On the occasion of Silver Jubilee Celebration of SPSI

International Symposium on Polymer Science and Technology

MACRO2015

January 23-26, 2015

Book of Abstracts

Indian Association for the Cultivation of Science
Kolkata, India

In association with

I am very happy to note that the Thirteenth Symposium on Polymer Science and Technology (Macro 2015) of the Society of Polymer Science, India is being held at the Indian Association for the Cultivation of Science, Kolkata, from January 23-26, 2014. The first such symposium was held at CSIR-National Chemical Laboratory, Pune in January 1991, which led to the formation of a national society dedicated to polymer science. Thus, 2015 also marks the beginning of the silver jubilee year of the Society.

The venue of the Thirteenth Symposium is most appropriate as IACS, Kolkata was the cradle of polymer science research in India. Professor Shanti Palit built the first school of polymer science in this institution in 1950. IACS is also one of India's oldest and venerated research institution, established in 1876, with a distinguished tradition of excellence in research in chemical and physical sciences.

The response to the symposium has been heartening with a large number of Indian and overseas delegates as well as students. I am particularly gratified to note that both, the American Chemical Society and the Royal Society, UK are participating in the symposium, bringing a global dimension to the meeting.

Polymer science and its application continue to be extremely relevant and significant to India. India, along with China is witnessing the fastest growth in consumption of polymers. Alongside with emerging needs in energy, water, health, housing, transportation and communications, advanced polymer materials are seeing a great resurgence. I am, therefore, confident that the Indian polymer science community will not be short of challenges with great opportunities beckoning them.

I wish the Symposium all success.

S. Sivaram

Dr. S. Sivaram
CSIR-National Chemical, Pune
President Socity of Polymer Science, India
Council Member, Federation of Asian
Polymer Societies

Message

On behalf of the organizing committee I take the opportunity to welcome you all at Indian Association for the Cultivation of Science (IACS) for this four days international symposium on Polymer Science & Technology – Macro 2015. IACS, founded by Dr. Mahendra L. Sirkar on 1876, is the oldest research institute of our country where Sir C.V. Raman discovered the Raman Effect winning Nobel Prize in physics in 1930. The polymer research in our country also started here under the leadership of the eminent Prof. S. R. Palit from 1947.

This conference is held under the umbrella of The Society for Polymer Science – India, celebrating its silver jubilee year, and is organized jointly by Kolkata and Kharagpur chapters of the society. Faculties of the leading institutes of eastern part of the country (IACS, Calcutta University, IISER Kolkata, Barasat State University and IIT Kharagpur) are involved in organizing the conference. In the event eminent polymer scientists from Asia, Australia, Africa, America and Europe are participating in delivering scientific and technical lectures along with discussions from some persons of polymer industries and instrument companies. The majority of scholars are involved in presenting their work in poster form. We wish a good scientific interaction & discussion between them and enjoyable& peaceful stay in Kolkata. We heartily thank them for taking pain for their long journey to come here and to discuss their valuable research findings amongst the participants.

It is important to mention here that American Chemical Society has sponsored the conference by giving eight poster prizes, advertisements and a lunch on meet of editors of Macromolecular Journals. Royal Society of Chemistry is also involved by sponsoring the conference. Dept. of Science & Technology and Dept. of Electronics & Information Technology of Govt of India have generously sponsored this conference. Also some polymer industries and instrument companies of the country have sponsored the conference and without these helps it would be difficult to manage the expenses of the conference.

To run this mega event of 650 registered participants our Director and Registrar have extended full infrastructural and technical supports from space, electricity, water and cleaning facilities. The effort of our students and staff members must be mentioned for arranging peaceful and smooth boarding, lodging and transports to the participants. The tireless efforts of my fellow colleagues, (T. K. Mandal, D. Chattaopadhyay, S. Malik and others), for the past few months have brought the conference to the light of the day. I take the humble opportunity not only giving thanks to all of them but I deeply appreciate their encouragement to make it a healthy and successful event. It would be the happiest and successful moment to the organizes if the participants, specially our younger colleagues, gain some new knowledge helping to envisage new ideas to cater the future research of polymer science in some newer directions for the benefit of human civilization.

Prof. Arun K. Nandi
FASc. Senior Professor & Head
Polymer Science Unit,
IACS Kolkata,
Chairman, Macro 2015

History

Prof. Arun K. Nandi
(Head) Polymer Science Unit
Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032
Email: psuakn@iacs.res.in

Introduction :

The field of polymer science is not very old and before 1930 only some naturally occurring polymers e. g. cellulose, starch, rubber etc. were present with a lack of distinct thoughts on their structures and properties. Graham, Ostwald, and others observed a slow diffusion rate of the material and called them as *"glue like"* or "*associative colloids"* arising from the secondary interaction of molecules of van der Walls type. In 1920 Staudinger a German scientist first proposed that polymers are *chain molecules* joined to each other by primary (covalent) valencies and surmised that the chain might contain more than 100 units. He relentlessly campaigned the primary valence view point with the observation that hydrogenation of rubber as well as its conversion with other derivatives does not destroy its colloidal properties. However, the view of Staudinger was not then widely accepted through criticism by other scientists mainly regarding its unit cell dimension that matches well with that of small molecules, etc. Staudinger proposed that a polymer chain may pass through many unit cells readily from one end of a crystallite to the other, passing through intermediate amorphous regions. In1929, Carothers used the simple organic reactions to produce Nylon and it was singularly successful to support the Staudinger's hypothesis of polymers produced from the covalent binding of chemical units. Later by theoretical calculations Khun, Mark and Meyer supported strongly the macromolecular hypothesis of Staudinger. For his *monumental work* of establishing polymer science Staudinger received the Noble Prize in 1953. Since then polymer science began to grow exponentially with the discovery of new synthetic polymers having diverse properties and major development in this field occurred during the Second World War. M. Gordon called this development of polymer science as a *"revolution in the chains"* and certainly it is a revolution that is regularly revitalized by new advances. Later on Ziegler and Natta (1963), P. J. Flory (1974), Shirakawa, Heeger and Macdiarmid (2000) obtained Noble Prizes for their work on stereoregular polymerization, fundamental understanding in the physical chemistry of polymers (both theoretical and experimental), and conducting polymers, respectively. In the following chapters we shall discuss how our beloved country contributed to the progress of this important field of science as one cannot think of a normal day without using any polymer. It is to be mentioned here that the author of this article is involved in polymer research since 1980 and here he has tried to produce a summary of polymer research at leading institutes, universities and industry of our big country and any unwanted mistake and omission may be excused due to his limitation of knowledge.

Initiation:

The history of polymer science in India started from 1947 onwards when Prof. S.R. Palit initiated research on polymers at the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032. His primary interest was the synthesis of polymers using different polymerization techniques eg. solution polymerization, emulsion polymerization, suspension polymerization etc. mainly using free-radical initiators. He measured the kinetics of polymerization to get an insight into polymerization mechanism and its dependence on reaction conditions. He characterized the polymers by viscometry, osmometry and spectroscopic techniques. His pioneering work on "chain transfer process" in collaboration with Prof. Sadahan Basu is usually led to a method for controlling the polymer molecular weight of addition polymers. Another seminal contribution of Prof. Palit was the end group analysis of polymer chains using the dye partition technique. Prof. Palit's other pioneering work on co-solvency, a phenomenon where the polymers being insoluble in two solvents but it becomes soluble in the mixture of two solvents, is an interesting phenomena that is used to alleviate the solubility problem of many polymers. Thus Prof. Palit made an outstanding contribution starting from polymer synthesis, solution thermodynamics, end group characterization etc. He published ~ 300 research publications and guided ~ 100 Ph.D. students during his academic carrier (1947-75). He died in 1981 leaving behind a host of his fellow polymer chemists to enrich polymer science in India and abroad. His works are well cited in the polymer classic 'Principle of Polymer Chemistry' written by P.J. Flory (Nobel laureate). Prof. M. Santappa is another individual who pioneered polymer research in India at the Department of Physical Chemistry at the then A.C. College of Technology, University of Madras. His major interests were in the area of synthesis and modification of polymers, kinetics of redox polymerization and photopolymerization. He later became Director of Central Leather Research Institute and contributed to development of polymers useful in leather processing and applications. He is now ~90 year old and resides at Chennai.

Growth:

Subsequent to initiation of polymer chemistry schools at two different parts of India the research in polymer science begins to propagate throughout the country. Here I shall start the journey again from IACS, Kolkata after Prof. Palit's period. Prof. B.M. Mandal made significant contribution in the fields of polymer synthesis particularly in solution and emulsion polymerization. He, in collaboration, with Prof. S.N. Bhattacharyya contributed to the fields of polymer blends and conducting polymers. He also contributed significantly to the new technique of living radical polymerization e.g. atom transfer radical polymerization (ATRP). Prof. Mandal has recently published a book on

'Fundamentals of Polymerization' published by World Scientific Publishers which is suitable for both students and researchers in this field. Another group at IACS was devoted to natural polymers like rubber, carbohydrate etc. It is important to mention here that the Calcutta University started a Department of Polymer Science and Technology at 1968 where both teaching and research in Polymers and Rubbers flourished with excellent contribution to create a cadre of students to cope with the demand of polymer and rubber industry in India. Here the contribution of Prof. P. Ghosh, an alumni of IACS, is noteworthy, particularly in the field of polymer synthesis. He also authored a book on polymer science suitable for the beginners of learning polymer science.

At National Chemical Laboratory(NCL), Pune under the able leadership of Dr. R.A. Mashelkar and Dr. S. Sivaram the polymer research expanded very significantly in the country. Both the scientists are well known for their individual contributions to polymer engineering and polymer chemistry, respectively. Dr. Mashelkar joined NCL in 1976 and built a school of research focused on polymer rheology, non-Newtonian flow and polymer gels. His publications related to volume phase transition of gels and self-healing gels by introducing supramolecular interactions are highly cited in literature. Dr. S. Sivaram is an eminent polymer chemist who joined NCL in 1988 after serving Indian Petrochemicals Corporation Ltd (IPCL) at Baroda (1973-1987) after his return to India. He successfully linked the polymer academic research with industry in the country, both Indian and Global. His main interests in academic research relates to polymer synthesis with tailor made properties using free radical, anionic and Ziegler Natta polymerization. His contribution to the synthesis of high performance polymers using new synthetic routes is also noteworthy. One of his significant achievement was to to built a good polymer research school encompassing all branches of polymer science: eg. polymer chemistry, polymer physics and polymer engineering. Many distinguised scientists (Drs. A Lele, C.Ramesh, K. Guruswamy, S.K.Asha, P.P Wadgoawkar and others) are working at NCL and have bought international recognition to this important branch of science.

At Indian Institute of Science (IISc), Bangalore research on Polymer Science began around 1970 under the able leadership of Dr. U.S. Nandi, an IACS alumni, who was interested on both biopolymers and also synthetic polymers. During his stay he was able to produce a number of good students who have since contributed significantly both in academia and industry. Amongst them Prof. D. Chatterji, (IISc Bangalore), Dr. C.K.S. Pillai, [RRL (now, NIIST, Trivandum] and Dr. Prabha Chatterjee, (IICT, Hyderabad and later GE, Bangalore) are the important personalities. Dr. U.S. Nandi, studied DNA-metal ion interaction, use of metal chelates in polymerization and polymerization mechanism. Prof. K. Kishore joined IISc at 1974 and persued research in the area of flame-retardant polymers, plasticization of polymers and polymer degradation. He contributed significantly to these areas publishing his work in very high quality journals. Presently S. Ramakrishnan is actively engaged in target oriented synthesis via condensation polymerization technique and in the structure property behaviors of these condensation polymers. He built an active school of research in this area. Also there are internationally recognized work on supramolecular polymeric architecture by Prof. S. Bhattacharyya and Prof. U. Maitra in the Organic Chemistry Department. In addition work of Prof. Giridhar Madras on polymer degradation and Prof. Satish Patil on clectroactive polymers are worthy of mention.

At several Indian Institutes of Technology (IITs) there are departments engaged in research in the fields of polymers and rubber materials and also engineering. At the oldest IIT at Kharagpur, the polymer research has made very high impact. At the chemistry department Prof. M. Biswas, an alumni of IACS, contributed to the synthesis of polymers, mechanism of polymerization and conducting polymers. The Rubber Technology Centre has been a good place to train students both in rubber and polymer science and it started with the leadership of Prof. S.K. De (alumni of IACS), a renowned scientist. The main interest of the Centre is to improve the processing and properties of rubber materials. Many eminent faculties have worked here and amongst them Prof. A. Bhowmik has made a significant contribution to the field of rubber science and technology and rubber-plastic blends. The Department continues to be a vibrant place of rubber research in the country guided by a number of eminent faculties (Dr. Nando, Dr. Khastagir, Dr. Singha & others). The Material Science Department of IIT Kharagpur has a sizable polymer program and the faculties are mainly interested in the synthesis of polymers, biodegradable polymers, photovoltaic application, composite materials etc. The contribution by Prof. S. Maiti (alumni of IACS), Prof. R.P. Singh and others (B.Adhikari, S. Banerjee, C.Das) at this department helped in the progress of polymer science in India. In 1984, Prof. S. Maiti founded the first Indian Journal on polymers *"J. Polymer Materials*" from here.

Amongst the other IITs, IIT Delhi and IIT Bombay have a long history of polymer research. Prof. Mrs. I.K. Verma and Prof. A. Mishra of IIT Delhi had contributed significantly to the chemistry and physics of polymers. They belonged to the Dept. on Polymer Science & Technology where the M. Tech degree is being offered in the area of polymer science and technology. The present faculties (V. Chowdhury, A. Ghosh, J. Jacob & others) of this department are keeping up high traditions of this department. This apart, research in polymer also occurs at the Dept. of Textile Technology, IIT Delhi where mostly applied research takes place. The history of polymer research at IIT, Bombay dates back to Prof. D.D. Deshpande who was mainly interested in the thermodynamics of polymer blends and polymer solutions. Later Prof. A. Misra, Prof. D. Khakkar and Prof. A. Kumar are contributing to the fields of polymer nanocomposites, conducting polymers etc. At IIT Madras the late Prof. Sundararajan, and Prof. Damodoron have contributed to the area of polymer synthesis using metal catalyzed polymerization and radical polymerization. At IIT Kanpur, research in the area of polymer science has recently gained considerable attention by Prof. A. Sharma of Chemical Engineering Department. He has contributed in the fields of meso- patterning of polymers, polymer thin films and polymer nanocomposites. Amongst the newer IITs, Prof. P.K.Iyer at IIT - Guwhati has contributed to the development of polymer based sensors and photovoltaics.

Amongst the Government funded research institutes of the country it is necessary to mention the contribution from Defence Research & Development Organization (DRDO, Kanpur, Delhi and Gwalior), Naval Research Institute at Bombay, Vikram Sarabhai Space Centre (VSSC) at Trivandrum where there is a long tradition of developing new polymeric materials for use in defense, naval and space research. The VSSC's main interest is to develop solid propellant using polymers as binder. The National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum has also a sizeable research group on polymer science and technology, working in the fields of conducting polymers, supramolecular polymers, polymer nanocomposites and crystallization of polymers. The contribution of Dr. C.K.S. Pillai to the area of cardinal derived polymers and that of Dr. Ajayaghosh to the field of supramolecular polymers are internationally recognized. At the Jawahar Lal Nehru Centre of Scientific Research (JNCSAR, Bangalore) Dr. Narayanan is actively engaged in research on conducting polymers and their photovoltaic applications and Dr. S. Gorge is in the area of supramolecular polymers. At the Indian Institute of Chemical Technology (IICT, Hyderabad) and National Physical Laboratory, Delhi there are small groups working in the fields of conducting polymers and polymer nanocomposites. Apart from these renowned institutions polymer research also takes place at CIPET a Central Govt. institute on plastic engineering and Technology, situated at Chennai, Bhubaneswar, and Haldia, mainly having the aim of improving the physical & mechanical properties of the polymers for application in engineering and household materials. Almost all the newly built Indian Institute of Science Education and Research (IISERs,) have some faculties interested in polymer research. Mention must be made of M. Jayakanan (IISER, Pune) P.Dey and Raja. Shunmugam (IISER Kolkata).

Apart from the Govt. funded research institutes researches in polymer science is also active in many industries. Amongst them are, General Electric (GE, now Sabic) India is the most important, consisting of a large number of polymer scientists working in the development of high performance polymers. Other companies where polymer research is active include Rliance Industries Limited), Haldia Petrochemicals Corporation Ltd. (HPCL), Haldia, Indian Oil Corporation, Faridabad, Ghardo Chemicals, Mumbai, Asian Paints, and Pidilite, Mumbai. There are a lot of Rubber industries in India where development of rubber materials along with polymers are taking place for direct application in automobile tyres and belts.

At some universities polymer research has gained good momentum in recent years. Amongst them, Calcutta University (D. Chatterjee, D. Banerjee, P. Kundu & others) Benaras Hindu University (N.Mishra, P. Maiti, B.Roy), Hyderabad Central University (T. Jana), M.S. University, Baroda (G. Murthy) and North Maharastra University, Jalgaon, Mahatma Gandhi University, Kottayam (S. Thomas), Cochin University, Anna University (P.Kannan), Jharkhand state University (B.Kuila), Tezpur University (N.Karak, S.Douloi) are few places where mainly academic research on chemistry and physics of polymers begins to emerge. Coming back to the *alma mater* of polymer research in India, the Polymer Science Unit of IACS is presently contributing significantly to the fields of polymer synthesis, physical and mechanical properties of polymers, conducting polymers, polymer nanocomposite, metal nanoparticle polymer hybrid, biomolecule-polymer hybrid, self-organized structure of polymer, supramolecular polymer and polymer photovoltaics. The present group (A.K.Nandi, T.K.Mandal, S. Malik and S. Ghosh) has kept alive the bright tradition of polymer research established by Prof. S.R. Palit.

Conclusion:

In conclusion, it may be inferred that the *"revolution in the chains"* is now spread all over the country and it is limited not only to the chemists, but to a large section of theoreticians, biologists, pharmacists, material physicists and engineers, biotechnologists and others, whose names are too numerous to mention here. They are involved in the *"revolution in the chains"* for the steady improvement of human civilization. I take the privilege to forecast that the *"revolution in the chains"* that stated from 1930, would expand further to every corner of our country in future due to its far reaching applications in energy, health care, food and food packaging, agriculture, medicine, water, housing, transportation as well as communication technologies.

Acknowledgement:

The author gratefully acknowledges Dr. S. Sivram, NCL,Pune for going through the manuscript and introducing necessary corrections.

Contents

The exciting and rewarding world of polymers

M. M. Sharma
Emeritus Professor of Eminence, ICT, Mumbai

"Just remember one word ...... PLASTIC"
From the motion picture The Graduate (1967)

The greatest contribution of Chemistry to society has been though plastics and it is appropriate to say that we live in Plastic Age. Plastics are hallmark of conservation of energy compared to steel and glass, and lend themselves for recycling. Plastics are environmentally friendly functional materials and conserve water. We are heading for production of polymeric materials at 1 mtpd.

The Plastic products have a fascinating, bewildering and even bizarre range of properties. Plastics can be rigid as well as flexible and provide barrier properties. The success of making available potable water from brackish and saline water, in a benign way, can be attributed to polymer based membranes. The full range of membrane separations from micro to ultra filtration, RO and now, in the course of last few years, nanofiltration which allows molecules of mol. wt. more than 200 to be retained and can distinguish between monovalent and divalent ions. The advent of Nafion membranes, a product required in the space programme, has allowed caustic/ chlorine to be produced in a neat way with reduction in energy consumption.

Plastics can be processed in a remarkably simple way. Emulsion polymers have made an extraordinary impact on the surface coating industry. Reactor designs are available to take care of very large variation in viscosity during polymerization. Recent success in free radical aqueous emulsion polymerization of ethylene with vinyl acctate/ethyl acrylate can be cited as yet another example. Even stearyl acrylate which is water insoluble has been emulsion polymerized with cyclodextrin as phase transfer agent. Block copolymers have been used for photolithography. Ionomers have been used for supramolecular polymer systems. Another success has come through the novel metathesis based polymerization. Thermoset resins which can be broken down are under development.

The quality of life has witnessed a remarkable change with the availability of superabsorbent polymers which are essential components of diapers and sanitary towels. Composites have led to reduction in weight of vehicles and aircrafts thereby resulting in energy conservation. Fiber glass reinforced plastics can be used in harsh environment. Elastomeric fibers made a major impact.

Polymers already feature in numerous biomedical applications, including drug delivery systems. Even hip joints depend on plastics. The use of membranes for kidney patients is a remarkable example of using in the form of hollow fibers.

The industry makes polyvinyl pyrolidone which is used in tableting in pharma industry. It is fascinating that we have medicines based on polyallylamines cross linked with epichlorohydnin for phosphorus containing substances to be removed for kidney patients. Similarly potassium in blood is managed by using polystyrene sulfonic acid.

Ion exchange resins have allowed purification of water to reduce dissolve salts to ppb level, as required in high pressure boilers for power generation. Cationic ion exchange resins as catalyst have made a great difference to homogeneous acidic catalysts to increase yield and prevent pollution.

Plastics have been very handy to make micro irrigation possible. PVC pipes and HDPE pipes are now used extensively and have replaced metals and alloys based pipes. Thermoplastic elastomers have allowed injection moulding and avoided unfriendly vulcanization of rubbers.

Plastics also epitomize more from less. Thus polyphenylene oxide is blended with much cheaper polystyrene to make processing possible. How fillers are useful in PP/PE? It is useful to look at polyaramid fibers which allow bullet proof chests. We are now witnessing use of polypropylene for currency notes, which will not soil.

Packaging industry has seen revolutionary challenges as exemplified by polyethylene films, woven sacks, foamed polystyrene, PET bottles for mineral water, oral medicines, etc. PET bottles are safe in kitchens compared to glass bottles which are not only very heavy put also pose a danger should they slip and fall. PET is recyclable.

Insulation has been made so much easier with polymeric substances and let us recollect how during the second war insulation of radar was made possible with polyethylene.

Polymers play a vital role in sports and entertainment from the classic table tennis balls to badminton and golf rackets, etc. Even turf for Olympics was made from polyethylene.

The broad field of macromolecular science has never been more vibrant. Driven by stunning fundamental advances in many fields: Methods of polymerization; interfacial polycondensation, including phase transfer catalysis; theory, simulation and modeling; methods of characterization. From an engineering point of view the use of fluidized bed reactors for large capacity LLDPE/HDPE/PP/EPR can be cited as a real advance in 1970’s. Polycarbonates can be made without phosgene. However, we are still humbled by nature which produces natural rubber at ambient conditions, formation of silk fiber directly, shellac, etc.

In the recent past there has been a penchant to use renewable raw materials and we have polylactic acid, polyhydroxyalkanoates, etc. However, we seem to have forgotten cellulose acetate/ butyrate and even ethyl cellulose which were used for a while for apparel wear. Nylon 11 was made from castor oil as a starting material. Many polyols for urethanes have been made from renewable raw materials like castor oil and other vegetable oils. We made LD polyethylene starting from ethyl alcohol but had to give up. Even butadiene was made from alcohol and given up. This area will witness developments and we have challenges to valorize bagasse, including lignin.

We need to recognise that several years have gone and we do not have any new plastic, synthetic fiber, and synthetic rubber. Known products have been modified and this includes some new polyesters, polyamides, etc. Recycling will come center stage.

It is heartening that a number of Nobel Prize have gone to Polymer Scientists: Herman STAUDINGER (1953); KARL ZIEGLER and GIULIO NATTA (1963); PAUL FLORY (1974); BRUCE MERRIFIELD (1980); PIERRE DEGENNES (1991); A. J. HEEGER, ALAN MACDIARMID and H. SHIRAKAWA (2000). Alas CAROTHERS could not be given for Nylon 66- the archetype of discovery and market driven product, as it is not given posthumously.

Halogen bonds, hydrogen bonds, and multivalent interactions for self-assemblies at different length scales

Olli Ikkala* and Nikolay Houbenov
Aalto University, Department of Applied Physics, P.O. Box 15100,
FIN-00076 Aalto, Espoo, Finland
Olli.Ikkala@aalto.fi

Polymeric self-assemblies incorporating supramolecular motifs allow hierarchies and tuning of the properties (1). However, polymeric self-assemblies do not typically render overall alignment or monodomain structures unless additional fields are imposed. In Politecnico di Milano/Aalto University collaboration we show that halogen bonding of iodoperfluoroalkanes to hydrophilic polymers allows self-assemblies in the nanometer periodicity that spontaneously align up to millimeter length scale (2). As structures exist also at smaller length scale due to the laterally packed fluorinated rods, the self-assembly is hierarchical. Self-assemblies involving larger length scale periodicities can be achieved by incorporating colloidal structural motifs. We incorporate cellulose nanocrystals as rod-like colloidal motifs. In Leibniz Institute/Aalto University collaboration, we show by high resolution transmission electron tomography that multivalent interactions based on maltose-decorated dendronized polymers allow wrapping around cellulose nanocrystals (3). This suggests routes towards supracolloidal self-assemblies. Finally we show that cellulose nanocrystals decorated by polyacrylate side chain brushes allow toughened materials, where cracks do not propagate catastrophically (4). This suggests design principles to incorporate sacrificial bonds within colloidal assemblies for synergistic mechanical properties for biomimetic materials.

References

[1] Ikkala, O.; Houbenov, N.; Rannou, P. In Handbook of Liquid Crystals, editors Goodby, J.W.; Collings, P.J.; Kato, T.; Tschierske, C.; Gleeson, H.; Raynes, P., **2014**, Vol VII, pp. 541-598.

[2] Houbenov, N.; Milani, R.; Poutanen, M.; Haataja, J.; Dichiarante, V.; Sainio, J.; Ruokolainen, J.; Resnati, G.; Metrangolo, P.; Ikkala, O. *Nat. Comm.,* **2014**, 5, 4043.

[3] Majoinen, J. Haataja, J; Appelhans, D.; Lederer, A.; Olszewska, A.; Seitsonen, J.; Aseyev, V.; Kontturi, E.; Rosilo, H.; Österberg, M.; Houbenov, N.; Ikkala, O. *J. Am. Chem. Soc.*, **2014**,136, 866–869.

[4] McKee, J.R. Huokuna, J.; Martikainen, L.; Karesoja, M.; Nykänen, A.; Kontturi, E.; Tenhu, H.; Ruokolainen, J.; Ikkala, O. *Angew. Chemie, Int. Ed*. **2014**, 53, 5049-5053.

Transporting Charged Macromolecules: Ubiquity and Conceptual Challenges

M. Muthukumar
University of Massachusetts, Amherst, MA 01003

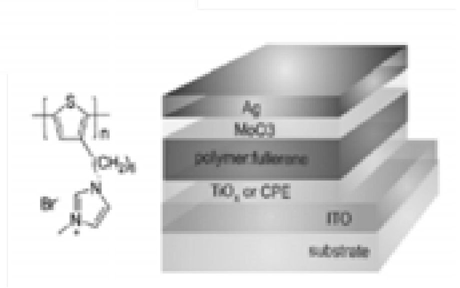
Movement of a charged macromolecule from one location to another is a vital process for the existence of life, as well as in executing myriads of technological applications. Yet, this ubiquitous phenomenon remains as one of the less understood phenomena in macromolecular science. The richness of the phenomenology on polymer movement in aqueous solutions will be illustrated with experimental data on diffusion and electrophoretic mobility, in both bulk solutions and through nanopores. The challenge in understanding their behavior lies on the coupling among several factors, such as macromolecular conformations, hydrodynamics, electrostatic forces, and confinement forces. These concepts will be described against a background of single-molecule electrophoresis experiments. Specifically, the movement of DNA/RNA, proteins, and synthetic polyelectrolytes in bulk and through protein/solid-state nanopores under an external electric field will be discussed. Implications on evolutionary issues and nanotechnology will be presented.

Conjugated Polyelectrolytes as Functional Interlayers of Electronic Devices

Ullrich Scherf
BergischeUniversität Wuppertal, Macromolecular Chemistry Group (buwmakro) and
Institute for Polymer Technology, Gauss-Str. 20, D-42119 Wuppertal, Germany
scherf@uni-wuppertal.de

The mission of organic electronics is to develop electronic and optoelectronic devices based on organic materials. The lecture presents a series of novel, conjugated polyelectrolytes (CPEs), including cationic, anionic as well as zwitterionic CPEs and their use as functional interlayers of organic electronics devices, especially bulk-heterojunction-type organic solar cells.

A key challenge towards stable and efficient organic solar cells is to develop solution-processed interlayers for improved and stable extraction of electrons and holes. The introduction of CPE-based interlayers (until now mostly cathode interlayers) can lead to a significantly improved charge extraction to the electrode, both for conventional [1,2] and inverted device architectures (see Scheme) [3-5].



References:

[1] J. H. Seo, A. Gutacker, Y. Sun, H. Wu, F. Huang, Y. Cao, U. Scherf, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.***2011**, *133*, 8416.

[2] U. Scherf, R. C. Evans, A. Gutacker, G. C. Bazan, All-Conjugated Rod–Rod Diblock Copolymers Containing Conjugated Polyelectrolyte Blocks, in: *Conjugated Polyelectrolytes: Fundamentals and Applications, Eds.* B. Liu, G. C. Bazan, Wiley-VCH, **2013**, chapter 2, pp 65–89.

[3] K. Zilberberg, A. Behrendt, M. Kraft, U. Scherf, T. Riedl, *Org. Electron.***2013**, *14*, 951.

[4] J. Min, H. Zhang, T. Stubhan, Y. N. Luponosov, M. Kraft, S. A. Ponomarenko, T. Ameri, U. Scherf C. J. Brabec, *J. Mater. Chem. A***2013**, *1*, 11306.

[5] *also as cathode interlayers for perovskite solar cells*: H. Zhang, H. Azimi, Y. Hou, T. Ameri, T. Przybilla, E. Spiecker, M. Kraft, U. Scherf, C. J. Brabec, *Chem. Mater.* **2014**, *dx.doi.org/10.1021/cm502864s*

Processing of PVDF Films

Devang Khakhar
Department of Chemical Engineering,
Indian Institute of Technology Bombay, Powai, Mumbai 400076

Poly (vinylidene fluoride) (PVDF) has excellent piezoelectric properties and used in applications such as sensors, actuators and switches. PVDF has several crystal phases of which the α-phase is mostcommonly obtained by melt processing. The β-phase, which has the required electrical properties, is obtained from the α-phase by cold drawing and electrical poling. The processing PVDF films by means of the blown film and cast film processes and their characterization will be reviewed. The drawing and poling of the films to obtain the β-phase with good piezo-electric properties will be discussed with reference to processing parameters. The role of nucleating agents to obtain the β-phase will be presented.

From Chain Folding to 2-D polymers

S. Ramakrishnan
Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560012
raman@ipc.iisc.ernet.in

Control of chain conformation in solution has several interesting ramifications – from mimicking the exquisite conformational control seen in biological macromolecules to understanding factors that govern the lamellar crystallite sizes in semi-crystalline polymers. During the past decade we have examined several aspects dealing with control of chain conformation in solution; and we have also attempted to translate this control towards regulating the morphological characteristics of the bulk polymer. The lamellar morphology that is often realized in these attempts leads to the layering of different types of immiscible domains; a closer examination of these layered structures prompted us to begin exploring the similarity between these systems and 2D polymers. 2D polymers have begun to attract the attention of several groups world-wide; although many early efforts have examined polymerization at air-water interfaces and also within vesicles, these do not typically constitute robust structures that would withstand exfoliation. One of the prime drivers of this field is graphene, which could be viewed as the archetypical 2D polymer – a robust and reasonably stiff system that can be readily exfoliated to generate single atom-thick carbon sheets. The remarkable properties of graphene amply justify the incredible attention that this class of materials has received during the past decade. As a polymer chemist one can ask – what are the possible design strategies to prepare 2-dimensional polymers? Evidently, folding of polymer chains does constitute one way to generate 2-D polymeric nano objects; the thickness of these sheets would be the height of a folded chain – something we have recently demonstrated. However, these are not robust structures that can be prepared in bulk and exfoliated. It is with this challenge that we have just begun to examine alternate approaches to prepare 2D polymers; broadly, our strategy is to pre-organize multi-segmented monomers bearing at least two polymerizable units at the segment junctions. The pre-organization is designed to be driven by segment immiscibility and strengthened by the strong interactions, such as crystallization, within the domains; polymerization of the double bonds in the solid or semi-molten state it was expected would lead to the formation of a cross-linked and reasonably stiff sheet that would represent a 2D polymer. By suitable choice of the outer segments, it was felt that exfoliation could be made feasible. In the talk, I shall describe our efforts beginning with chain folding and I shall end with our recent foray into 2D polymers.

Boronic Acids Block Copolymers: Sugar-Responsive Delivery Agents and Dynamic-Covalent Biomaterials

William L. A. Brooks,[1] Soma Mukherjee,[1] Abhijeet P. Bapat,
[2]Brent S. Sumerlin[1]*
[1]George & Josephine Butler Polymer Research Laboratory,
Center for Macromolecular Science & Engineering,
Department of Chemistry, University of Florida, Gainesville, Florida, USA
[2]Department of Chemistry, Southern Methodist University, Dallas, Texas, USA
sumerlin@chem.ufl.edu

This presentation will discuss our results in two areas of responsive polymeric nanomaterials that derive their responsive utility from boronic acid functionality. The first topic of the presentation will discuss glucose-responsive polymers and their potential to be employed in the area of sugar-induced release of diabetes therapeutics. Boronic acid-containing block copolymers were shown to be both pH- and glucose-responsive in aqueous media, which led to unique adaptive self-assembly behavior. Polymeric micelles and vesicles constructed from these block copolymers were capable of encapsulating model therapeutics and allowing their release upon an increase in the surrounding glucose concentration. The second topic of the presentation involves our recent results in the area of dynamic-covalent nanomaterials. Macromolecules of various complex topologies were constructed via dynamic-covalent linkages, including boronic esters, Diels-Alder adducts, disulfides, and hydrazones. Diblock copolymers with one reactive block and one "passive" block were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization. Addition of a complimentary difunctional small molecule led to intermolecular crosslinking of the reactive block to result in star copolymers with cores crosslinked via dynamic-covalent bonds. The kinetics of self-assembly and the morphology of the resulting stars were investigated as a function of block copolymer and crosslinker concentrations and stoichiometry. The reversible nature of the crosslinks within the cores allowed the stars to reversibly reconfigure their macromolecular topology via competitive exchange reactions or by manipulation of the dynamic-covalent equilibrium.

Next Gen. Polymeric Materials : Growth Strategies and Technological Opportunities

Ajit Sapre
Reliance Research and Development Centre, Reliance Industries Limited,
Reliance Corporate Park, Navi Mumbai 400 701 India

Exponential growth in different sectors such as Auto, Agriculture, Medicals, Packaging, Space, Electrical & Electronics etc. has provided impetus for the development of next generation high performance polymeric materials with different functionalities. Furthermore, alternative feed-stocks such as renewable and use of biotechnology are creating opportunities for newer polymeric materials. The present talk will cover current polymeric materials and emerging trends in next generation polymeric materials with possible alternative feed-stocks. Multidisciplinary approach involving chemical and biological sciences in combination with engineering & advanced modeling, and effective public private partnerships for driving frontiers of innovation to create new value added products could speed up the development cycle from Mind to Market.

New materials from simple transformations of an amino-substituted polysiloxane by addition of carboxylic acids

Yong He[1,2] , Hui Zhao[1,2] and Richard G. Weiss[2,3*]
[1]College of Materials Science and Engineering,
Beijing University of Chemical Technology, Beijing 100029, China.
[2]Department of Chemistry and [3]Institute for Soft Matter Synthesis and Metrology,
Georgetown University, Washington, DC 20057-1227, USA.
*weissr@georgetown.edu

Changes in rheological, adhesive, and some preliminary swelling properties are reported when a variety of mono- and di-carboxylic acids is added to 6-7PSil, a polysiloxane in which 6-7 % of the side groups contain a primary amine functionality. Although the specific properties of the resultant quaternary salts depend on the amount of added acid, most of the studies here have been conducted on materials made at 1:1 amine:acid ratios. The salts are found to behave very differently than the unquaternized precursor, 6-7PSil. The changes are correlated with (especially) the structures of the 7 mono- and 6 di-carboxylic acids added. In addition, the nature of the materials made from *in situ* photo-polymerization of unsaturated carboxylic acids that were added to the 6-7PSil are reported. The results demonstrate that a simple transformation of the amino functionalities of a polysiloxane, such as 6-7PSil, to their quaternized form, leads to materials with significantly enhanced rheological and adhesive properties. Furthermore, those properties can be modulated by the acid structure, the amount of acid added, and by polymerizing unsaturated carboxylates *in situ*, creating interpenetrating networks. The potential for applying the methodologies employed here to other polymers and non-carboxylic acids is noted. The results will be compared with those from addition of CO_2 or CS_2 to 6-7PSil [1].

Reference:

[1] Yu, T.; Wakuda, K.; Blair, D. L.; Weiss, R. G. J. Phys. Chem. C **2009**, 113, 11546-11553.

Biomimetic polymersomes from controlled self-assembly of block copolymers

S. Lecommandoux*
LCPO, UMR CNRS 5629,Université de Bordeaux,
Bordeaux-INP, 33600 Pessac, France
*Lecommandoux@enscbp.fr

Polymersomes are among the most attractive systems for drug delivery applications. We report here an overview on the self-assembly in water of amphiphilic block copolymers into polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules. We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles. These copolymers that mimic the structure and function of glycoproteins represent an example of the effectiveness of a biomimetic strategy in implementing materials design. In addition, magnetic polymersomes, including iron oxide γ-Fe_2O_3 nanoparticles are currently investigated, together with their potential applications as contrast agent for imaging and as therapeutic nanoparticles using hyperthermia. *In vitro* and *in vivo* efficacy results on different cancer models will be presented. Finally our recent advances in using "biomimicry approaches" to design complex, compartmentalized materials will be proposed. Such a system constitutes a first step towards the challenge of structural cell mimicry and functionality.

References:

[1] (a) Upadhyay, KK.; Bhatt, A.N.; Mishra, A.N.; Dwarakanath, B. S.; Jain, S.; Schatz, C.; Le Meins, JF.; Farooque, A.; Chandraiah, G.; Jain, AK.; Misra, AK.; Lecommandoux, S.*Biomaterials***2010**, 31, 2882. (b) C. Bonduelle, S. Lecommandoux. Biomacromolecules**2013**, 14, 2976-2983. (c) Bonduelle, C. ; Huang, J. ; Ibarboure, E. ; Heise, A. ; Lecommandoux, S. *Chem. Commun.***2012**, 48, 8353. (d) Huang, J. ; Bonduelle, C. ; Thévenot, J.; Lecommandoux, S. ; Heise, A. *J. Am. Chem. Soc.***2012**, 134, 119.

[2] (a) Sanson, C. ; Diou, O. ; Thevenot, J. ; Ibarboure, E. ; Soum, A. ; Brulet, A. ; Miraux, S. ; Thiaudiere, E. ;Tan, S. ; Brisson, A. ; Dupuis, V. ; Sandre, O. ; Lecommandoux, S. *ACS Nano***2011**, 5, 1122. (b) Oliveira, H. ; Pérez-Andrés, E. ; Thevenot, J. ; Sandre, O. ; Berra, E. ; Lecommandoux, S. *J. Control. Release***2013**, 169, 165. (c) Pourtau, L. ; Oliveira, H. ; Thevenot, J. ; Wan, Y. ; Brisson, A. ; Sandre, O. ; Miraux, S. ; Thiaudiere, E. ; Lecommandoux, S. *Advanced HealthcareMaterials***2013**, 2, 1420-1424.

[3] Marguet, M.; Edembe, L.; Lecommandoux, S. *Angew. Chem. Int. Ed.* **2012,** 51, 1173. (b) Marguet, M.; Sandre, O.; Lecommandoux, S. *Langmuir***2012,** 28, 2035. (c) Marguet, M. ; Bonduelle, C. ; Lecommandoux, S. *Chem. Soc. Rev.***2013**, 42, 512-529. (d) R. J. R. W. Peters, M. Marguet, S. Marais, M. W. Fraaije, J. C. M. Van Hest, S. Lecommandoux. *Angew. Chem. Int. Ed.***2014,** 53, 146-150.

Surface and Interface Engineering with Polymer Brushes

Harm-Anton Klok
Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux
Laboratoire des Polymères, Station 12, CH-1015 Lausanne (Switzerland)
**harm-anton.klok@epfl.ch*

Thin polymer coatings are of great importance to control the interactions of synthetic materials with other materials (lubrication, wear), the environment (corrosion) as well as biology (marine antifouling). Modern polymer science offers unprecedented opportunities to chemically engineer the properties of surfaces and interfaces. This presentation will discuss three aspects. The first part of the presentation will introduce modern controlled/"living" radical polymerization techniques and "polymer brushes" (chain-end tethered monomolecular assemblies of densely grafted polymer chains) and present the scope and possibilities of these approaches to chemically modify surfaces and interfaces. The second part of the presentation will address the need for accurate surface chemical characterization and the challenges related to the precise determination of the localization and distribution of functional groups in thin polymer films. The presentation will end with 3 brief showcases that illustrate the use of modern polymer science tools to develop ultrathin polymer films that possess sensory properties, which can be used to control fluid flow or to template the controlled growth of metallic or non-metallic inorganic films on complex, 3D structured substrates.

References:

[1] R. Barbey, L. Lavanant, D. Paripovic, N. Schüwer, C. Sugnaux, S. Tugulu, H.-A. Klok, Polymer brushes via surface-initiated controlled radical polymerization: synthesis, characterization, properties and applications, Chem. Rev. **2009**, 109, 5437.
[2] N. Schüwer, T. Geue, J. P. Hinestrosa, H.-A. Klok, Neutron reflectivity study on the postpolymerization modification of poly(2-hydroxyethyl methacrylate) brushes, Macromolecules **2011**, 44, 6868.
[3] R. Barbey, V. Laporte, S. Alnabulsi, H.-A. Klok, Postpolymerization modification of poly(glycidyl methacrylate) brushes: An XPS depth-profiling study, Macromolecules **2013**, 46, 6151.
[4] N. Schüwer, H.-A. Klok, A potassium-selective quartz crystal microbalance sensor based on crown-ether functionalized polymer brushes, Adv. Mater. **2010**, 22, 3251.
[5] C. Sugnaux, L. Lavanant, H.-A. Klok, Aqueous fabrication of pH-gated, polymer-brush-modified alumina hybrid membranes, Langmuir **2013**, 29, 7325.

Linear and hyperbranched polymers for organic electronic applications

Brigitte Voit, Tim Erdmann, Anton Kiriy, Robert Pötzsch,
Maria Heuken, Qiang Wei
Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany
voit@ipfdd.de

The microelectronics industry and especially the organic electronics industry continue to demand new innovative materials. Besides the active (conducting and semiconducting) materials, also the insulating materials in between, the dielectrics, as well as materials with special optoelectronic properties are highly important since they determine significantly the final performance of the device. Recently, the development of the Kumada Catalyst-Transfer Polycondensation (KCTP)[1] allowed for preparing conjugated polymers of high molar mass precision in a living manner enabling end group control and eventually block copolymer formation. We will demonstrate how KCTP has been effectively used for the preparation of new donor-acceptor block copolymers involving Nitroxide-Mediated Radical Polymerization (NMRP) and effective cesium-mediated polymer analogous esterification.[2] Furthermore, the successful controlled preparation by KCTP of dithienosilole (DTS) based conjugated polymers as well as block copolymers with thiophene could be realized using this protocol.[3] These structures are highly interesting as stable active materials of printed organic field effect transistors (OFETs).

In the area of insulating materials high performance hyperbranched (hb) polymers (e.g. hbpolyphenylenes, hb-PPh) offer significant potential in the application as gate dielectric material which can be adopted for high performance OFETs by design-matching with the respective semiconducting material. The branching provides the highly needed solubility and allows solution processing or even processing by printing techniques. For multilayer device preparation, we also developed suitable crosslinking strategies which can be thermally or photochemically induced.[4] Furthermore, hyper-branched polyvinylsulfides through thiol-yne addition[5] proved to be excellent candidates for high refractive index materials well suited for efficient light out-coupling from OLEDs.

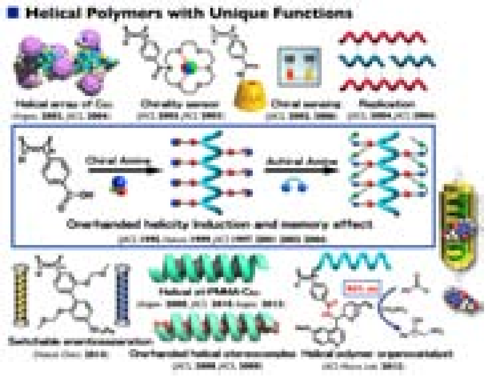
References:

[1] a) T. Yokozawa et al., Macromol. Rapid Commun. **2004**, 25, 1663-1666. b) McCullough et al., Macromolecules 2005, 38, 8649. b) A. Kiriy et al. Macromol. Rapid Commun. **2011**,32, 1503.
[2] M. Heuken, H. Komber, T. Erdmann, V. Senkovskyy, A. Kiriy, B. Voit, Macromolecules, **2012**, 45, 4101.
[3] T. Erdmann, J. Back,b R. Tkachov, A. Ruff, S. Ludwigs, B. Voit, and A. Kiriy, A, Polymer Chemistry, **2014**, 5, 5383
[4] R. Pötzsch, B. Voit, Macromol. Rapid Commun. **2012**, 33, 635.
[5] Q. Wei, R. Pötzsch, H. Komber, D. Pospiech, B. Voit, POLYMER, 2014, DOI: 10.1016/j.polymer.**2014**.07.030 (in print)

Functional Helical Polymers and Oligomers as Unique Chiral Materials

Eiji Yashima
Department of Molecular Design and Engineering, Graduate School of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan
yashima@apchem.nagoya-u.ac.jp

The helix is a central structural motif for biological macromolecules and plays a key role in their sophisticated functions, such as chiral and molecular recognitions, enantioselective catalysis, and replication. Here we present unique macromolecules and oligomers that fold into a preferred-handed single- or double-stranded helical conformation induced by chiral pendants covalently bonded to the main-chains or external chiral stimuli followed by memory of the helical chirality [1]. The direct observations of helical structures of synthetic helical polymers, foldamers, and supramolecular helical assemblies by atomic force microscopy (AFM) will be also presented [2]. A series of double helices composed of different components and sequences that exhibit specific functions, such as chirality sensing, chiral recognition, enantioselective asymmetric catalysis, and anisotropic spring-like motion are also described [3].

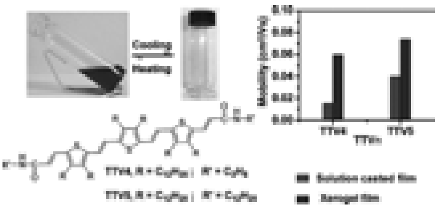


References:
[1] Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102 – 6211.
[2] Kumaki, J.; Sakurai, S.-i.; Yashima, E. *Chem. Soc. Rev.* **2009**, *38*, 737-746.
[3] Furusho, Y.; Yashima, E. *Macromol. Rapid Commun.* **2011**, *32*, 136-146.

Electronic Properties of Thiophene Based Supramolecular Polymers and Organogels

Ayyappanpillai Ajayaghosh
CSIR-National Institute of Interdisciplinary Science and Technology
(CSIR-NIIST), Trivandrum-695 019, India
ajayaghosh@niist.res.in

Supramolecular polymers are a class of nonconventional macromolecular architectures formed by the "bottom-up" self-assembly of organic molecules. While a large number of different molecular systems have been used as the building blocks, linear π-systems such as *p*-phenylenevinylenes, and *p*-phenyleneethynylenes are of interest due to the formation of supramolecular architectures of different size, shape and properties.[1] In this context, thiophene derived molecular building blocks have attracted the attention of chemists due to their inherent electronic properties such as electrical conductivity and charge carrier mobility. These self-assembled macromolecular structures are of interest to the design of organic electronic devices.[2] A challenge in this area is the control on the morphological features of the p-type assembly when mixed with n-type semiconductors. It has been found that the nature of the conjugated backbone and the attached functional groups play an important role in controlling the morphology and the electronic properties of the supramolecular structures. For example, the charge carrier mobility[3] of donor-acceptor type self-assemblies that form gels are found to be significantly different when compared to the ill-defined structures. Upon increasing the conjugation length they show very high conductivity.[4] We have demonstrated this with gel forming thienylenevinylenes which results in fibrous structures with high conductivity. These donor gelators upon mixing with an acceptor, PBI, forms self-sorted assemblies at molecular level and self-aligned fibers at supramolecular level, resulting in co-axial heterojunctions with enhanced photoconductivity and charge carrier mobility.[5] These systems may be appropriate to the design of bulk heterojunction photovoltaic devices. Details of these studies will be presented.



Reference:

[1] Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. *Chem. Rev.* **2014,** *114*, 1973.

[2] Babu, S. S.; Prasanthkumar, S.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 1766.

[3] Prasanthkumar, S.; Saeki, A.; Seki, S.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2010**, *132*, 8866.

[4] Prasanthkumar, S.; Gopal, A.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2010**, *132,* 13206.

[5] Prasanthkumar, S.; Ghosh. S.; Nair, V. C.; Sakei, A.; Seki, S.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2014**, *52*, 0000 (in press).

Tubular Supramolecular Polymer Brushes

Sébastien Perrier,[1,2]
[1]Department of Chemistry, The University of Warwick, CV4 7AL, UK
[2]Faculty of Pharmacy and Pharmaceutical Sciences, Monash University,
381 Royal Parade, Parkville, VIC 3052, Australia.
s.perrier@warwick.ac.uk

We recently developed a novel approach to engineer unique supramolecular polymer brushes (SPBs) which structure is controlled at the molecular level.[1-5] Our process relies on the conjugation of well-controlled polymeric chains to cyclic peptides (CPs) comprised of alternating L- and D- amino acids.[6,7] By assembling *via* β-sheet-like antiparallel hydrogen-bonding interactions, the cyclic peptides direct the assembly of the polymeric chains into polymer brushes. An additional feature of these systems is that they can also be used as nanotubes, due to the inherent internal channel formed by the stacking of the CPs. In this respect, they are unique in that they provide access to internal diameters of sub-nm dimensions (typically between 0.7 to 1.2 nm), since the channel size is based on the diameter of the peptide cycle. Our strategy to attach polymeric chains to cyclic peptides *prior* to assembly into polymer brushes provides structures that exhibit a unique combination of features, which make them ideal candidate to form functional supramolecular systems. The synergy between the cyclic peptide, which directs the formation of the SPBs and the polymer conjugate, which provides functionality, opens the route to a wealth of functional structures. The library of materials available is further increased by the modular approach that permits to mix conjugates within one SPBs structure (similar to a statistical copolymer). Such structures have found applications as drug delivery vectors for cancer therapy and transmembrane channels.[8]

References:

(1) Chapman R, Jolliffe KA, Perrier S *Polym Chem*, **2011**, 2, 1956; Chapman R, Jolliffe KA, Perrier S *Aust J Chem*, **2010**, 63, 1169; Poon CK, Chapman R, Jolliffe KA, Perrier S *Polym Chem*, **2012**, 3 (7), 1820-1826
(2) Chapman R, Warr GG, Perrier S, Jolliffe KA *Chem Eur J*, **2013**, DOI: 10.1002/chem.20120360
(3) Chapman, R.; Bouten, P. J. M.; Hoogenboom, R.; Jolliffe, K. A.; Perrier, S. *Chem. Commun.*, **2013**, 49 (58), 6522 – 6524
(4) Chapman, R.; Koh, M. L.; Warr, G. G.; Jolliffe, K. A.; Perrier, S. *Chem. Sci.* **2013**, *4*, 2581
(5) Chapman, R.; Jolliffe, K.A.; Perrier, S. *Adv. Mater.*, **2013**, 25, 1170–11724
(6) Ghadiri MR, Granja JR, Milligan RA, McReeDR, Khazanovich N, *Nature*, **1993**, 366, 324
(7) Ghadiri MR, Granja JR, Buehler, LK *Nature*, **1994**, *369*, 301; Fernández-López S, Kim H-S, Choi, EC, Delgado M, Granja JR, Khasonov A, Kraehenbuehl K, Long G, Weinberger DA, Wilcoxen K, Ghadiri MR *Nature* **2001**, 412, 452
(8) Danial, M.; My-Nhi Tran, C.; Young, P.G.; Perrier, S.; Jolliffe, K.A. *Nat. Commun.*, **2013**, 4:2780 DOI: 10.1038/ncomms3780

Responsive Polymer Assemblies

S. Thayumanavan
Department of Chemistry, University of Massachusetts,
Amherst, MA 01003, USA
thai@chem.umass.edu

Molecular designs that afford tunable supramolecular assemblies are of interest in a variety of applications, including catalysis and sensing. When these assemblies are nanoscopic in size and are responsive to specific stimulus, then the interests in these nanoscale scaffolds are even higher. We have developed macromolecule-based amphiphilic supramolecular assemblies, which not only exhibit these features, but also can bind guest molecules efficiently. We have also shown that these non-covalently bound guest molecules can be released in response to specific triggers. The molecular design principle is versatile enough to be adapted for physical, chemical, or biological stimuli. From a fundamental perspective, we divulge the structural factors that underlie the stimuli-responsive behavior of supramolecular assemblies. From an application perspective, the implications are numerous.

References:

[1] Guo, J.; Zhuang, J.; Wang, F.; Raghupathi, K.; Thayumanavan, S. *J. Am. Chem. Soc.* **2014**, *136*, 2220-2223

[2] Zhuang, J.; Chacko, R.; Amado Torres, D.; Wang, H.; Thayumanavan, S. *ACS Macro Lett.* **2014**, *3*, 1-5.

[3] Wang, F.; Gomez-Escudero, A.; Ramireddy, R. R.; Murage, Thayumanavan, S.; Vachet, R. W. *J. Am. Chem. Soc.* **2013**, *135*, 14179-14188.

[4] Amado Torres, D.; Garzoni, M.; Subrahmanyam, A.; Pavan, G. M.; Thayumanavan, S. *J. Am. Chem. Soc.* **2014**, *136*, In press.

[5] Yuan, C.; Raghupathi, K.; Popere, B. C.; Ventura, J.; Dai, L.; Thayumanavan, S. "*Chem. Sci.***2014**, *5*, 229-234.

[6] Fuller, J.; Raghupathi, K.; Ramireddy, R. R.; Subrahmanyam, A.; Yesilyurt, V.; Thayumanavan, S. *J. Am. Chem. Soc.* **2013**, *135*, 8947-8954.

[7] Gonzalez-Toro, D.; Ryu, J.-H.; Chacko, R.; Zhuang, J.; Thayumanavan, S. *J. Am. Chem. Soc.* **2012**, *134*, 6964-6967.

[8] Amado Torres, D.; Azagarsamy, M.; Thayumanavan, S. "*J. Am. Chem. Soc.* **2012**, *134*, 7235-7237.

[9] Wang, F.; Klaikherd, A.; Thayumanavan, S. *J. Am. Chem. Soc.* **2011**, *133*, 13496-13503.

[10] Yesilyurt, V.; Ramireddy, R.; Thayumanavan, S. *Angew. Chem. It. Ed.***2011**, *50*, 3038-3042.

When Nanoparticles meet Macromolecules…

Anil K. Bhowmick
Rubber Technology Center, Indian Institute of Technology, Kharagpur- 721302, India
anilkb@rtc.iitkgp.ernet.in

Nanoparticles (Nano) are highly researched topic in recent times. These are used in macromolecules (Macro) to improve their properties even at low loading. However, most of the nanoparticles are inorganic in nature or having distinct surface characteristics, while macromolecules are mostly organic. What happens when nano is forced to meet macro? Would the properties of nanoparticle change? How would macromolecules embrace these particles? Would there be an interface? How thin or thick would be this? Would the nanoparticles adsorb or delaminate immediately? If so, when and to what extent? What would be the driving force? If a third component is used to assist interaction, what would be its role? Could the compatibility between nano and macro be changed? What happens when macro and nano are bound by permanent forces? If they grow together right from their inception, would it make a difference? If macromolecule is attacked by a swelling agent, would the neighboring nanoparticles protect? How do they do? The present lecture would attempt to give answer to the above questions.

The nanoparticles that would be referred here are mostly nanoclay, silica, expanded graphite, carbon nanotubes, nanofibers, hydroxyapatite etc. The macromolecules are either polar or non-polar polymers having various structures. Together, under certain conditions, they form nanocomposites. Polymer nanocomposites reinforced with low volume fraction of nanofillers have attracted great interest due to their fascinating properties. Incorporation of nanofillers such as layered and fibrillated silicate clays, carbon nanotubes and nanofibers, calcium carbonate, metal oxides or silica nanoparticles into polymers improve significantly their mechanical, thermal, dynamic mechanical, electrical, aging, barrier, adhesion and flame retardancy properties. What is the mechanism? These also significantly alter rheological behavior of a polymer even at low filler loading. The properties of nanocomposites depend greatly on the structure of polymer matrices, nature of nanofillers, and the method by which they are prepared. It has been established that uniform dispersion of nanofillers in polymer matrices is a general prerequisite for achieving desired mechanical, rheological and physical characteristics. In this paper, some recent developments on polymer nanocomposites reinforced with various nanoparticles from our laboratory will be addressed. Finally, new insights into understanding the properties of these nanocomposites and morphology development will be discussed. Some of the applications of these nanocomposites, developed or currently under development will be highlighted in this lecture.

Multi-responsive polymers for sensors, logic gates and drug delivery

Richard Hoogenboom*
[1]Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry,
Ghent University, Krijgslaan 281-S4, 9000 Ghent Belgium
**Richard.hoogenboom@ugent.be*

The development of “smart” functional polymers that respond to changes in the environmental conditions has been the target of many research groups in recent years. Such ‘smart’ materials are promising candidates to be used in a wide range of applications varying from biotechnology, drug delivery, to optical sensing. Commonly, stimuli-responsive polymers are investigated that exhibit a solution phase transition upon application of an external stimulus, such as temperature, pH or concentration of a certain molecule.

In this contribution, we will discuss our efforts to further enhance the complexity and application potential of such smart polymeric materials by making them responsive to multiple stimuli, such as temperature and pH, temperature and light as well as temperature and ionic strength. The use of these materials will demonstrated for dual sensing applications, where a single UV-vis measurement of the polymer solution allows determination of both the pH and temperature of the solution [1]. In addition, an AND Boolean logic gate will be reported based gold nanoparticles coated with thermoresponsive polymers. The color of this solution only changes [output] when two stimuli are applied simultaneously, namely increasing the temperature [input1] and adding 50mMNaCl [input2] [2,3]. A further example will be discussed for pH induced drug delivery, for which a dual responsive polymer is developed that both undergoes dehydration and collapse upon heating and pH degradation under slightly acidic conditions [4,5]. The main advantage of this system is that it allows homogenous dissolution of the polymer at low temperatures, useful for conjugation to proteins as well as for drug loading, while it collapsed to shield the protein or entrap the drugs. The slow pH degradation in the collapsed state at 37 °C then induces slow release of the cargo.

References:
[1] C. Pietsch, R. Hoogenboom, U. S. Schubert, Angew. Chem. Int. Ed. **2009**, 48, 5653-5656.
[2] Z. Zhang, S. Maji, A. da Fonseca Antunes, R. De Rycke, Q. Zhang, R. Hoogenboom, B. G. De Geest,Chem. Mater. **2013**, 25, 4297-4303.
[3] V. R. De la Rosa, Z. Zhang, B. G. De Geest, R. Hoogenboom, submitted.
[4] Q. Zhang, N. Vanparijs, B. Louage, B. G. De Geest, R. Hoogenboom, Polym. Chem. **2014**, 5, 1140-1144.
[5] Q. Zhang, B. Louage, N. Vanparijs, B. G. De Geest, R. Hoogenboom, submitted.

Novel Romp-Based Polymers That Mimic Protein Activity

Gregory N. Tew
Polymer Science and Engineering Department, University of Massachusetts,
Amherst, 120 Governors Dr. Amherst, MA 01003

Our primary research aim is to create new materials using a combination of principles, many of which are inspired by biology.[1-10] In addition, the design of simple molecules that mimic the complex structures and functions of biology is at the heart of our work. In this presentation, we will illustrate some of these principles including facially amphiphilic polymers based on conformationally flexible backbones that are antimicrobial. These synthetic polymers mimic the essential physiochemical properties of natural host defense peptides, like Magainin and Defensin. We will discuss our newest results in which we have successfully mimicked that biological activity of protein transduction domains like HIV-TAT. The versatility of these synthetic mimics provides the opportunity to discover analogs with superior properties compared to their native sequences. Here we report the first detailed structure-activity relationship of a new PTD family of polymers based on a completely abiotic backbone.[7] The synthetic approach easily allows doubling the density of guanidine functional groups, which increases the transduction efficiency of the sequences. Cellular uptake studies on three different cell lines (HEK 293T, CHO, and Jurkat T cells) confirm that these synthetic analogs are highly efficient novel protein transduction domain mimics (PTDMs), that are more effective than TAT_{49-57} and nonaarginine (R9) and also highlights the usefulness of polymer chemistry at the chemistry-biology interface.

References:

[1] Zha, Y.; Disabb-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493.
[2] Som, A.; Reuter, A.; Tew, G. N. *Angew. Chem., Int. Ed.* **2012**, *51*, 980.
[3] Cui, J.; Lackey, M. A.; Madkour, A. E.; Saffer, E. M.; Griffin, D. M.; Bhatia, S. R.; Crosby, A. J.; Tew, G. N. *Biomacromolecules* **2012**, *13*, 584.
[4] Colak, S.; Tew, G. N. *Langmuir* 2012, *28*, 666.
[5] Zhang, K.; Lackey, M. A.; Wu, Y.; Tew, G. N. *J. Am. Chem. Soc.* **2011**, *133*, 6906.
[6] Zhang, K.; Lackey, M. A.; Cui, J.; Tew, G. N. *J. Am. Chem. Soc.* **2011**, *133*, 4140.
[7] Tezgel, A. O.; Telfer, J. C.; Tew, G. N. *Biomacromolecules* **2011**, *12*, 3078.
[8] Som, A.; Tezgel, A. O.; Gabriel, G. J.; Tew, G. N. *Angew. Chem., Int. Ed.* **2011**, *50*, 6147.
[9] Rathfon, J. M.; Cohn, R. W.; Crosby, A. J.; Tew, G. N. *Macromolecules* **2011**, *44*, 134.
[10] AL-Badri, Z. M.; Maddikeri, R.; Zha, Y.; Dobriyal, P.; Shunmugam, R.; Russell, T. P.; Tew, G. N. *Nature Comm* **2011**, *2*, DOI: 10.1038/ncomms1485.

Development of a Range of Functional Materials Based on Polyacryloyl Hydrazide

Anuj Kumar, Rewati Raman Ujjwal and Umaprasana Ojha*
Department of Chemistry, Rajiv Gandhi Institute of Petroleum Technology Rae Bareli

A range of functional materials with potential application in coatings, sensors, controlled delivery, and enhanced oil recovery were developed using polyacryloyl hydrazide (PAH) as the precursor. The swift reactivity of hydrazide functional moiety present in the polymer as a pendant group was effectively used to synthesize the above materials through hydrazide based click reactions. PAH was cured with BADGE epoxy crosslinker to form transparent and defect free resins with adequate tensile stress (2 – 40 MPa) and excellent ultimate elongation (8-50%). The resin possessing 1:2 (wt:wt) ratio of PAH:BADGE exhibited significantly higher UTS = 40 MPa compared to conventional resins (UTS = 31 MPa) synthesized using triethylene tetramine crosslinker. Synthesis and characterization of a series of injectable and stimuli responsive hydrogels based on PAH were accomplished using dimethyl 2,2'-thiodiacetate, acrylic acid, diethyl malonate and polyethylene glycol as the cross-linkers through chemical or dual cross-linking pathway. The yield stress of the gels synthesized using cross-linker concentrations up to 0.7 mol/L was observed above 10% strain and the viscosity decreased by at least two orders of magnitude upon increasing the shear rate by 1000 times suggesting the gels may be smoothly injected through the needle. The gels released up to 10–84% of the total encapsulated Rhodamine B in a controlled manner over a period of 120 h under physiological conditions. An azo dye with aldehyde functionality was covalently attached the polymer through hydrazone linkage under ambient conditions and the dye labeled polymers exhibited colorimetric pH sensing ability. Additional material development using PAH as the precursor is currently under progress.

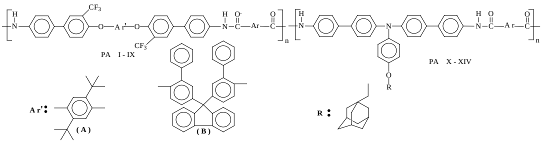
References:

[1] Kumar, A.; Samal, S.; Dash, R.; Ojha, U. J. Mater Chem. B, **2014**, 2, 7429-7439.
[2] Kumar, A.; Ujjwal, R. R.; Mittal, A.; Bansal, A.; Ojha, U. ACS Appl. Mater. Interface, **2014**, 6, 1855-1865.

Polymers containing bulky pendant groups: Superior membrane materials for gas separation application

Susanta Banerjee[1*], Parthasarathi Bandyopadhyay[1], Debaditya Bera[1]
1Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
*susanta@matsc.iitkgp.ernet.in

Membrane-based gas separation has established as a superior, economical and efficient separation technique over other conventional methods [1,2]. However, the inherent trade-off between gas permeability(P) and selectivity(α) for a pair of gases limits the large scale applications of this technique [3]. However, there is no strict "design rules" for the polymers to obtain optimal gas separation efficency. But, by incorportaing structural moiety which simultaneously enhanced the polymer rigidity and fractional free volumes (FFV), can be possible to achieve superior membrane materials for gas permeation applications. Among several other polymeric materials, aromatic polyamides (PAs) due to their excellent mechanical and thermal properties can be used as an alternative membrane materials . Considering the above facts, we have designed and synthesized several organo-soluble PAs containing different bulky groups like, fluorenone, adamantane, tert-butyl, triphenylamine (TPA)etc. All the membranes showed high thermal and mechanical stability. Basically, the effect of these bulky groups on gas permeation and diffusion processes of four different gases (e.g., CH4, N2, O2 and CO2) were investigated at 35 oC and at applied pressure of 3.5 bar. High gas permeability was obtained with PAs containing bulky tert-butyl group (PCO2 = 173 and PO2 = 44 Barrer), where as, rigid propeller shaped adamantane substituted TPA moiety yielded PAs with high permselectivity (PCO2/PCH4 = 63.00 and PO2/PN2 = 11.67). The incorporation of the fluorenone moiety effected in enhancement of both permeability and permselectivity(PCO2 = 67.42 and PO2 = 15 Barrer, PCO2/PCH4 = 50.69 and PO2/PN2 = 8.82).



References:

[1] Barillas, M. K.; Enick, R. M.; O'Brien, M.; Perry, R.; Luebke, D. R.; Morreale, B. D. J. Membr. Sci. **2011**, 372, 29–39.

[2] Yampolskii, Y. Macromolecules. **2012**, 45, 3298-3311.

[3] Robeson, L. M. J. Membr. Sci. **2008**, 320, 390-400.

Polyfluoroacrylate and its Nanocomposite via RAFT Polymerization

Nikhil K. Singha
Rubber Technology Centre, IIT Kharagpur 721302, India

Polyfluoroacrylates have high thermal stability and they are oleophobic as well as hydrophobic in nature. In this investigation tailor-made polyfluoroacrylate was prepared via reversible addition fragmentation chain transfer (RAFT) polymerization. In this case, random as well as amphiphilic block (Am-BCP) copolymers of heptafluorobutyl acrylate (HFBA) were prepared and their properties were studied. The Am-BCPs were used as surf-RAFT agent for emulsion polymerization of styrene. Polyfluoroacrylate/clay nanocomposites were also prepared via in situ RAFT polymerization. Importantly, these nanocomposites showed armored morphology in which nanoclay was exfoliated in the polymer matrix with the help of a reactive additive, as evidenced by TEM and DLS analyses. These composites showed much improved properties like, greater hydrophobicity, higher thermal stability etc. These polymer composites can have potential application in hydrophobic paints and coating materials.

Unnatural Information-containing Macromolecules

Jean-François Lutz*
Precision Macromolecular Chemistry, Institut Charles Sadron,
23 rue du Loess, 67034 Strasbourg, France
*jflutz@unistra.fr

Information-containing macromolecules are polymers that contain a message encrypted in their comonomer sequences. The archetypal example of such a polymer is DNA, which is used in biology to store genetic information.[1]However, DNA is certainly not the only polymer that can contain molecular information.[2] In principle, a string of information can be created in any copolymer using two comonomers defined intentionally as 0-bit and 1-bit (Figure 1). However, such polymers have to be monodisperse and perfectly sequence-defined. In addition, the message encoded in their chains should be easily read.

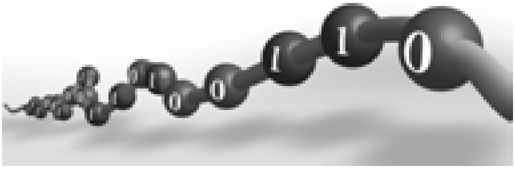


Figure 1. Schematic representation of an information-containing macromolecule containing a monomer-encoded binary code.Reprinted from reference 2.Copyright Nature Publishing Group 2014.

In this lecture, I will present recent achievements obtained in my laboratory for the synthesis of information-containing macromolecules. Recent progress in the field of sequence - controlled polymers allows synthesis of unnatural macromolecules with precisely controlled primary and secondary structures.[3-6] For instance, monodisperse sequence-defined polymers were prepared using chemoselective iterative strategies. Furthermore, the readability of these polymers will be presented. For instance the sequencing of unnatural sequence-defined copolymers by tandem mass spectrometry will be discussed.

References:

[1] Lutz, J.-F., Ouchi, M.; Liu, D. R.; Sawamoto, M. Science **2013**, 341, 628
[2] Colquhoun, H. M.; Lutz, J.-F. Nature Chem. **2014**, 6, 455-456
[3] Giuseppone, N.; Lutz, J.-F. Nature **2011**, 473, 40-41
[4] Lutz, J.-F. Nature Chem. **2010**, 2, 84-85
[5] Ouchi, M.; Badi, N.; Lutz, J.-F.; Sawamoto M. Nature Chem. **2011**, 3, 917-924
[6] Zamfir, M.; Lutz, J.-F. Nature Commun. **2012**, 3, 1138

Reversible Umpolung Interconversion of Growing Nature during Vinyl Polymerizations

Kotaro Satoh[1,2]* and Masami Kamigaito[1]
[1]Department of Applied Chemistry, Graduate School of Engineering,
Nagoya University, Nagoya, Japan
[2]Precursory Research for Embryonic Science and Technology (PRESTO)
Japan Science and Technology Agency (JST), Japan
*satoh@apchem.nagoya-u.ac.jp

Tremendous developments on livingor "controlled/living" polymerization technique have been achieved over the last couple of decades in polymer chemistry [1]. Now that livingpolymerizations have been developed through various intermediates, such as radical, cationic, anionic, or metal coordination polymerization, one can access numerous kinds of polymers with tailor-made macromolecular architectures, such as block and graft copolymers. However, since chain-growth polymerization of vinyl monomers is implemented via appropriate active species depending on the monomer structure, there are always limitations of polymerizable monomers inherent to the mechanisms. An efficient and versatile mechanistic transformation reaction between different polymerizations would be a candidate for developing unprecedented copolymers. In this work, we examined reversible mechanistic transformation between two different active species during controlled/living polymerizations by using dormant covalent bonds, which have been used just for controlling the propagation reaction. Especially, reversible mechanistic transformation of radical species was investigated from or into ionic species, such as cationic and anionic intermediates [2–4].

References:

[1] Handbook of Radical Polymerization;Matyjaszewski, K.; Davis, T. P., Eds.; Wiley-Interscience: New York, 2002.
[2] Kumagai, S.; Nagai, K.; Satoh, K.; Kamigaito, M. Macromolecules**2010**, 43, 7523-7531.
[3] Aoshima, H.; Uchiyama, M.; Satoh, K.; Kamigaito, M.Angew. Chem. Int. Ed.**2014**, 53, 10932-10936.
[4] Aoshima, H.; Satoh, K.; Kamigaito, M. ACSMacro Lett.**2013**, 2, 72-76.

Linear and block copolymers containing acrylate and styrene units via Controlled Radical Polymerization

Pavan Karkare, C. N. Murthy
Macromolecular Materials Laboratory, Applied Chemistry Department, Faculty of Tech. & Engg., PO BOX 51, Kalabhavan, The M. S. University of Baroda, Vadodara-390001, India
chivukula_mn@yahoo.com

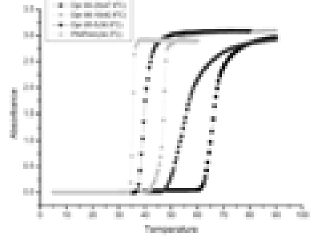
The atom transfer radical polymerization has been successfully applied for the synthesis of Poly(t-butyl acrylate-b-styrene-b-t-butyl acrylate) (PTBA-b-PS-b-PTBA) and poly(methyl methacrylate-b-t-butyl acrylate-b-polystyrene-b-t-butyl acrylate-methyl methacrylate) (PMMA-b-PTBA-PS-PTBA-PMMA) linear, tri and penta block copolymers in solution. Here, a difunctional polystyrene macroinitiator that contains bromide end-group was prepared by ATRP of styrene with dimethyl-2,6-dibromoheptanedioate (DMDBHD). The mole ratio of initiator (DMDBHD) and monomer has significant effect on the initiation of styrene polymerization which could be seen from the C13-NMR analysis of the polymers obtained. Certain ratios of the monomer:initiator gave a macroinitator where as in some cases an uncontrolled polystyrene with broad molecular-weight distribution was obtained. Similarly, linear, tri and penta block copolymers were successfully synthesized using activators generated in situ. Here, the synthesis of block copolymer was done using different types of reducing agents along with known ascorbic acid, triphenyl phosphine, 2-mercaptoethanol in solution, whereas L-cystine, D-glucose were carried out in mixed water/solvent system. The formation of block copolymers were confirmed by gel permeation chromatography (GPC), Nuclear magnetic resonance (13C-NMR), Differential scanning calorimeter (DSC) and Thermo Gravimetric analysis (TGA). These results will be discussed in this presentation.

References:
1. S. Kumar, J-S Lee, C. N. Murthy, Macromol. Res., **2011**, 19, 1022
2. T. Sabru, T. Pintauer, B. Mackenze, K. Matyjaszewski, J. Poly. Chem.**, 2002**, 40, 3153
3. H. Dong, K. Matyjaszewski, Macromolecules, **2008**, 41, 6868.

Synthesis, Characterization and Thermal studies of New thermo-responsive glycopolymers and their Copolymers with Poly (*N*-isopropylacrylamide)

Vaishali S. Shinde, Archana B. Dhumure, Anuja S. Kulkarni
Department of Chemistry, SavitribaiPhule Pune University
(Formerly University of Pune), Pune-411007
E-mail: vsshinde@chem.unipune.ac.in

Galactose containing glycomonomer was prepared by copper catalyzedazide-alkyne cyclo-additionreaction of 1,2,3,4 di-isopropylidene 6-azido D-galactoseand propargyl acrylate.The synthesized monomer was characterized by NMR, IR, MS techniques. The monomer was subjected for homopolymerization and copolymerization withN-isopropylacrylamide (NIPAm) in different compositionby free radical polymerization using 2, 2′-azobis-isobutyronitrile (AIBN)as an initiator.The composition of the copolymer was determined with1H-NMR spectroscopy. On acid hydrolysis, water-solubledeprotected polymers were obtained.The polymers were characterized by NMR,IR,TGA,DSC, GPC and thermal analytical techniques.The protectedand deprotected copolymers showed a sharp cloud-pointtemperature. A linear correlation was obtained betweenthe lower critical solution temperatures and the concentrationof glycomonomer in the copolymers.The TGA curvesclearly revealedtwo weight loss processesin the degradation behavior of the copolymers whose sharpness and intensity was varied with composition.DSC experiments were also run for deprotected polymers and the resulting Tg data are plotted.



Cloud point measurements of Glycopolymer

References:

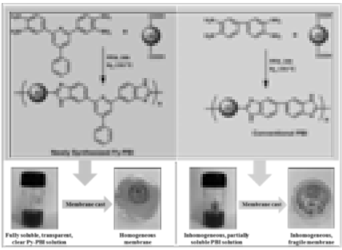
1) Vishwas Pawar, Vaishali. S. Shinde, J.Appl.Poly.Sci.,**2009**, 111, 2607.
2) Stacy Slavin, James Burns, David M.Haddelton, C.Remzi Becer,European polymer journal**2011**,47, 435-446.
3) Ahmed M.Eissa, Ezat Khosravi,European polymer journal**2011**,47, 61-69.

A new class of imidazole based polymers and block copolymers: Synthesis, structure and their use as proton conducting membrane in fuel cell

Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad, India
tusharjana@uohyd.ac.in

Since the inception, polybenzimidazole (PBI)has been studied enormously and utilized in numerous application areas owing to its superb thermal, mechanical and chemical stability, and excellent film forming capability makes it an attractive choice to be used as membrane.Despite the availability of myriad number of publications and patents on PBI, there are number of limitations in regard to the synthesis of PBI.A careful review and analysis of the literature reports unequivocally suggests that the most challenging bottlenecks which PBI chemistry is suffering at this point of time are the solubility, processability of PBI and the availability of suitable, inexpensive tetraamine monomer to synthesize the PBI frameworks.

Keeping these observations in the context of PBI synthesis, we have built various synthetic strategies to construct the PBI structures which not only fully resolved the existing limitations but also enhanced various properties especially proton conductivity of acid doped PBI membrane. I will discuss of our recent synthesis of a new tetraamine monomer called, *2,6-bis(3′,4′-diaminophenyl)-4-phenylpyridine (Py-TAB)*,which was found to be an efficient, readily accessible, inexpensive alternative monomer for synthesizing PBI and its copolymer with very high solubility and significantly high proton conducting behavior than the conventional PBI. Another example I will focus on is our synthetic route to make a series of *segmented block copolymers* of PBI with various structural motifs and block lengths. These block copolymers displayed considerably higher conducting behavior than random copolymers and hencebelieved to be more suitable for PBI based PEM for the use in fuel cell.



References:

1. Maity, S; Jana, T. Macromolecules **2013**, 46, 6814 – 6823.
2. Maity, S; Jana, T. ACS Appl. Mater. Interfaces **2014**, 6, 6851−6864.
3. Maity, S; Jana, T. Polym. Int. **2014**(DOI 10.1002/pi.4830)

Biodegradable Polymers from Renewable Resource Materials

Bhaskar B. Idage, Susheela B. Idage, Ashish K. Lele, S. Sivaram
Polymer Science & Engineering Division, National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune - 411 008, INDIA
E-mail: bb.idage@ncl.res.in

In recent decades, significant research has focused on reducing fossil-fuel dependence and building a more sustainable future, specifically through the use of polymers from renewable resources. One approach toward sustainability has been to investigate feedstock's that have short carbon cycles, such as plants, as alternatives to petroleum-based feedstock. A more elegant solution is to develop materials that both come from renewable resources and can be easily recycled into their feedstock, thus creating a cradle-to-cradle life cycle. However, the challenge is to develop biodegradable materials that can compete with conventional polymers in terms of processability, mechanical and thermal properties, durability and cost.

The environmental concerns have led to the development of biorenewable polymers with the ambition to utilize them at an industrial scale. Poly(lactic acid) and poly(hydroxyalkanoates) are semi-crystalline, biorenewable polymers that have been identified as the most promising alternatives to conventional plastics. However, both are inherently susceptible to brittleness and degradation during thermal processing. In the present work, we discuss several approaches to overcome these problems to create a balance between durability and biodegradability. For example, the preparation of copolymers and blends can increase ductility and the thermal-processing window. Furthermore, chain modifications such as branching or crosslinking, the processing techniques such as fiber drawing or annealing, or additives such as plasticizers or nucleating agents can improve the mechanical properties and prevent the thermal degradation during processing.

References:
[1] Tsui A.; Wright Z.C.; Frank C.W. Annu. Rev. Chem. Biomol. Engg. **2013**, 4, 143-170.
[2] Tschan M.J.L.; Brule M.; Haquette P.; Thomas C.M. Polym. Chem. **2012**, 3, 836-851.
[3] Auras R.A.; Lim L.T.; Selke S.E.M.; Tsuji H.; Poly(lactic acid) : Synthesis, Structures, Properties, Processing and Applications, **2010**, John Wiley and Sons, USA.

Photo-Induced Organotellurium-Mediated Radical Polymerization (TERP) and Radical Coupling Reaction

Shigeru Yamago
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, JAPAN
yamago@scl.kyoto-u.ac.jp

Organotellurium compounds are activated under photo irradiation reversibly generating the corresponding carbon-centered radicals.[1] This photochemical activation was successfully applied to organotellurium-mediated living radical polymerization (TERP);[2] the polymerization proceeded in a controlled manner by applying low intensity light source under mild conditions.[3] On the other hand, radical coupling reaction (RC) of living polymers prepared by TERP in the presence of dienes and styrenes as coupling agents (*c*) selectively took place by employing high intensity light source (Scheme 1).[4]Due to the high versatility of TERP and high compatibility of functional groups, symmetric mid-chain functional polymers from various monomers with rich functionalities were successfully synthesized in a controlled manner. Synthetic aspects and application of the conditions to elucidate the mechanism of radical polymerization will be discussed.

Scheme 1. Synthesis of structurally well-controlled telechelic, mid-chain functionalized polymers by successive TERP and RC

References:

[1] Yamago, S.; Miyazoe, H.; Yoshida, J. *Tetrahedron Lett.***1999**, *40*, 2339.

[2] a) Yamago, S. *J. Polym. Sci. Part A: Polym. Chem.***2006**, *44*, 1. b) Yamago, S. *Chem. Rev.***2009**, *109*, 5051.

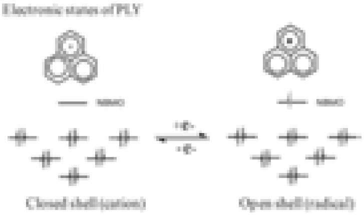
[3] a) Yamago, S.; Ukai, Y.; Matsumoto, A.; Nakamura, Y. *J. Am. Chem. Soc.***2009**, *131*, 2100. b) Nakamura, Y.; Yamago, S. *Beilstein J. Org. Chem.***2013**, *9*, 1607. c) Yamago, S.; Nakamura, Y. *Polymer*, **2013**, *54*, 981.

[4] a) Nakamura, Y.; Arima, T.; Tomita, S.; Yamago, S. *J. Am. Chem. Soc.***2012**, *134*, 5536. b) Nakamura, Y.; Arima, T.; Yamago, S. *Macromolecules***2014**, *47*, 582.

Switching Open to Closed State of Phenalenyl: From Polymerization Catalysis to Spin Electronics

Swadhin Mandal
Department of Chemical Sciences, Indian Institute of Science
Education and Research - Kolkata, Mohanpur-741246, India
E-mail: swadhin.mandal@iiserkol.ac.in

Open shell phenalenyl chemistry started more than half century back and the first solid state phenalenyl radical was realized only about a decade ago highlighting the synthetic challenges associated in stabilizing carbon based radical chemistry though it has great promise as building blocks for molecular electronics and multifunctional materials. Alternatively, we developped in recent years that a stable closed shell phenalenyl has great potential as this can be utilized to create in situ open shell state by external spin injection.[1-3]In this way, we have prepared a new route to closed shell phenalenyl based organometalliccatalysts for ring opening polymerization of various cyclic esters which can further be extended to a variety of organic transformations,[1] organocatalysts[2] and molecular spin memory device[3]. In this presentation, I shall emphasize how our initial understanding of closed state of phenalenyl influenced the outcome in polymerization catalysis and further developped to a new route to design novel materials for useful application.



References:

[1] (a) Mukherjee *et al.Chem. Eur. J.,***2012**, *18*, 10530–1054 (b) Sen*et al.Chem. Eur. J***2012**, *18,* 54-58. (c) Sen*et al.Dalton Trans.,***2013**,*42*, 1893–1904; (d) Mukherjee *et al.Scientific Reports,***2013**, *3*, 2821*;* (e) Mukherjee*et al.Organometallics,* **2013** *32*, 7213–7224.

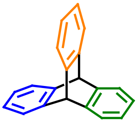
[2] Roy *et al.ACS CatalysisASAP***2014.**

[3] Raman*et al.Nature,* **2013**, *493*, 509–513.

Synthesis and Characterization of Triptycene Based Polymer

Snehasish Mondal and Neeladri Das*
Department of Chemistry, IIT Patna
*neeladri@iitp.ac.in

Iptycene is a class of molecules wherein several arene rings are connected together by a [2.2.2] bicyclic bridge. Triptycene is the simplest member (having three benzene ring) of this family of compounds that was first synthesized by Bartlett and coworkers in 1942.[1] Due to its highly symmetric three dimensional (3D) rigid structure, triptycene has been extensively used in various research fields that include but is not limited to supramolecular chemistry, nanotechnology (molecular machines), and polymer chemistry.[2-5] Swager and others have extensively explored polymers bearing triptycene scaffold.[6] Incorporation of 3D triptycene motif in polymer backbone was found to enhance the properties of polymers with respect to thermal stability, organosolubility, mechanical strength, dielectric properties, and optical properties.[2-6]



Triptycene

Herein, various polymers synthesized from triptycene monomers will be described. For the first time, we have synthesized non-conjugated but fluorescent polymers bearing triptycene motif in polymer backbone. The interaction of fullerene C_{60} with these polymers will be discussed.[7] Synthesis and characterization of wholly-aromatic and semi-aromatic polyamides containing triptycene units will also be illustrated. The effect of hydrogen bonding and interchain interaction on the polymer morphology will be discussed. Finally, a series of triptycene based and triazole bridged organosoluble polymers will be depicted. Application of these triazole linked triptycene based polymers in sensing nitroaromatic compounds will be shown.

References:

1. Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.
2. Jiang, Y.; Chen, C.-F. *Eur. J. Org. Chem.* **2011**, *32*, 6377-6403.
3. Chen, C.-F. *Chem. Commun.* **2011**, *47,* 1674–1688.
4. Zhao, L.; Li, Z.; Wirth, T. *Chem. Lett.* **2010**, *39*, 658-667.
5. Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301–3315.
6. Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1181–1189.
7. Mondal, S.; Chakraborty, S.; Bhowmick, S.; Das, N. *Macromolecules* **2013,** *46*, 6824–6831.

Probing the reactivity of 1,1-disubstituted functional olefin in insertion copolymerization

Shahaji S. Gaikwad[2], Satej S. Deshmukhand Samir H. Chikkali[1]*
[1]Polyolefin Lab, Polymer Science and Engineering Division, CSIR-National
Chemical Laboratory, Pune, India
**s.chikkali@ncl.res.in*

Polyethylene (PE) is inherently a long-chain of hydrophobic methylene repeat units without any functional groups on the backbone. This partly limits the potential application of PE in adhesives, binders, paints, printing ink, dying etc. Incorporation of even small amount of functional groups in PE can significantly enhances these material properties and can further broaden the PE application window. Recently, significant progress has been made by using phosphine-sulfonate palladium catalysts in copolymerization of ethylene(ET) and several polar monomers including acrylic acid, esters, acrylonitrile, vinyl ethers, ketone and vinyl halides.[1] Despite this progress 1,1-disubstituted functional monomers remain elusive and unexplored. The talk will present the first copolymerization ET with Ethyl-2-cyanoacryalate (ECA) using acetonitrile ligated phosphine-sulfonate palladium complex (**3**) leading to functional copolymers.[2]

References:

[1] Gaikwad, S. R.; Deshmukh, S. S.; Chikkali, S. H.J. Polym. Sci. Part A: Polym. Chem. **2014**, 52, 1 – 6.
[2] Gaikwad, S. R.; Chikkali, S. H.Insertion copolymerization of functional olefins catalysed by phosphine sulphonate complex, CSIR- National Chemical laboratory, Pune, Provisional filing no. 2587DEL2014-09-11, Provisional filing date : 10th Sept.**2014**.

Stimuli-Responsive Formation/Transition/Disintegration of Polymer Nanoparticles: Investigation by Energy Transfer and Potential Application as Drug Delivery Vehicles

Rakesh Banerjee, Chiranjit Maiti, Saikat Maiti, Dibakar Dhara*
Department of Chemistry, Indian institute of Technology Kharagpur,
West Bengal 721302, India
Email: dibakar@chem.iitkgp.ernet.in

Formation, disintegration and transition of polymeric nanoparticles in response to external stimuli are important phenomena that have been widely explored for a variety of biomedical applications. In this presentation, we describe the RAFT-mediated synthesis of various di/tri-block copolymers that spontaneously formed various self-assembled nanoparticles, like micelles and vesicles, in aqueous medium in response to external stimuli such astemperature and pH.Formation of these nanoparticles was confirmed by different characterization techniques viz. transmission electron microscopy, dynamic light scattering and steady-state fluorescence measurements.The stimuli-responsive formation-degradation process or structural changes were monitored by following the energy transfer between various donor-acceptor pairs embedded in the polymeric nanoparticles and/or by release of dye/drug molecules from nanoparticles.

The copolymers were further utilized to synthesize core cross-linked nanoparticles by reacting with two and four-arm cross-linkers by applying three different types of organic reactions including green chemistries. The encapsulation efficiencies of these nanoparticles for different drug and dye molecules were investigated and found to be dependent of pH and temperature.The core cross-linked nanoparticles were shown to be non-toxic and capable of undergoing pH-induced controlled degradation that reflected in the controlled release of drug/dye molecules that werepre-loaded in the core.Thus, we demonstrated various possibilities of synthesizing polymeric nanoparticles potentially useful for controlled drug delivery applications.

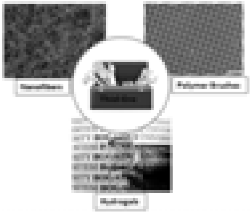
Reference:

[1] Maiti, C.; Dey, D.; Mandal, S.; Dhara, D. *J. Phys. Chem. B.***2014,***118*, 2274-2283.
[2] Banerjee, R; Dhara, D. *Langmuir* **2014**, *30*,4137–4146
[3] Banerjee, R.; Maiti, S.; Dhara, D. *Green Chem*. **2014**, *16*, 1365-1373.

Design of Novel Functional Polymeric Materials using Thiol-based Conjugations

Amitav Sanyal*
[1]Department of Chemistry, Bogazici University, Istanbul, Turkey
[2]Center for Life Sciences and Technologies, Bogazici University, Istanbul, Turkey
**amitav.sanyal@boun.edu.tr*

Efficient methodologies for fabrication and functionalization of reactive polymeric materials based on ‘click’ type transformations have become increasingly prevalent due to the simplicity and versatility of these reactions. Appropriately designed reactive polymeric materials find various biomedical applications such as substrates for sensing applications, scaffolds for tissue engineering and drug delivery vehicles. Over the past several years our research has focused on the design of novel polymeric platforms such as hydrogels, polymer brushes, nanofibers and nanoparticle coatings that allow functionalization via efficient thiol-based conjugations. We recently utilized thiol-ene reactions to obtain cyclodextrin containing hydrogels that can be used for controlled drug delivery. The presentation will outline several examples where thiol-based conjugation chemistry is utilized to fabricate and functionalize polymeric materials.



Acknowledgement: The author thanks The Scientific and Technological Research Council of Turkey (TUBITAK 114Z139) for financial support.

References:

[1] Arslan, M.; Gevrek, T. N.; Lyskawa, J.; Szunerits, S.; Boukherroub, R.; Sanyal, R.; Woisel, P.; Sanyal, A. Macromolecules **2014**, 47, 5124.
[2] Gevrek, T. N.; Bilgic, T.; Klok, H.-A.; Sanyal, A. Macromolecules **2014**, 47, DOI:10.1021/ma5015098.
[3] Arslan, M.; Gevrek, T. N.; Sanyal, A.; Sanyal, R. Eur. Polym. J. **2015**, 62, DOI:10.1016/j.eurpolymj.2014.08.018.
[4] Arslan, M.; Gevrek, T. N.; Sanyal, A.; Sanyal, R. RSC Advances **2014**, 4, 57834.

Block copolymer–small molecule supramolecular assembly in thin film for creating large scale controllable periodic arrays of nanomaterials

Pallavi Gupta, Koomkoom Khawas and Biplab Kumar Kuila*
Center for Applied Chemistry, Central University of Jharkhand
Brambe, Ranchi-835205, Jharkhand, India
biplab.kuila@yahoo.com

Supramolecular assembly (SMA) of block copolymer and small molecule has received enormous research interest due to their formation of fascinating set of periodic structures in the nanoscopic length scale [1.2].Block copolymer supramolecular assembly where a low molar mass additive is associated with one of the blocks by noncovalent interactions is a simple and powerful technique to introduce new functionalities into the block copolymer system as well as fine-tune its morphology [3].The advantages of using supramolecular system over the pure block copolymer are easy tuning of morphology by changing the small molecule composition, introduction of new functionality into the block copolymer layer by using non-covalent interaction and simple removal of the minor component by dissolution from the block copolymer layer to transform it into a porous nanotemplate. In the last few years, we have extensively studied block copolymer–small molecule supramolecular assembly in thin film and developed some novel SMA systems mostly with an aim to fabricate polymer nanotemplates for creating large scale periodic arrays of nanomaterials.

References:
[1] Ikkala, O. ten Brinke, G. Chem. Commun. **2004**, 2131.
[2] Kuila, B. K. Gowd, E. B. Stamm, M. Macromolecules **2010**, 43, 7713.
[3] Sidorenko, A. Tokarev, I. Minko, S.; Stamm, M. J. Am.Chem. Soc. **2003**, 125, 12211.

Renewable Feedstock for the Synthesis of Functional Materials

Ramaswamy Nagarajan[1]*, Jayant Kumar[2], Zhiyu Xia[1], Weeradech Kiratitanavit[1], Ankita Singh[1], Zarif Farhana Mohd. Aris[1]
[1] Department of Plastics Engineering,
[2] Department of Physics and Applied Physics, Center for Advanced Materials,
University of Massachusetts Lowell,
Lowell, MA 01854 USA

The development of macromolecules has often been driven by the need for new functionality that has not been achieved using existing materials and composites. Materials design and development is also being increasingly driven by sustainability considerations.

Biological systems reveal elegant molecular design that meet functionality as well as degradability/end-of-life considerations. Biobased materials provide valuable insights into structure property-relationships that can help us fashion the next generation of functional materials. They can also serve as a renewable hydrocarbon source. This concept is illustrated with two classes of alternative bio-inspired safer materials.

First, the development of non-halogenated flame retardant materials inspired by fire resistant biomass will be presented. We have demonstrated that naturally occurring phenols can be oligomerized to yield additives that have excellent char forming characteristics. One of the raw materials used is cardanol - a waste byproduct of the cashew nut industry with no competing food value.

Biobased and bio-inspired surfactants are the second class of materials that will be discussed. Non-ionic surfactants such as nonylphenol ethoxylates (NPE), are being phased out due to their aquatic toxicity. Inspired by oil eating bacteria, A. Calcoaceticus, also known as RAG-1, we have developed a new class of polysaccharides based surfactants. These surfactants are derived from fruit waste and exhibit surface activity similar to that of NPE. Here again, bio-inspiration had lead to the conversion of a waste product into a sustainable and safe alternative surfactant.

The benefits for the pursuit of materials research using renewable feedstock transcends sustainability considerations and reveals exciting possibilities through bio-inspiration, rendering it worthwhile from both scientific and commercial perspective.

Highly branched stimulus responsive polymers

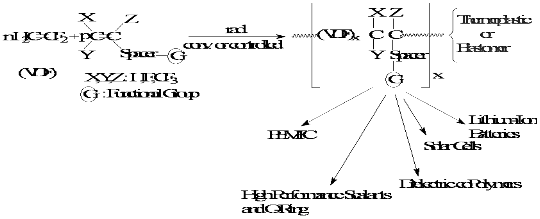
Stephen Rimmer*[1], Thomas Swift[1], Richard Hoskins,[1] Richard Penderleith,[1]
Pavintorn Teratanatorn[1], Sheila MacNeil,[2] Ian.Douglas[3]
[1]Polymer and Biomaterials Chemistry Laboratories, Department of Chemistry. University of Sheffield, Sheffield, UK S3 7HF.
[2]Department of Materials Science & Engineering, The Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield, S3 7HQ, UK.
[3]School of Clinical Dentistry, UniVersity of Sheffield, Sheffield S10 2TA, U.K.
*s.rimmer@sheffield.ac.uk

Highly/hyper branched polymers have a large number of end groups that are positioned towards the outside of the polymer coil in solution. In this respect they are very different to linear functional polymers with functional groups along the main chain. These structural features mean that in water if highly branched polymers become desolvated (in a coil-to-globule transition) it is possible to maintain availability of the functional groups on the outside of the desolvated globules. On the other hand, when linear polymers become desolvated the functional groups are masked by the desolvated chain segments. We have used this phenomenon to design poly(N-*iso*propyl acrylamides) that respond, in a coil-to-globule transition, to binding bacteria. The response on binding to bacteria occurs as the solvation of the functional end groups is perturbed on binding. The degree of branching in these polymers is critically related to the nature of the response to bacteria and, for the most active polymers, we present evidence for a core shell type structure composed of a desolvated core and a swollen shell. It is the interactions of the end groups with the bacteria that produce a coil-to-globule transition on binding. The data suggest that the end groups penetrate into the coil for a limited distance and that binding of certain cellular targets results in a segmental conformational change rather than full transition from coil to globule. High sensitivity differential calorimetry shows that the main transition may not shift with binding but instead secondary events occur in which segments pass through a coil-like confirmation to a desolvated segmental coil.

Recent Advances in the Controleld Radical Copolymerization of Fluoroalkenes

Bruno Ameduri,
Department of Chemistry, Institute Charles Gerhardt
Ecole Nat. Sup. Chime de Montpellier, 34296 Montpellier, France
*bruno.ameduri@enscm.fr

Fluorinated polymers[1] are a remarkable polymers because of their thermal, chemical and oxidative stability making them useful in specific applications such as non-sticky paints and coatings, chemically resistant O-rings and seals, membranes for fuel cells, separators and binders for Lithium ion batteries, wires and cable insulation, and so on. They are mainly synthesized by radical (co)polymerization of fluoroalkenes. Among fluorinated polymers, poly(vinylidene fluoride) (PVDF)[2] is one the most often used since it can be synthesized according to usual radical pathways, just like VDF containing–copolymers that lead to many applications, as displayed in Scheme 1.



Scheme 1: radical copolymerization of VDF with synthesized fluorofunctional monomers

Only four main routes of CRP of fluorinated alkenes are possible so far[3]: iodine transfer polymerization (ITP)[4] that this the oldest by far, MADIX[5], and more recently, that involving specific transition metal complex under photoinitiation.[6] More details on both first strategies will be applied on the radical copolymerization of vinylidene fluoride with other fluoromonomers opening various applications ranging from surfactants to fuel cell membranes.

1. Ameduri, B. and Boutevin B., Well Architectured Fluoropolymers: Synthesis, properties and Applications, Elsevier, Amsterdam, 2004.
2. Ameduri, B.; *Chem. Rev.,* **2009**, *109*, 6632-6686.
3. Ameduri, B; *Macromolecules* **2010**, *43*, 10163-10184.
4. a) Tatemoto, M.; The first Regular Meeting of Soviet-Japanese Fluorine Chemists, Tokyo, February 15-16, **1979**; b) Tatemoto; M.; US **1979**/4158678, (assigned to Daikin Kogyo Ltd).
5. a) Patil, P.; Ameduri, B. *Polym. Chem.* **2013**, *4*, 2783-2799; b) Kostov, G. ; Boschet, F. Buller, J.; Badache, L. ; Brandtstadter, S. *Macromolecules*, **2011**, *44*, 1841-1855.
6. Asandei A. *et al*. *J. Amer. Chem. Soc.,* **2012**, *134*, 6080-6083.

WAXS/SAXS/USAXS investigation of orientation induced by deformation in semi-crystalline polymers

Frédéric Bossan[1]*, Sandra Desvergne[1], Pierre Panine[1],
Manuel Fernandez-Martinez[1], Yongfeng Men[2], Yaotao Wang[2]
[1]R & D, Xenocs, Sassenage, France - Frederic.Bossan@xenocs.com
[2]State Key Lab Polym. Phys. Chem, Changchun Inst. Appl. Chem, Changchun, China

During the industrial transformation, most polymers are involved in specific processes resulting in the macromolecular chain orientation. Such orientation is appearing from the local phase to the mesophase and sometimes even up to the macroscopic phase. Small Angle X-Ray Scattering (SAXS) is a technique well suited for investigating nano-materials and nano-structures of polymers. Information is collected on sample structure parameters such as particle shape or size, size distribution, orientation, surface to volume ratio… in the range from 1 nm to beyond 100 nm. Moreover, orientational functions can be derived from 2 dimensional x-ray patterns. Length-scales down to 0.1 nm can also be investigated in combination with Wide Angle X-ray Scattering (WAXS). In the case of samples with internal structures larger than 200 nm, USAXS (Ultra Small Angle X-Ray scattering) experimental conditions are required. USAXS allows to access heterogeneities about some hundreds of nanometers while providing the opportunity to investigate the large-scale structure evolution during the deformation of polymeric materials [1].

The progress in the performances of x-ray components and subsequent assembly offers such characterization methods in the laboratory. Hence, investigation of an injected semicrystalline polymer has been performed, emphasizing the nanostructure orientation and processing relationships. Further, recent results obtained on in-situ stretched Polybutene-1 (PB-1) [Figure 1] illustrate the capability to perform lab measurement equivalent to Synchrotron USAXS [2] highlighting microscopic structural evolution and macroscopic strain-whitening phenomenon correlation.

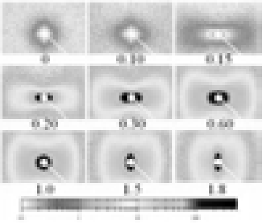


Figure 1: 2D-USAXS patterns of PB-1 crystallized at 60°C stretched at 30°C as a function of engineering strain - 50s exposure time. Stretching direction horizontal. Data courtesy of Pr. Men and Y. Wang

References:

[1] Y. Men et al, Macromolecules **2004** 37, 9481.

[2] Y. Men et al, under submission **2013**

Imaging & Characterization of Polymers using TEM and SEM

Dr. Michael Felsmann, Gatan GmbH
Munich, Germany

Polymers can be characterized using different methods in TEM and SEM. While the Cryo TEM allows to examine and study the morphology of polymers, Spectroscopic technique such EELS can give additional information on the carbon bonding by showing different variations in the near edge fine structure of the polymers. Another spectroscopic technique, is the analysis of cathodoluminescence (CL) spectrum in the SEM, which enables the identification of many organic compounds through spectroscopy of the light emitted. Another approach is the reconstruction in 3 dimensions and characterisation of large area, using serial block face scanning electron microscopy.

These different methods will be explained with illustrative examples.

Hyperbranched Polymers with High Refractive Index Prepared by Metal-Free Thiol-Yne Click Polymerization

Qiang Wei[1,2,3], Robert Pötzsch[1,2,3], Xiaoling Liu[1,2], Hartmut Komber[1], Doris Pospiech[1], Anton Kirly[1], Brigitte Voit[1, 2, 3*]
[1]Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany
[2]Chair of Organic Chemistry of Polymers, TechnischeUniversität Dresden, Germany
[3]Center for Advancing Electronics Dresden (cfaed), TU Dresden, Germany
*voit@ipfdd.de

The growing demand for High Refractive Index (HRI) polymers has attracted intense attention from industry and academia, due to their excellent performance as OLED encapsulates and in other optoelectronic areas. According to Snell's Law of Refraction, HRI polymers, when applied as OLED's encapsulates, can expand the critical angle of incident ray from OLED's inner layers and therefore enhance the external efficiency ($\boldsymbol{\eta}_{\mathrm{EL}}$). Up to date, RI values of most HRI polymers (RI≤1.76)stand still below expectation. Moreover, HRI polymers with residual metallic catalysts also have the limitations to optical and biomedical applications.

In the present study, in order to obtain HRI polymers without metal residues, 1,3,5-tris(naphthylethynyl) benzene with two aromatic moieties (naphthalene and benzene) was designed as B3 monomer. Through "A2+B3" metal-free thiol-yne click polymerization, B3 monomer could react efficiently with benzene-1,4-dithiol (A2 monomer) in three different molar ratios (B3 : A2 = 1:1, 2:3, 1:2), yielding hyperbranched polymers PIa, PIb and PIc respectively. For the produced polymers, due to the steric effects of the bulk naphthalene moiety, only mono-adducted structures of thiols and alkynes were regioselectively generated. At the same time, the characteristic of branched structure ensured these polymers to exhibit good solubility and thereafter processibility. Furthermore, the high proportions of aromatic and sulfide groups, also endowed PIa, PIb and PIc with both high RI values (1.7839, 1.7778, 1.7683 respectively) and highT_gs (141, 172, 147). Besides, in the range of visible light, no absorbance was observed in these polymers' solutions and films. With all these thermal and optical properties, the obtained HRIhyperbranched polymers are novel promising materials to be applied as OLED encapsulates or in other optoelectronics areas.

References:

[1] J.-g. Liu and M. Ueda, Journal of Materials Chemistry **2009**, 19, 8907.
[2] Z. B. Wang, M. G. Helander, QiuJ, D. P. Puzzo, M. T. Greiner, Z. M. Hudson, WangS, Z. W. Liu and Z. H. Lu, Nat Photon **2011**, 5, 753-757.
[3] J. M. Ziebarth, A. K. Saafir, S. Fan and M. D. McGehee, Advanced Functional Materials **2004**, 14, 451-456.
[4] M. Stroisch, T. Woggon, C. Teiwes-Morin, S. Klinkhammer, K. Forberich, A. Gombert, M. Gerken and U. Lemmer, Optics Express **2010**, 18, 5890-5895.
[5] C. K. W. Jim, A. Qin, J. W. Y. Lam, F. Mahtab, Y. Yu and B. Z. Tang, Advanced Functional Materials **2010**, 20, 1319-1328..
[6] B. I. Voit and A. Lederer, Chemical Reviews **2009**, 109, 5924-5973.

Novel bench scale slurry propylene polymerization technique: Evaluation of Ziegler Natta catalyst under severe conditions

Harshad R. Patil*, Priyanshu B. Vyas
Reliance Research and Development Centre, Reliance Corporate Park,
Reliance Industries Limited, Ghansoli, Mumbai
*Harshad.Patil@ril.com

Polypropylene (PP) is second largest polymer globally in term of volume.Currently PP is produced by three major propylene polymerization processes – slurry, gas and bulk polymerization. Magnesium dichloride supported titanium Ziegler Natta (ZN)catalyst is used commercially for majority of PP production.Gas phase polymerization has economic advantage [1-3] among peers. However, catalyst system used for gas phase polymerization process has to be operated in prescribed operating temperature. Increasing reaction temperature can lead to run away reaction and can result into agglomerated product formation as well as upsetting large scale reactor. It is therefore imperative to have laboratory scale slurry polymerization technique to measure catalyst performanceunder run away conditions.In the prior art method, PP catalyst performance is evaluated through bench scale polymerization experiments carried out at 70°C, 90°C and 110°C or by using normalized method [4].

We have developed single step slurry polymerization technique by changing reaction parameters to evaluate catalyst under severe condition.Three catalysts [5]– low (3.1 KgPP/gcat), medium (6.3 KgPP/gcat) and high activity (9.6 KgPP/gcat)- were evaluated at 70°C in 4 L jacketed stirred stainless steel reactor to create base data. Novel technique included purposefully avoiding the removal of heat from the reactor to create severe condition like run away reaction. When catalyst A is subjected to sever conditions, it was observed that maximum temperature reached to 77.5°C with 7.5 °C rise. Catalyst B showed89°C with 19° C rise while Catalyst C indicated maximum 102 °C with 32°C rise (Fig. 1). CAT A, B and C have taken 50, 15 and 10 min timedemonstrating high activity catalyst is prone to achieve high temperature very fast.This technique gives quantitative measure to understand severity of magnesium supported titanium ZN catalyst.

Fig 1: Polymerization temperature profile of Catalyst A, B and C under run away conditions

References

[1] Vyas,P. B.; Kaur, S.; Patil, H.R.; Gupta, V. K. J. Polym. Res. **2011**, 18, 235-239.
[2] Qiao, J.; Guo, M.; Wang, L.; Liu,D.; Zhang, X.; Yu, L.; Songab, W.; Liu, Y. Polym. Chem. **2011**,2,1611-1623.
[3] Cai,P.; Chen, L.; Egmond, J.; Tilston, M. Particuology**2010**, 8, 578-581.
[4] Chen, L.;Campbell, J.; Richard, E.United States Patent 7989383, **2011**.
[5] Gupta, V.K.; Patil, H. R.; Naik, D.G., United States Patent 8283424, **2012**.

Preparation and applications of Polythiophene based dual stimuli responsive graft copolymers: Effect of graft chain hydrophobicity

Dhruba P. Chatterjee[1], Sandip Das[2] and Arun K. Nandi[2]
[1]Dept. of Chemistry, Presidency University, Kolkata, [2] Polymer Science Unit, IACS, Kolkata
dhruba.chem@presiuniv.ac.in

Design and synthesis of water soluble smart polymeric materials have emerged as a very important area of research. These materials find diversified applications as solar cells (1), chemical or biological sensors (2), molecular thermometers (3) logic gates (4) etc. applications as chemical or biological sensors require water soluble polymeric systems where mostly in the literature optical signals have been chosen as output. This is due to the high degree of sensitivity of optical signals coming from single molecular level (5). In this respect polymers are proved to be better candidates than monomeric systems due to signal amplification. Different strategies including attachment of small amount of fluorescent moieties on the polymer backbone, preparation of block copolymers having one of the constituting block containing pendant fluorescent group have been adopted in this respect. However, one very interesting strategy has been the grafting of stimuli responsive block copolymers on the fluorescent active conjugated backbone polymer like polythiophene. Grafting on polythiophene hinders aggregation of polythiophene chains and therefore changes in optical response of polythiophene systems may be linearly corroborated with the changes effected on grafted polymeric chain conformations by variation in the system conditions (input signals). Polythiophene contains π electron excess thiophene units therefore; they interact electronically with the π deficient species (donor -acceptor interactions) say polynitro compounds (explosives!). This report deals with synthesis and characterizations of water soluble polythiophene based graft copolymeric systems where grafted chains on polythiophene backbone show dual stimuli response against temperature and pH. Synthesized materials show operation like 'AND' logic gate using temperature and pH as two inputs and fluorescent optical signal as output. Grafted chains constituted random block copolymers of thermo sensitive polydiethyleneglycolmethylether metrhacrylate (PDEGMEM) showing LCST at about 210C in aqueous solution and polydialkylaminoethyl methacrylate as pH sensitive block. Effect of introduction of various alkyl groups on the polydialkylaminoethyl methacrylate has been studied in respect of the application of the graft copolymeric materials as logic gates or sensors for electron deficient polynitro compounds.

References:

1) Routh P, Das S, Shit A, Bairi P, Das P and Nandi AK, ACS Appl Mater Interfaces **2013,** 5: 12672-12680.
2) Chen L, McBranch DW, Wang H-L, Helgeson R, Wudl F and Whitten Dg, Proc Natl Acad Sci USA **1999**, 96:1228712292.
3) Uchiyama S, Matsumura Y, de Silva AP, and Iwai K, Anal Chem **2003,** 5926-5935.
4) Nilsson KPR and Inganas O, Nat Matter **2003**, 2, 419-424.
5) Valeur B, Molecular Fluorescence Principles and Applications. **2001**, Weinheim.

Synthesis and Characterization of polybenzobisoxazole copolymers containing thiophene moiety in the main chain

Swati Chopra*, Sarfaraz Alam
Polymer Science Division , DMSRDE, Kanpur - 208 013, India

Polybisbenzoxazoles are a class of rigid rod polymers known for their extremely high tensile strength, modulus, thermal and flame resistance. These polymers are soluble only in very strong acids and therefore pose processability problems. Extensive research has been done by modifying the monomer base unit with a view to improve processability and compressive properties of this class. In this work, novel copolymers of polybenzobisoxazole containing thiophene moiety have been synthesized by polycondensation of diaminoresorcinol dihydrochloride (DAR) with various ratios of terephthaloyl chloride and 3,4-propylenedioxy thiophene -2,5 –dicarboxylic acid in polyphosphoric acid in an inert atmosphere. The monomer DAR has also been synthesized by usual high pressure reduction method of 1,3-dibenzyloxy-4,6-dinitrobenzene. The polymers have been characterized by Infrared Spectroscopy, Nuclear Magnetic Resonance Spectroscopy, X-ray diffraction and elemental analysis and their solubility behaviour has been studied. Thermogravimetric analysis revealed thermal stability upto approximately 550°C while Differential Scanning Calorimetry revealed absence of glass transition temperature in all the polymers.

References:

[1] Wolfe, J.F.; Arnold, F.E. Macromol **1981** 14, 909-915.
[2] Kumar, S.; Dang, T-D.; Arnold, F.E.; Bhattacharya, A.R.; Min, B.G.; Zhang, X; Vaia, R.A.; Park, C.; Adams, W.W; Hauge, R.H.; Smalley, R.E.; Ramesh, S; Willis, P.A. Macromol **2002** 35 9039-9048.
[3] Saxena, R.; Kandpal, L.D.; Mathur, G.N. J Polym Sci Part A: Polym Chem **2002** 40, 3959-3966.
[4] Saegusa, Y. ;Horikiri, M.; Sakai, D.; Nakamura, S. **1998** J Polym Sci Part A: Polym Chem 36, 429-435.

Thermal and Optical Modulation of Ionic Conductivity in Main Chain Liquid Crystalline Polyesters

Chinmay G. Nardele[1], Vishal M. Dhavale[2], K. Sreekumar[2] and S. K. Asha[1]*
[1]Polymer Science and Engineering Division, CSIR-NCL, Pune- 411 008, India
[2]Physical Chemistry Division, CSIR-NCL, Pune- 411 008, India
*sk.asha@ncl.res.in

Three series of main chain thermotropic liquid crystalline azobenzene polyesters were synthesized using azobenzene twin molecules as the AA monomer and diols like diethylene glycol (DEG), tetraethylene glycol (TEG) and hexaethylene glycol (HEG) as the BB comonomer. The twin azobenzene units had the structure Phenylazobenzene - oligooxyethylene spacer – Phenylazobenzene (**PnP**), where the spacer length 'n' was chosen from 2, 4 and 6 oxyethylene units. The terminal azobenzene moieties were functionalized with –C(O)OMe units to facilitate transesterification with diols to form polyesters. The twin molecular design reduced the melting temperature and also improved the solubility as well as miscibility in the molten reaction medium thereby enabling melt polycondensation. All polymers were exhibited stable smectic mesophases and most of the polymers showed higher ordered smectic mesophase transition. One of the polymers - **Poly(P4PTEG)** was chosen to prepare composite polymer electrolytes with $LiCF_3SO_3$ and ionic conductivity was measured by a.c impedance spectroscopy. The polymer/0.3 Li salt complex exhibited a maximum ionic conductivity in the range of 10^{-5} S cm^{-1} at room temperature (25 °C), which increased to 10^{-4} S cm^{-1} above 65 °C. The temperature dependence of ionic conductivity was compared with the phase transitions occurring in the sample and it was observed that the glass transition had a higher influence on the ionic conductivity compared to the ordered liquid crystalline phase. Reversible ionic conductivity switching was observed upon irradiation of the polymer/0.3 Li salt complex with alternate UV and visible irradiation. An increase in ionic conductivity was observed for UV light irradiation whereas visible light irradiation resulted in reduction in conductivity.

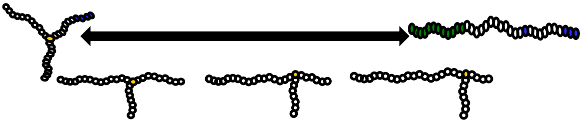
References:

[1] Tokuhisa, H.; Yokoyama, M.; Kimura, K. *J. Mater. Chem.* **1998**, 8, 889-891.
[2] Kishimoto, K.; Suzawa, T.; Yokota, T.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2005**, 127, 15618-15623.
[3] Nardele, C. G.; Asha, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, 50, 2770-2785.

Exploring the Continuum between 3-Arm Star and A-B-C-Linear Triblock Copolymers

Rohit Gupta, HuseyinTas and E. Bryan Coughlin*
Department of Polymer Science and Engineering, University of Massachusetts Amherst
*Coughlin@mail.pse.umass.edu

Multiblock copolymers with complex architectures offer opportun ities to create a diversity of ordered phases due to their greatly enlarged parameter space[1]. The studies on multiblock copolymer architectures are primarilylimited to theoretical investigations of 3-arm star and A-B-C linear triblock copolymers[2].A versatile synthetic strategy has been designed to synthesize a series of graft copolymers which lie along the continuum between 3-arm star and A-B-C linear triblock copolymers. The synthetic methodology includes the synthesis of block copolymer using RAFT polymerization, followed by a single insertion of a pentafluorophenyl-maleimide ester (PFPMI)monomer[3], and subsequentchain extension. Finally, the third polymer chain is grafted to the polymer backbone through reaction with the PFPMI activated ester[4,5]. The synthesized graft copolymershave been fully characterized, and the effect of the variations in molecular architectureon the macromolecular self-assembly has beenstudied. The spontaneous self-assembly of such "imprecise"graft copolymers can be further exploited to produce highly ordered morphologies that could be utilized in a variety of applications.



References:

[1] Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. Science, **2012**, 336, 434-440.

[2] Xu, W., Jiang, K., Zhang, P., Shi A.C. J. Phys. Chem. B, **2013**117, 5296–5305.

[3] Zamfir, M., Lutz, J. F. Nature, **2012**, 3, 1138.

[4] Kakuchi, R., Zamfir, M., Lutz, J. F., Theato P. Macromol. Rapid Commun.,**2012**, 33, 54–60.

[5] Jochum, F. D., Theato, P. Chem. Soc. Rev., **2013,** 42, 7468-7483.

Compartmentalization of Single Polymer Chains by Stepwise Intramolecular Cross-linking of Sequence-Controlled Macromolecules

Raj Kumar Roy, Jean-François Lutz*
Precision Macromolecular Chemistry Group, Institut Charles Sadron,
University Of Strasbourg, France

In the past few decades, polymers have revolutionized our life. Their low price, easy processability, exceptional mechanical properties have led to the use of polymers in variety of applications. However we are still far behind to mimic the nature's complex machinery system for example photosynthesis,enzymatic activity, signalling, recognition etc., and we realized that their function relies on the higher order structure. 1 Inspired by nature, there is a significant activity in material chemistry to emulate complex biological structure in order to accomplish the comparable functions.2 In the last two decades there is significant advancement towards the direction of bio-mimicking for example, the basic secondary structures of biopolymers such as single-chain helices, double helices, and sheets have been reproduced with synthetic stereoregular polymers and foldamers. 3It was also recently shown that atactic polymer chains, which generally adopt an amorphous random coil configuration in solution, can be "structured" into more defined objects usingintramolecular interactions. 4 For instance, a number of systems have been reported wherein synthetic polymer chains are compacted into single-chain nanoparticles by covalent bond formation. 5These kinds of compacted chains could be viewed as a pseudo-tertiary structure of the polymer. In this regard, the major differences between synthetic polymer and biopolymer lies in the primary structure itself. The sequence defined primary structure in biopolymerisessential to form higher order structure of proteins, enzymes etc. So one of the major challenges in this area are to have a macromolecule with controlled primary structure, necessitate a synthetic route which can offer control positioning of the different monomer within the polymer chains.In this presentation, the synthetic technique for preparing sequence control macromolecules which was established few years ago in our lab6 will be discussed. In the same direction, our recent effort on the synthesis and predictable folding (by intramolecular crosslinking) of a sequence controlled copolymer wherein the crosslinkable moieties are located precisely at the two end of the polymer chain will also be addressed.Intramolecular double compactions of the precursor polymer allow us to create single chain polymeric nanoparticle having distinct crosslinked subdomains as shown in scheme 1.7

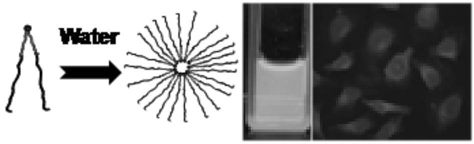
References

(1) (a) Perutz, M. F. *Nature***1942**, *149*, 491. (b) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *Nature***1985**, *318*, 618. (c) Garcia-Viloca, M.; Gao, J.; Karplus, M.; Truhlar, D. G. *Science***2004**, *303*, 186.
(2) (a) Breslow, R. *Science***1982**, *218*, 532. (b) Lehn, J.-M. *Science***2002**, *295*, 2400.(c) Aida, T.; Meijer, E. W.; Stupp, S. I. *Science***2012**, *335*, 813.
(3) (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.***2001**, *101*, 3893. (b) Ghosh, S.; Ramakrishnan, S. *Angew. Chem., Int. Ed.***2004**, *43*, 3264. (c) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.***2009**, *109*, 6102. (d) Guichard, G.; Huc, I. *Chem. Commun.***2011**, *47*, 5933.
(4) (a) Ouchi, M.; Badi, N.; Lutz, J.-F.; Sawamoto, M. *Nat. Chem.* **2011**, *3*, 917. (b) Lutz, J.-F. *Kobunshi***2013**, *62*, 509.
(5) (a) Harth, E.; Horn, B. V.; Lee, V. Y.; Germack, D. S.; Gonzales, C. P.; Miller, R. D.; Hawker, C. J. *J. Am. Chem. Soc.***2002**, *124*, 8653. (b) Altintas, O.; Barner-Kowollik, C. *Macromol. Rapid Commun.***2012**, *33*, 958.(b) Sanchez-Sanchez, A.; Perez-Baena, I.; Pomposo, J. A. *Molecules***2013**, *18*, 3339.
(6) Lutz, J.-F. *Acc. Chem. Res.* **2013**, *46*, 2696.
(7) (a) Roy, R. K.; Lutz, J.-F. *J. Am. Chem. Soc.* **2014**, *136*, 12888 (Highlighted in *Nature Nanotechnology* **2014**, *9*, 748).

Designing of Fluorescent Amphiphilic Polymer-Peptide Bioconjugates for Cell Imaging

Mrinmoy Biswas, Madhab Dule, Anupam Saha and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India

The tremendous effort of the present decade in designing of bio-relevant functional polymer already come up with application in the domain of drug delivery, cell-growth media, tissue scaffolding.[1] Our group is also actively involved in the design and synthesis of peptide-polymer conjugates via control polymerization from peptide-based initiator through 'grafting from' strategy that impart remarkable effect on their aggregation behavior and physical properties.[2,3] Attachment of a fluorescent unit in the bioconjugate is contemporary approach adopted by us to design a superior probe for live cell imaging. Thereby, we have reported fluorescent triblock conjugate PEG-tripeptide-Fluorophore-tripeptide-PEG prepared using 'grafting to' technique based on Schiff base coupling chemistry. The micellar aggregation behavior of the amphiphilic polymer conjugate was investigated. On the other hand, HeLa cell endocytosis experiment showed its potential as macromolecular probe for cell imaging.[4] Further extension in this area led to the designing and successful synthesis of fluorescent polymer-peptide bioconjugate from a cysteine-based dipeptide initiator. Simple thiol-ene polymerization of this dipeptide with 1-vinylimidazole and successive attachment of fluorescein isothiocyanate (FITC) led to formation of amphiphilic FITC-dipeptide-polyvinylimidazole conjugate. The final conjugate molecules undergo self-assembly into micelles in water as studied via DLS and fluorescence spectroscopy. The critical micellization concentration of the polymer is observed to be affected with the variation of pH. In addition, the invitro analysis of the polymer is under thorough investigation to explore its viability and potential for imaging different types of cells.



References:

[1] Place, E. S.; George, J. H.; Williams, C. K.; Stevens, M. M. Chem. Soc. Rev. **2009**, 38, 1139-1151.

[2] Paira, A. S., Sanjib Banerjee, Tamalika Das, Pradip Das,; Nikhil R. Jana, T. K. M. Macromolecules **2010**, 43, 4050-4061.

[3] Paira, T. K.; Banerjee, S.; Mandal, T. K. J. Polym. Sci., Part A: Polym. Chem. **2012**, 50, 2130-2141.

[4] Paira, T. K.; Saha, A.; Banerjee, S.; Das, T.; Das, P.; Jana, N. R.; Mandal, T. K. Macromol. Biosci. **2014**, 14, 929-935.

Surface Modified Cellulose Nanowhiskers as Nucleating Agent for Poly (lactic acid)

Susheela B. Idage, Bhaskar B. Idage, Ashish K. Lele, S. Sivaram
Polymer Science & Engineering Division, National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune - 411 008, INDIA
E-mail: sb.idage@ncl.res.in

Poly(lactic acid) (PLA) is biocompatible and biodegradable polymer derived from renewable sources and having potential properties as compared to petroleum based synthetic plastics. One of major the disadvantages of PLA is its brittleness which restrict its use in many applications. Several strategies have been tried to improve the brittleness of PLA.

Biocomposite materials have received considerable scientific and technical interest. Cellulose whiskers (CNW) have focused attention as reinforcing fillers in nanocomposite materials as a combination of their high surface area and unique morphology as well as good mechanical response upon stress. The problem in cellulosic materials is weak interactions between hydrophilic cellulose and hydrophobic polymer matrices.

Now a day the environmental concern has lead to growing interest in substitute traditional material with greener alternatives. One of the main drawbacks of CNW is their high propensity to agglomeration (or film forming) as soon as they are dried. An interesting approach providing improved surface chemistry control is grafting of monomers on to the surface of CNW. The use of CNW in PLA gave several advantages such as biodegradability, low cost, low density and improved mechanical properties. The ε-caprolactone, L-lactide and D-lactide were chemically grafted on to the surface hydroxyl groups of cellulose by ring opening polymerization (ROP).

In the present work, the surface modified CNW's were prepared by *in situ* surface grafting via ROP method using lactide enantiomers and ε-caprolactone. The CNW's were characterized by CP MAS ^{13}C NMR, FTIR spectroscopy, scanning electron microscopy (SEM) and X-ray photon spectroscopy (XPS). The grafted CNW's were used as nucleating agent for PLA. The impact of chemically modified CNW was studied on the nucleation and crystallinity of PLA.

References:

[1] Goffin A.L.; Raquez J.M.; Duquesne E.; Siqueira G.; Habibi Y.; Dufresne A. Biomacromol. **2011**, 12(7), 2456 - 2465
[2] Sanchez-Garcia M., Lagaron J. Cellulose **2010**, 17(5), 987 - 1004.
[3] Siqueira G.; Fraschini C.; Bras J., Dufresne A.; Prud'Homme R., Laborie M.P.; Eur. Polym. J. **2011**, 47(12), 2216 - 2227.
[4] Raquez, J.M.; Murena Y.; Goffin A.L.; Habibi Y.; Ruelle B.; DeBuyl F.; Dubois P. Comp. Sci. and Technol. **2012**, 72(5), 544 - 549.

Recovery of harmful metal ions from aqueous solution using novel chelating terpolymer resin: Synthesis and characterization

R. Azarudeen
Department of Chemical Engineering,
Coimbatore Institute of Technology, Coimbatore – 641 014, Tamil Nadu, India
azarudeen.rs@gmail.com

An effectual chelating resin was synthesized for the detoxification of hazardous metal ions using a synthesized resin involving anthranilic acid/4-nitroaniline/formaldehyde. The resin was characterized by FTIR, ^{1}H & ^{13}C NMR spectroscopy and its morphology was established through SEM and XRD. The resin was analyzed by TGA to assess the thermal stability, in which the resin could be used in high temperature aqueous solutions for the elimination of harmful metal ions. The ion-exchange property of the resin was evaluated by batch technique for specific metal ions *viz.* Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}. The study was extended to three variations such as effect of metal ion uptake in presence of various electrolytes in different concentrations, effect of pH and effect of contact time. The outcome proved that the resin can be used as a strong cation-exchanger to remove various metal ions from the solutions. The resin could be regenerated using inorganic acid and could be reused with quantitative recovery of metal ions for few cycles. On comparison with the commercial resins, the reported resin has found excellent capability of metal ion recovery.

References:

[1] Azarudeen, R.S.; Subha, R.; Jeyakumar, D.; Burkanudeen, A.R. Sep. Purif. Technol. **2013**, 116, 366-377.
[2] Azarudeen, R.S.; Ahamed, M.A.R.; Subha, R.; Burkanudeen, A.R. J. Chem. Technol. Biotechnol. **2014,** doi: 10.1002/jctb.4528.
[3] Azarudeen, R.S.; Burkanudeen, A.R. Res. Chem. Intermed. **2012**, 38, 2155-2173.

Oligomerization of olefins: A mechanistic study

Rajshekhar Ghosh*, Ashis Ranjan Bandyopadhyay, Rakshvir Jasra and Maniya Milan Gagjibhai
Reliance Technology Group, Reliance Industries Limited,
Vadodara Manufacturing Division,Vadodara Gujarat India
*Rajshekhar.Ghosh@ril.com.

A mechanistic study on oligomerization of olefins of isomeric octenes is reported using Lewis acidic ionic liquid as catalysts. This was aimed at understanding the effect of the position as well as geometry of the double bond on the probable pathway of the reaction and the properties of the final product. We have observed an interesting reactivity pattern in the oligomerization of a mixture of olefins where there is selectivity for the cis isomer over the trans isomer. Another interesting observation made in the study is that the final oligomer obtained starting from a mixture of olefins isomers displays better properties as compared to an oligomer obtained starting from exclusively the □olefin. Kinetic studies were carried out with individual isomers of octenes and their mixtures towards oligomerization. Subsequently, analyses of the structural properties of the final oligomerized and hydrogenated product were undertaken.

References:

[1] Ghosh, R.; Bandyopadhyay, A. R.; Jasra, R.; Gagjibhai, M. M. Ind. Eng. Chem. Res., **2014**, 53, 7622-7628

Epoxidized Castor oil toughened epoxy nanocomposites: Synthesis and Characterizaion

Nagarjuna Reddy Paluvai[1,2,*], Smita Mohanty[2], Sanjay K Nayak[1,2]
[1]Advanced Research School for Technology & Product Simulation (ARSTPS), Central Institute of Plastics Engineering and Technology (CIPET), Chennai, India
[2]Laboratory for Advanced Research in Polymeric Materials (LARPM), Central Institute of Plastics Engineering and Technology (CIPET), Bhubaneswar, India
Email: nag1987@gmail.com

The present investigation highlights the synthesis and characterization of Epoxidized castor oil (ECO) toughened DGEBA epoxy nanocomposites. Toughened nanocomposites was synthesized using ECO as a reactive diluent for Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin. DGEBA / ECO nanocomposites prepared by incorporating organo modified montmorillonite (OMMT) clays and (3-aminopropyl) triethoxysilane to the DGEBA/ECO system using sol-gel process. Their chemical structures were identified using FTIR and ^{1}HNMR. The Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the homogeneous dispersion of clays within the nanocomposites. The Methylhexahydrophthalic anhydride (MHHPA) and benzyltriethylammonium chloride (TEBAC) cured DGEBA/ECO/OMMT (8:2:0.1) nanocomposites exhibited tensile strength (56 MPa), tensile modulus (1933 MPa), flexural strength (132 MPa), flexural modulus (2518 MPa) and elongation (23.1%). The DGEBA/ECO/OMMT (6:4:0.1) nanocomposites can easily bend up to 360° without any damage, similarly 8:2:0.1 nanocomposites can bend up to 180°.

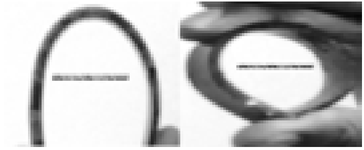


Figure: Flexibility/Bending behavior of 3mm thickness (a) DGEBA/20wt%ECO/OMMT, and (b) DGEBA/40wt%ECO/OMMT nanocomposites.

References

1. Park, S.J., Fan-Long, J., and Lee, J.R. (2004) *Macromol. Chem. Phy.,* 205, 2048.
2. Reddy, P.N., Mohanty, S., and Nayak, S.K. *Polym. Plast. Technol. Eng.,* DOI:10.1080/03602559.2014.919658.
3. Srikanta, D., Anand, V.P., Vaibhav, V.G., and Narayan, C.P. (2008) *Bioreso. Technol*., 99, 3737.
4. Gaston, F., Francisco, C., and Nathan, W.M. *J. Appl. Polym. Sci*., DOI,10.1002/APP.38380.
5. Gunter, W., Arunjunai, R.M., Muller, U., Andreas, K., and Alfred, T. (2012) *J. Polym. Environ.,* 20, 1063.
6. Ravindra, D.K., Priya, S.D., Sujay, U.M., and Pramod, P.M. (2013) *Indu. Crop. Prod.,* 49, 586.
7. Esmat, M., Mohamed, K.A., and Nik, M.N.S. (2013) *Appl. Ener*., 104, 905.
8. Oliver, K., Tommy, T., and Michael, A.R.M. (2011) *Euro. Polym. J*., 47, 1804.
9. Altuna, F.I., Esposito, L.H., Ruseckaite, R.A., and Stefani, P.M. (2011) *J. Appl. Polym. Sci*., 120, 789.

Synthesis and Characterization of novel Polyimides containing 1, 2, 3-Triazole By Click Reaction

R. Bala subramanian and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai-600025, India
msrde2000@yahoo.com

Initially, 4-aminophenyl propargyl ether (APPE) containing alkynyl group and diazides monomers were synthesized for the click reaction. Novel 1, 2, 3-triazole containing diamine monomers were synthesized by 1, 3-dipolar cycloaddition reaction in the presence of Cu (I) catalyst by click reaction and which was used to prepare a novel polytriazoleimide by polycondensation reaction with aromatic dianhydride. The chemical structure of the monomers and polymers were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra techniques. Polytriazoleimides were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), and dielectric constant. These polymers are readily soluble in highly polar organic solvents. Furthermore the incorporation of 1, 2, 3-triazole significantly improves the glass transition temperature, thermal stability and storage modulus of the polymer. The click coupling is the effective approach to develop the structural and functional polyimides.

Keywords: Polyimide-triazole- click reaction- thermal properties-mechanical properties

References

[1] Xiao'an Zhou; Liqiang Wan; Yanpeng, E.; Farong Huang;Lei Du. Polymer Journal **2010**, 42, 216-222
[2] Abdol, R; Hajipour; Fateemeh Abrishami. Journal of Applied Science **2012**, 124, 1757-1763
[3] Yanpeng, E.; Liqiang Wan; Xiao'an Zhou; Farong Huang; Lei Du. Polym.adv.technol. **2012**, 23, 1092-1100
[4] Tarek Agag; Tsutomu Takeichi. Macromolecule **2001**, 34, 7257-7263

Hyperbranched Polyimides based on New Triamine and Dianhydrides

M. Fathima Rigana and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai-25
E-mail : msrde2000@yahoo.com

A new triamine monomer 1,3,5-tris[4-(4′-aminophenoxy)phenoxy]benzene, was synthesized by a two step process using hydroquinone, 1-chloro-4- nitrobenzene and 1,3,5-trichlorobenzene. It was successfully polymerized into hyperbranched polyimides (HB PIs) with commercially available dianhydrides [3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA)] by A_2+B_3 method. Different monomer addition methods and different monomer molar ratios resulted in hyperbranched polyimides with amino and anhydride end groups. The structure of the resulting hyperbranched polyimides were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopic analysis. Glass transition temperature (Tg) and thermal stability were moniterd by DSC and TGA analysis respectively. Dielctric constant and dielectric loss measurements were carried out with the help of impedence analyzer.The resulting polymers have good solubility and thermal properties.

Keywords: Hyperbranched polymer, polyimides, poly(etherimides), condensation polymerization

References:

[1] Chen, H.; Yin, J. J. Polym. Sci. Part A: Polym. Chem. **2002**, 40, 3804- 3814.
[2] Fang, J.; Kita, H.; Okamoto, K. Macromol. **2000**, 33, 4639-4646.
[3] Xu, Z.; Xiong, X.Q.; Cheng, L. Chin. Chem. Lett. **2008**, 19, 1127-1130.
[4] Park, S-J.; Li, K.; Jin, F-L.; Mater. Chem. Phys. **2008**, 108, 214-219
[5] Fang, J.; Kita, H.; Okamoto, K. J. Membr. Sci. **2001**, 182, 245-256.

pH and Thermoresponsive Amino Acid-Based Zwitterionic Polymers

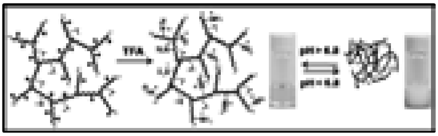
Tanmoy Maji, Sanjib Banerjee, and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India

L-serine-based zwitterionic polymers, poly(L-serinnyl acrylate)s (PSAs) of varying molecular weights and low polydispersities are synthesized via controlled RAFT polymerization in water-based solvent. The obtained PSA is highly sensitive to the solution pH due to the presence of pendent amine and carboxylic acid group in ach repeating unit. The isoelectric point of PSA in aqueous solution is around 2.9, thus within a very short pH range of 2.4 to 3.3, the aqueous PSA solution becomes as two phase system due to the intermolecular ionic interaction. In that pH range, the aqueous PSA solution also exhibits upper critical solution temperature (UCST) which decreases with the decrease of molecular weight of the polymer. The UCST behavior of PSA solution can also be altered by adding brine solution. Thus, this is an unique example of synthesis of duel-stimuli responsive zwitterionic homopolymer whose solution properties can easily be altered by altering temperature and pH.

Side-chain amino acid based pH responsive hyperbranched and star polymers *via* SCVP-RAFT

Saswati Ghosh Roy and Priyadardi De*
Polymer Research Centre, Department of Chemical Sciences, IISER Kolkata,
Mohanpur - 741246, Nadia, West Bengal, India
**p_de@iiserkol.ac.in*

Among the various polymer chain architectures, *e.g.,* linear, grafted, hyperbranched, dendrimers, comb-, brush- and star-shaped; hyperbranched and star polymers showed several interesting unique properties, such as enhanced solubility in wide range of solvents, low melt and solution viscosities, reduced hydrodynamic volume, and critical phase behavior. Besides, branched polyetheleneimines (PEIs) are widely explored synthetic cationic polymeric carrier for the plasmid DNA (pDNA) to cell due to high transfection efficiency of PEI/pDNA complexes. However, the PEI based delivery systems is highly toxic due to strong positive surface charge. Therefore, synthesis and study of pH responsive cationic amino acid based hyperbranched polymers may make them interesting and competitive candidates with respect to branched PEI for non-viral gene delivery. Here, we report design and synthesis of hyperbranched polymers *via* combination of self-condensing vinyl polymerization (SCVP) and reversible addition- fragmentation chain transfer (RAFT) polymerization from Boc-L-valine acryloyloxyethyl ester (Boc-Val-HEA) and *S*-(4-vinyl) benzyl *S*′-butyltrithiocarbonate (VBBT) with variable degree of branching (DB), molecular weight (M_n) and chain end functionalities. These hyperbranched polymers with tuneable M_n and DB have been further employed *via* successive RAFT polymerization for the synthesis of star polymers with variable arm numbers and lengths. Removal of Boc groups from the polymers results water soluble pH responsive cationic hyperbranched architectures with tuneable pH responsiveness (pH = 6.8 - 7.5), due to the incorporation of varied degree of hydrophobic chain end functionalities with different monomer feed compositions.



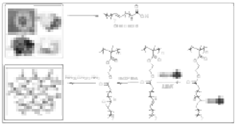
References:

[1] Roy, S. G.; Haldar, U.; De, P. *ACS Appl. Mater. Interfaces* ***2014***, *6*, 4233.
[2] Roy, S. G.; Bauri, K.; Pal, S.; De, P. *Polymer Chemistry* **2014**, *5*, 3624.
[3] Roy, S. G.; Acharya, R.; Chatterji, U.; De, P. *Polymer Chemistry* **2013**, *4*, 1141.
[4] Roy, S. G.; De, P. *Polymer Chemistry* **2014**, *5*, In press.

Post-polymerization modification of side-chain oleic acid containing polymerssynthesized *via* RAFT technique

Binoy Maiti, Sudhansu Sekhar Jena and Priyadarsi De*
Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur - 741246, Nadia, West Bengal, India
**p_de@iiserkol.ac.in*

Synthesis of polymers from renewable resources is receiving an increasing attention for both academic and industry world due to their low cost, sustainability biocompatibility and biodegradability.Methacrylate derivative of oleic acid, 2-(methacryloyloxy)ethyloleate (MAEO), has been synthesized and polymerized by reversible addition-fragmentation chain transfer (RAFT) technique. The corresponding polymer, PMAEO,is capable of subsequent chain extension to form well-defined block copolymers *via* RAFT technique. Double bonds in oleate side-chains in PMAEO are further functionalized by various organic thiol compounds *via* thiol–ene based Michael addition reactions. The ^{1}H NMR spectroscopy was used to determinethe quantitative conversion of double bonds with ethanethiol, butanethiol, dodecanethiol and 3-mercaptopropanoic acid, whereas 2-mercaptoethanol gave ~90% thioether product after prolonged reaction time. The side-chain double bonds of PMAEO were also quantitatively epoxidized using *meta*-chloroperbenzoic acid, which was further cross-linked by 1, 3-diaminopropane. Therefore, side-chain oleate pendants are ideal for various post-polymerization modification reactions to prepare renewable resource derived controlled macromolecular architectures with potential practical applications in the field such as paints, adhesives, electrical insulators, thermoplastics, etc.



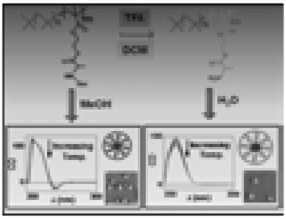
References:

[1] Xia, Y.; Larock, R. C. *Green Chem.***2010**, *12*, 1893–1909.
[2] Maiti, B.; De, P.*RSC Adv.***2013**, *3*, 24983–24990.

Polyisobutylene containing block copolymers with pH-responsive cationic side-chain amino acid moieties: synthesis, self-assembly and chiroptical properties

Kamal Bauri, Kapil Dev Sayala and Priyadarsi De*
Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur campus - 741246, Nadia, West Bengal, India
*p_de@iiserkol.ac.in

The rational synchronization of living carbocationic and reversible addition-fragmentation transfer (RAFT) polymerization has successfully enabled the synthesis of novel diblock chiral copolymer consisted of polyisobutylene (PIB) and *tert*-butyloxycarbonyl (Boc) protected amino acid based monomers such as Boc-L-alanine methacryloyloxyethyl ester (Boc-L-Ala-HEMA) and Boc-L-leucine methacryloyloxyethyl ester (Boc-L-Leu-HEMA). The block composition and molecular weight could be controlled while maintaining a narrow molecular weight distribution. Deprotection chemistry strategy has been used to make them smart pH-responsive materials having positive surface charges. Specific rotation and circular dichroism (CD) studies confirmed higher order helical secondary structure of protected and Boc-deprotected block copolymers in organic solvent and water, respectively. Boc-protected block copolymers self-assemble to core-shell micellar structure in methanol, which is a good solvent for side-chain amino acid block but non solvent for PIB. The amphiphilic nature of the deprotected diblock copolymer enabled formation of self-assembled structures in water, which was confirmed by atomic force microscope (AFM), scanning electron microscopy (SEM), ^{1}H NMR and DLS measurements.



References:
[3] Bauri, K.; Roy, S. G.; Pant, S.; De, P. Langmuir. **2013**, 29, 2764.
[4] Bauri, K.; Pant, S.; Roy, S. G.; De, P. Polym. Chem. **2013,** 4, 4052.
[3] Bauri, K.; De, P.; Shah, P. N.; Li, R.; Faust, R. Macromolecules. **2013**, 46, 5861.

“Poly(arylene ether)-co-polysiloxane multi block copolymers”

This study focuses on the synthesis and evaluation of novel, linear,poly(arylene ether)-polysiloxane (PPE-Siloxane)multiblock copolymers prepared by the reaction of ahydroxyl terminated oligomericbifunctional poly(aryleneether), a hydroxyl terminated telechelicbifunctionalpolysiloxane, and an aromatic diacid chloride. This synthesis overcomes disadvantages of known syntheses of poly(arylene ether)-polysiloxane block copolymers. The poly(arylene ether)-polysiloxanemultiblock copolymer is useful for improving the melt processibility of poly(arylene ether) compositions. Theresulting copolymer chains has multi (greater than orequal to 2) siloxane blocks and multi arylene-etherblocks. The overall siloxane incorporations were variedand at high levels (>60 wt %) yielding flexiblecompositions with improved flow, ductility, flameretardancy and low smoke generation during burn.

Synthesis of Poly(2-ethyl-2-oxazoline)-Based Photolabile Block-Copolymer via Combination of Cationic ROP and ATRP

Somdeb Jana, Anupam Saha and Tarun K. Mandal*
Polymer Science unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India

Now a days, much research interest devotes to block copolymer (BCP) micelles that respond to environmental conditions or stimuli such as pH, temperature, etc.[1]Recently, there has been emerge attention in photoresponsive BCP micelles whose aggregation state in solution can be disrupted by illumination.[2,3]Herein, we report the synthesis of a new type of photo-cleavable poly(2-ethyl-2-oxazoline)-*block*-poly(2-nitrobenzyl acrylate) (PEOX-*b*-PNBA) copolymer with varying compositions via microwave-assisted cationic ring-opening polymerization (CROP) followed by atom transfer radical polymerization (ATRP). The synthesized block copolymer is characterized through NMR, GPC and FTIR. The self-assembly of this block copolymer (PEOX-*b*-PNBA) in water/THF results in the formation of well-dispersed spherical micelles (<100nm) as observed through FESEM image. The effects of other solvents/solvent mixtures, molecular weight and composition of PEOX-*b*-PNBA block copolymer on the self-assembly and the formed self-assembled structures are described. The photo-solvolysis of 2-nitrobenzyl moieties of the PNBA block ofblock copolymer(PEOX-*b*-PNBA) is taken place upon UV-irradiation at 350nm, which converts the hydrophobic PNBA block to hydrophilic poly(methacrylic acid) block. Thus, the photo-solvolysis process leads to the formation of double hydrophilic poly(2-ethyl-2-oxazoline)-*b*-poly(acrylic acid) copolymer. Dissociation of nitrobenzyl group upon UV irradiation (350nm) of the PEOX-*b*-PNBA is successively monitored by UV spectroscopy.

References:

[1] Liu, S.; Armes, S.P.J. Am. Chem. Soc.**2005**, 127, 17982–17983.

[2] Jiang, J.; Tong, X.; Zhao, Y. J. Am. Chem. Soc.**2005**, 127, 8290-8291.

[3] Jiang, J.; Tong, X.; Morris, D.; Zhao, Y. Macromolecules **2006**, 39, 4633-4640.

Formation of Polymer Hydrogels and Nanoparticles Composites

Reena Bhadani
Department of chemistry, Ranchi Women's College, Ranchi
Ranchi University, Ranchi, Jharkhand
E-mail:-reenabhadani@yahoo.com

Polymer hydrogels are cross-linked hydrophilic polymers which are insoluble but absorb, swell and retain large amount of water. They exhibit both liquid and solid like properties. Such polymers have wide range applications in biotechnology, biomedical, pharmaceutical, agriculture, water treatment and many other areas. We carried out a free radical polymerization of acrylamide in an aqueous solution of HNO_3 where no other initiator was present. The acidic medium itself acts as an initiator. A highly crossed linked polymer gel was obtained .The dried gels were brittle and glassy in appearance. They swell in water and equilibrium swelling is obtained after several days. The water intake of the gels substantially increased when the polymer was subjected to an alkaline saponification. The water absorbency of hydrolyzed polymer was found to be more than 1000 times their own mass. The unhydrolyzed polyacrylamide is neutral and has a randomly coiled configuration having consequently low swelling. On the other hand, the hydrolysed polymer has ionic character with an extended chain configuration. Such polymers display a better swelling behaviour. The degree of swelling of prepared polyacrylamide hydrogels depend on pH.

The properties of hydrogels are greatly enhanced by mixing them with metal nanoparticles. Such materials have great promise for technology. We also carried out the formation of polyacrylamide hydrogels-metal nanoparticles composites by electrochemical method. The simultaneous reduction of a solution of acrylamide in water and metal ions occurred. Polymer-metal nanoparticles composites appeared to be formed *insitu* at the cathode. Silver, Zinc, Nickel, Iron, Copper metals were used as electrodes, anode and cathode being of the same metals. Yields of materials are dependent on the nature of electrode metals. A reaction mechanism is also proposed.

Keywords: Polymerization, Electrochemical polymerization, polyacrylamide, cross linked hydrogels, initiator, nitric acid and Polymer-metal nanoparticles composites.

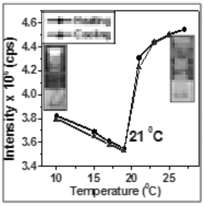
Reference

1. Kunzler J. F. Hydrogels in Encyclopedia of Polymer Science and Technology, John Willey & Sons, New York. **2002,** 2, 691-722.
2. Osada Y. and Kanjiwara Kanji, Editors, Gel Handbook, Academic Press, USA. **2000**
3. Magathaes A. S. G., Manuel P. A. N., Bezerra M. N. and Feitosa J. P. A. J. Braj. Chem. Soc. **2013, 24**, 1-12.
4. Chatterji S., Kwon H. K. and Park k. Prog. Polym. Sci. **2007**, **32**, 1083 – 1122.
5. Reena Bhadani, U. K. Mitra. Asi. J. Res. Che. 2014, 7, 345-348.
6. Rangareddy P., Mohnaraju K., SubbaramiReddy N. Chem. Sci. Rev. Lett. **2013**, 1**,** 228-235.
7. KhaydarovRashid A., KhaydarovRenat R., Gapurova Olga, Estrin Yuri,Scheper Thomas, **2009**, 11, 1193-1200.

Temperature responsive water soluble poly(ethylene glycol) based polythiophene graft copolymers

RadhakantaGhosh, Sandip Das, Sanjoy Samanta,
Dhruba P. Chatterjee[1] and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700032
[1]Department of Chemistry, Presidency University, Kolkata 700073
Email-psuakn@iacs.res.in

Abstract: Diethyleneglycolmethylethermethacrylate(MeO2MA) and oligoethylene glycol methylethermethacrylate(OEGMA) are polymerized on polythiophene(PT) backbone to produce water-soluble PT-g-PMeO2MA(PTD) and PT-g-P(MeO2MA-co-OEGMA)(PTDO) using atom transfer radical polymerization. They are characterized by 1H NMR and GPC techniques. TEM micrographs indicate that PT-chains self-organize as nanospheres and atomic force micrographs suggest that aggregated PT-chains are present at the centre surrounded by dispersed PMeO2MA fibers producing miceller type aggregates. Dynamic light scattering study indicates an initial decrease followed by sharp increase of Z-average particle size of PTD with temperature for attaining lower critical solution temperature(LCST) at 200C. The LCST increases with OEGMA concentration in PTDO. The temperature dependent PL emission of PTD shows a minimum at 190C, followed by a sharp increase till 210C and in the cooling cycle it shows a complete reversibility. In the PTDO copolymers the PL intensity shows the hike at progressively higher temperatures due to the increase of LCST with increasing OEGMA concentration.



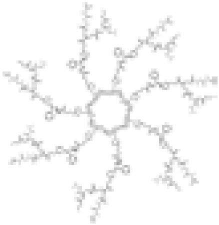
References:

[1] Das, S.;Samanta, S.;Chatterjee, D.P.; Nandi, A.K. J PolymSci A Polym Chem**2013**, 51, 1417–1427.

A novel dendrimer like star polymer, based on β-Cyclodextrin, with ABC type miktoarm star polymeric arms

Kranthikumar Tungala, P.Adhikary, Venkanna Azmeerea,
Krishna Kumar, S.Krishnamoorthi*
Department of Chemistry, Banaras Hindu University, Varanasi 221005, U.P., India

So far many miktoarm star polymers, through different polymerization techniques, have been reported. We have synthesized a novel dendrimer like star polymer, based on β-cyclodextrin, in which the primary alchoholic arms of β-cyclodextrin core are linked to ABC type miktoarm star polymers. Intern, 6-heptaazido-6-deoxy-β-cyclodextrin (7-N_3-β-CD), synthesized from β-cyclodextrin, is clicked with alkyne terminated polystyrene which is synthesized through atom transfer radical polymerization (ATRP) technique to form β-CD-PS-Br. β-CD-PS-N_3 has been synthesized from β-CD-PS-Br through azidation. Further a mikto functional initiator having alcohol, xanthate and alkyne functionalities is used in ring opening polymerization (ROP) of D, L-Lactide, reversible addition-fragmentation chain-transfer (RAFT) polymerization of N-Isopropylacrylamide and then click reaction with β-CD-PS-N_3. The synthesized star polymer has been well characterized by ^{1}H NMR, FTIR and GPC.



References:
[1] Tungala, K.; Adhikary, P.; Krishnamoorthi, S. Carbohydr. Polym, **2013**, 95, 295-298.
[2] Altintas, O.; a. Demirel, L.; Hizal, G.; Tunca, U. J. Polym.Sci., Part A: Polym. Chem. **2008**, 46, 5916–5928.
[3] Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U. J. Polym.Sci., Part A: Polym. Chem. **2008**, 46, 4459–4468.

Kinetic study of the esterification of Phthalic Anhydride with 1,4 Butendiol. Tetrabutyl Orthotitanate as a Catalyst

Shyam Dev Maurya[1]*, Surendra Kumaravanshi[1],
Smita Mohanty[1] and Sanjay K. Nayak[1]
[1]Laboratory for Advanced Research in Polymeric Materials (LARPM)
Central institute of plastics engineering & Technology, Bhubaneswar, India
*shyam4ucipet@gmail.com

The kinetics of the esterification of phthalic anhydride (PA) with 1,4 butenediol (BDO) in the presence of tetrabutyl orthotitanate as a homogenous catalyst was studied in semibatch reactor and produced 1,4 butanediol ortho-phthalate. Investigation of intrinsic rate constant carried out uder varied with the reaction temperature, agitator speed, reaction time and effect of catalyst were studied. Extent of reaction is confirmed by end group analysis i.e. acid value determination of reaction product and reaction kinetics mechanism is proposed for the different temperature sets. The maximum conversion, approximately 80% was obtained at 200^{0}C for molar ratio of 2 BDO/PA. It was found the increasing temperature of the reaction, decrease the rate constantand conversion of certain mole ratio, that is due to the transeterification is endothermic. The experimental data shows overall rate of reaction followed a second order kinetics. The composition of polyols were determined by fourier transform infrared (FT-IR).

References:

[1] J.Skrzypek; J.Z. Sadlowski; Chem. Eng. and Proc. 35 **1996**, 283-286
[2] L. Gao; L. Zhou; S. Fang; C. Wu; L. Guo; G.Sun; M. Hu; C.Liu; S. Ma; **2011** J Polym Res (2011) 18:833–841

Living Free Radical Polymerization of N-Vinyl Pyrrolidone by new CTA reagent A Kinetic study

Deepak[1], Ashok Kumar[1], Rajesh Kumar*[1] and Arti Srivastava[2]
[1] Department of Chemistry, Centre of Advance Studies in Chemistry,
Faculty of Science, Banaras Hindu University, Varanasi-221005, UP, India
[2] Department of Chemistry, School of Physical Sciences,
Guru Ghasidas Vishwavidyalaya, Bilaspur-495009 (CG), India
*E-mail: reach2arti@yahoo.co.uk

The reversible addition-fragmentation chain transfer (RAFT) polymerization of N-vinyl pyrrolidone (NVP) has been investigated in the presence of prop-2-ynyl morpholine-4-carbodithioate (PMDC), a chain transfer agent (CTA). The influence of several experimental parameters, such as temperature, monomer concentration [M], dithioester to initiator molar ratio ([CTA]/[AIBN]) and monomer to dithioester molar ratio ([M]/[CTA]), has been studied with respect to polymerization duration, conversion limit. This study evidences the parameters leading to an excellent control of M_W and molar mass distribution. Kinetics of the reaction strongly influenced by both temperature and [CTA]/[AIBN] ratio and to a lesser extent by monomer concentration. A high [CTA]/[AIBN] ratio resulted in a long induction time. Surprisingly, the control over M_W and molar mass distribution was improved by an increase in temperature from 45 to 65°C. Moreover, an increase of the [CTA]/[AIBN] molar ratio from 2 to 10, also improved the M_W control. Chain-end analysis by ^{1}H NMR shows that polymerization started with radical forming out of dithiocarbamate agent. The activation energy (E_a= 36.96 kJ mol^{-1}) and enthalpy of activation($\Delta H^{\ddagger}$= 39.94 kJ mol^{-1}) were in a good agreement to each other and negative entropy of activation($\Delta S^{\ddagger}$= -201.04 J mol^{-1}K^{-1}) supports the highly ordered transition state during polymerization.

Supported Ziegler Natta catalyst for Highly trans-1,4 Selective Polymerization of Butadiene

Virendra kumar Gupta*, Umesh Makwana, Hiren Bhajiwala
Reliance Research and Development Centre, Reliance Technology Group,
Reliance Industries Limited, Hazira-Surat
*virendrakumar.gupta@ril.com

There are many efforts have been made to develop new catalyst systems for regio- or stereoselective polymerization of conjugated dienes to get higher amount of cis-1,4 polybutadiene for elastomer industry1-2. In the meantime, an interest in trans-1,4- regulated polymer has emerged as a thermoplastic or an important component of high-performance rubbers and the variety of catalyst systems have been designed for the trans-1,4- selective polymerization of isoprene, such as Ziegler-Natta catalysts based on Ti and V metals3. The trans-polymerization of butadiene has been in turn less explored since the pioneer disclosures of Natta4. The resulting trans-1,4- regulated polymer displays good hardness and abrasion resistance 5-6, which motivated the search for the development of new trans-selective catalytic systems. Magnesium dichloride supported titanium Ziegler Natta (ZN) catalyst is used commercially for majority of polyolefin production but it is still less explored for butadiene polymerization as trans-selective catalytic systems.

In this study we have explored magnesium dichloride supported titanium catalyst containing an ester moiety as an internal donor for 1,3-butadiene polymerization using triethyl aluminium as co catalyst. The polymerization performance was optimized by varying the Al/Ti molar ratio and we found that at higher molar ratio the, %conversion of 1,3-butadiene to polybutadiene increases. Similarly, we have also studied the effect of external donor on 1,3-butadiene polymerization performance. However in all cases the polymer obtained is having more than 95% trans-1,4- regulated polymer and thus the we have established that the catalytic system used is trans-selective in various conditions of polymerization.

References

[1] Porri, L.; Giarrusso, A.; Ricci, G. Prog. Polym.Sci. 1991, 16,405.
[2] Shen, Z.; Gong, Z.; Zhong, C.; Ouyang, J. Chin. Sci. Bull. 1964,4, 335.
[3] Natta, G.; Porri, L.; Carbonaro, A. Makromol. Chem. 1964, 77,126.
[4] Natta, G.; Porri, L.; Corradini, P.; Morero, D. Chim.Ind.1958,40,263.

High Melt Flow Polypropylene byZiegler Natta Catalyst using External Donor System

Bhavesh Desai, Umesh Makwana and Virendra kumar Gupta*
Reliance Research & Development center, Reliance Industries Ltd, Hazira, Surat-395410
Virendrakumar.gupta@ril.com

The $MgCl_2$-supported Ziegler-Natta catalyst is multi-component system including catalyst, co-catalyst, andelectron donors.The roles of internal and external electron donors have been discussed in various studies for $MgCl_2$-supported $TiCl_4$ catalysts for propylene polymerization.Thepolymerization process efficiency and product characteristicsare the function of nature of external donors and its composition. The developed external electron donor (EED) provides higher productivity and gives higher hydrogen response which results in reduction in consumptions of hydrogen and co catalyst amount compared to known classical Ziegler Natta Catalyst system. The particular external electron donor systems is useful for specific application such as homo polypropylene used for slit tape application, injection moulding grade, high stiffness application and also for impact copolymer grades.

In this study we have explored EED system containing isopropyl Myristate (IPM) and cyclohexylmethyl dimethoxy silane (C-Donor) mixture for monoester catalyst system. The influences of EED system during slurry phase propylene polymerization performance as well as its effects on polymer properties were studied with monoester type Z-N catalyst.We have optimized the mixture of EED by varying the composition of silane compound and also through different Al/D ratios.The EED system was found to influence on thehigh productivityand it has also higher hydrogen response compared to knownexternal donor system (PEEB). For detailed understanding of the system, we have also used various long chain aliphatic carboxylic esters and different alkyl alkoxy silane compounds.

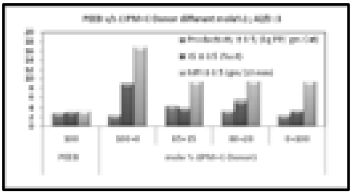


Figure 1: Polymerization performance of PEEB v/s EED at different mole%.

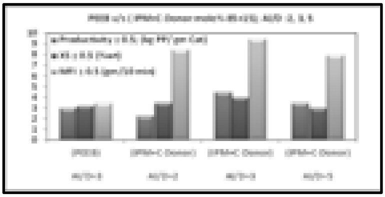


Figure 2: Polymerization performance of EED at different Al/D mole ratios.

Polyacryloyl hydrazide: A robust polymeric reducing agent

Anand Pratap Singh, Umaprasana Ojha*
Department of Chemistry, Rajiv Gandhi Institute of Petroleum Technology,
Raebareli, Ratapur Chowk, UP-229316, India
*Email - uojha@rgipt.ac.in

Polyacryloylhydrazide (PAH) synthesized by a robust method was used as the reducing agent for azo, nitrile and nitro group. The reduction of N=N bond of various azo dyes was smooth under room temperature condition. Visual color change and UV-Vis spectroscopic analysis suggested successful reduction. The IR peak for N=N bond (1591cm^{-1}) disappeared in the product after reduction supporting the conversion. The post reduction purification was smooth as the polymer catalyst was separated easily by simple precipitation in methanol. Structural similarity with hydrazine hydrates makes it a suitable reducing agent for wolff-kishner type reduction. Furthermore, the biocompatibility of the PAH makes it a robust & cost effective alternative to replace biocatalysts agent such as microorganism mediated redox conversion of poisonous soluble Cr(VI) into insoluble Cr(III). The above studies are currently under progress and will be presented during the symposium.

Key words : Polyacryloylhydrazide, azo dyes, ketoreductase.

Polyacryloyl hydrazide based hydrogels with tunable properties

Anuj Kumar, Umaprasana Ojha*
Department of Chemistry, Rajiv Gandhi Institute of Petroleum Technology Raebareli,
Ratapur Chowk, UP-229316, India
*uojha@rgipt.ac.in**

Polyacryloyl hydrazide (PAH) based hydrogels through chemical or dual cross linking pathway were prepared and studied. PAH was synthesized from polymethyl Acrylate (PMA) through nucleophilic substitution reaction with hydrazine hydrate in presence of tetra-n-butyl ammonium bromide. The hydrogels based on PAH with different cross linkers such as dimethyl 2,2'-thiodiacetate (DTDA), acrylic acid (AA), diethyl malonate (DEM) and polyethylene glycol (PEGDA) were synthesized at room temperature or70 °C. The swelling ratio study of hydrogels was carried out at room temperature as well as higher temperature. These hydrogels showed swelling ratio in the range of 20- 800% depending on type and concentration of the cross-linker as well as temperature and pH of the medium. The injectibility of hydrogels containing cross linker concentration up to 0.7 mol/L were confirmed by observed yield stress above 10% strain and the viscosity decreased by at least two orders of magnitude upon increasing the shear rate by 1000 times. Moreover, under physiological conditions hydrogels released up to 84% of the total encapsulated Rhodamine B in a controlled mode over a period of 120 h. Among these hydrogels, the hydrogels synthesized with AA and PEGDA as a cross linkers are potential candidates for controlled delivery, conformed by exhibited excellent cytocompatibility.

Novel approach for synthesis of core-shell nanofibers of polyvinyl alcohol by ethylene polymerization using titanium chloride incorporated Electrospun PVA nanofiber

Hiren M Bhajiwala[1], Bhavesh K Desai[1], H. R. Imam Khasim and Virendrakumar Gupta[1]
[1]Reliance Research & Development center, Reliance Industries Ltd, Hazira, Surat-395410

Surface functionalized Nano fiber(NFs) with cores sheath nanostructures have attracted a lot of attention in variety of applications including catalysis, tissue engineering,[1] photonics, microfluidics[2] and enzyme applications.[3] Synthesis of such structures becomes important in transforming them into different Nano templates like nanotubes, nanowires etc. electrospining is easy, simple and cost effective method for preparation of nano fiber, NFs have enhanced properties compared to conventional fibers because of their large surface area to volume ratios. Previous attempts on surface functionalization of NFs have been achieved via co-axial electrospining[4]. In this work, we demonstrate a unique approach to prepare core-shell PVA/PE Nano fibers

Core-Shell electrospun Nano fibers of polyethylene (PE) / polyvinyl alcohol (PVA) is synthesized by polymerizing ethylene using titanium chloride incorporated PVA (NF) precursor in presence of methylaluminoxane as cocatalyst in hexane slurry phase. The shell of Polyethylene over PVA core is noted as evidenced from SEM and EDX data. Thermal analysis of core-shell Nano fiber also indicates presence of polyethylene due to observation of melting peak at 134 °C. The Nano fiber precursor is prepared by reaction of PVA electrospun fiber with titanium tetrachloride. The obtained titanium incorporated PVA was found to be insoluble in protonic solvent due to reaction of OH group in PVA with titanium tetrachloride leading formation of cross-linked mat. This methodology is useful for synthesizing incompatible class of polymers with core-shell morphology at Nano scale.

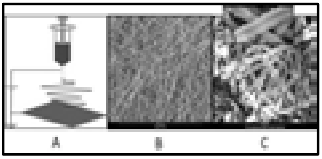


Figure 1: A. Schematic setup for solution electrospining B. SEM micrograph of pure PVA Nanofiber spun C. PVA Nanofiber treated with TiCl4 and ethylene polymerized at 110^{0}C

References

1. Linh, N. T.; Min, Y. K.; Song, H. Y.; Lee, B. T. J Biomed Mater Res B Appl. Biomater, **2010**, 95, 184-191.
2. Chang, H. C.; Yeo, L. Y. Electrokinetically driven microfluidics and nanofluidics; Cambridge University Press: Cambridge ; New York, **2010**.
3. Haghi, A. K.; Zaikov, G. E. Electrospining of nanofibers from introduction to application; Nova Science Publishers: Hauppauge, N.Y, **2011**.
4. Fu, G. D.; Lei, J. Y.; Yao, C.; Li, X. S.; Yao, F.; Nie, S. Z.; Kang, E. T.; Neoh, K. G. Macromolecules**, 2008**, 41, 6854-6858.

Development of Highly efficient Graft Copolymers based on xanthan gum and vinyl monomers for Organic dye removal from waste water

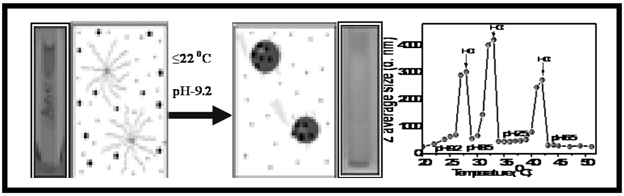
Arti Srivastava[1*], Pratibha Mondal[1] and Rajesh Kumar[2]
[1*] Department of Chemistry, School of Physical Sciences,
Guru Ghasidas Vishwavidyalaya, Bilaspur-495009 (CG)
[2] Department of Chemistry, Faculty of Science, Banaras Hindu University,
Varanasi-221005, UP, India
*E-mail: reach2arti@yahoo.co.uk**

This presentation will highlight some of our recent research work on the synthesis of various graft copolymer materials using free radical polymerization techniques. Different types/grades of graft copolymers based on natural polysaccharide *viz*. Xanthan gum and vinyl monomers *viz.* acrylamide, and 2-acrylamido-methane-1-propane sulphonic acid, were synthesized by varying the amount of vinyl monomers and natural substrates by graft copolymerization methodology. The graft copolymers were used to remove organic dyes from waste water, coal suspended particles from aqueous solution by flocculation process and by UV analysis. Different types/grades of graft copolymers were studied for adsorption of heavy metal ions (Pb^{2+}, Cd^{2+} , Hg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, As^{2+}) from the contaminated waste water. Among the different graft copolymers, the ionic graft copolymer based on AMPS show best performance in the dye removal and heavy metal ion adsorption. The synthesized graft copolymers adsorb good amount of organic dyes. Therefore, synthesized graft copolymer can be utilised as adsorbent for organic dye removal and also metal ion sorption and has applicability to the method of separation of various dyes and metal ions for analytical and technological purposes such as the treatment of waste water.

Poly-methacrylate Based 'Smart' Polymeric Material as Targeted Drug Delivery Vehicle for Malignant Tissues

Sandip Das, Dhruba P. Chatterjee,[‡] Radhakanta Ghosh and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032
‡Dept. of Chemistry, Presidency University, Kolkata-700 073
Email-psuakn@iacs.res.in

Three arms star initiator based dual (pH and temperature) responsive block 3A-(PDEGMEM-b-PDMAEMA) and random 3A-(PDEGMEM-stat-PDMAEMA) copolymer are synthesized by ATRP using diethylene glycol methyl ether methacrylate and N, N dimethyl amino ethyl methacrylate monomer at 30 ^{0}C. They are characterised by ^{1}H NMR and gel permeation chromatography (GPC) techniques. Both the polymers show excellent aqueous solubility at low temperature but at high temperature they are insoluble due to the lower critical solution temperature (LCST) of PDEGMEM at ~26 ^{0}C and a sharp increase of particle size is observed from dynamic light scattering (DLS) data. The star shaped random block copolymer of PDEGMEM and PDMAEMA also exhibit reversible micellization / dissociation (multistep micellization) at varied temperature and pH conditions.This system requires increased temperature for micellization with decreasing pH of the medium. This system has shown micellar state of aggregation at pH values near 7 under physiological temperature range and at this temperature when the pH is lowered micellar dissociation operates. Therefore, this polymeric system should perform better for delivery of hydrophobic drug molecules in the malignant tumour tissues having pH range 5 to 7.

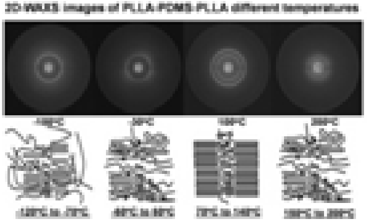


Reference: [1] Yamamoto, S.I.; Pietrasik, J.; Matyjaszewski, K. Macromolecules 2008, 41,7013-7020.

Synthesis of Poly (L-lactide-*b*-dimethyl siloxane-*b*-L-lactide) Triblock Copolymers: Crystallization and Phase Transition Behaviour of PLLA and PDMS

S.Nagarajan and E. Bhoje Gowd*
Materials Science and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology
Thiruvananthapuram - 695019, Kerala, India

Poly(L-lactide-*b*-dimethyl siloxane-*b*-L-lactide) (PLLA-*b*-PDMS-*b*-PLLA) triblock copolymers with different block ratios were synthesized by ring opening polymerization of L-lactide using Sn(Oct)$_2$ and bis(hydroxyalkyl) terminated PDMS as a co-initiator. The block copolymers were immiscible in the melt, the break out and preservation of the nanostructure of the triblock copolymer has been investigated by variable temperature wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) using samples with different thermal histories. This situation allowed us to investigate the crystallization and melting behaviors of PDMS component and PLLA component in triblock copolymers. At the same time, the effects of block ratio and the isothermal cold crystallization temperatures on the melting and polymorphic behavior of PLLA were investigated. In the case of higher volume fractions of PLLA, it was found that PLLA crystallized into disordered and ordered α form depending on the isothermal cold crystallization temperature. In contrast, PLLA crystallized into the ordered α form irrespective of the isothermal cold crystallization temperature in lower volume fractions of PLLA.



References:

[1] Ho C.H., Jang G.W., Lee Y.D. Polymer **2010**, 51, 1639-1647.

[2] Zhang J., Duan Y., Sato H., Suji H., Noda I., Yan S., Ozaki Y., Macromolecules **2005**, 38, 8012-8021.

Study of aging properties of PU adhesive on different substrate in different medium based on aliphatic isocyanate

Swarnalata Sahoo[1], Smita Mohanty[2], S. K Nayak[2]
Laboratory of Advance Research in Polymeric Materials (LARPM), Bhubaneswar
Central Institute of Plastic Engineering and Technology (CIPET,Bhubaneswar)
Email: sahoo.swarnalata@gmail.com

Synthesis of bio based polyurethanes(PU) are widely used in the field of adhesive and coatings due to there high reactivity & high flexibility.As polyurethane adhesive (PU) free of volatile organic component is less toxic and avoid environmental pollution, for that biobased PU adhesive synthesized by reacting castor oil based polyester polyol with partially biobased HDI. This can be confirmed by lap shear test. Effect of catalyst can be verified by the dsc curing kinetics. Degradation behavior can be studied by UV, lap shear, mechanical, SEM. Solvent resistance of PU adhesive was investigated by keeping the sample in different media. The thermal stability of these polymers was determined by the TGA.

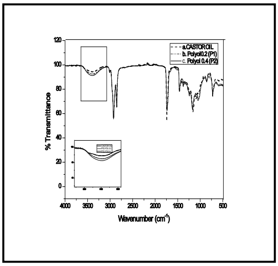
References:

[1] Ida Poljanšek, Ema Fabjan, Darko Molders, Dolores Kukanja International Journal of Adhesion & Adhesives 51 (2014) 87–94
[2] Hansol Kim , Ryu-Un Kim, Koo-Hyun Chung, Joong-Hyok An b,Hong-Gyu Jeon b, Byung-Joo Kim bPolymer Testing 40 (2014) 13-23
[3] Dakai Ren, Charles E. Frazier, International Journal of Adhesion & Adhesives, S0143-7496(13)00076-6
[4] NI Xiaoxue, LI Xiaogang , ZHANG Sanping, QIU Dajian, Vol.24 No.6 *NI Xiaoxue et al: The Aging Behavior of Polyurethane 892 Adhesive…*

Effect of castor oil modification on the thermal, chemical, morphological and mechanical properties of partially bio based polyurethane elastomers

Sonalee Das[1], Smita Mohanty[1], S.K.Nayak[2]
[1]Laboratory for advanced research in polymeric materials, LARPM,
CIPET, Bhubaneswar -751024, India
[2]Head Office, Central Institute for plastic Engineering and Technology (CIPET),
Chennai-600032, Tamil Nadu, India

Recent years has witnessed the increasing demand for natural resources and products in polyurethane synthesis because of global warming, sustainable development and oil crisis. For this purpose, different plant oils such as soybean oil, castor oil and linseed oil are extensively used. Moreover, the isocyanate used for the synthesis of polyurethane is derived from petroleum resources. In this present work attempts have been made for the successful synthesis of biobased isocyanate from castor oil modified and unmodified with partially biobased isocyanate in presence of catalyst dibutyltin dilaurate (DBTDL).The goal of the present study was to investigate the thermal, mechanical, morphological and chemical properties of the synthesized polyurethane in terms of castor oil modification. The transesterified polyol showed broad and higher hydroxyl value as compared to castor oil which was confirmed by FTIR studies. The FTIR studies also revealed the successful synthesis of bio based polyurethane by showing characteristic peaks at 3300cm^{-1}, 1715cm^{-1} and 1532cm^{-1} respectively. The thermogravimetric (TGA) results showed three step degradation mechanism for the synthesized polyurethane from modified and unmodified castor oil. However, the modified polyurethane exhibited higher degradation temperature as compared to unmodified one. The mechanical properties also demonstrated higher tensile strength for modified polyurethane as compared to unmodified one.



FTIR Graph of (a) Castor oil and Transesterified Castor oil (b) Polyol 0.2 (c) Polyol 0.4

References

[1] Manuel F Valero and Adriana Gonzalez.Journal of Elastomers & Plastics **2012**, 44,433–442.

[2] Valero M, Pulido J, Ramı´rez A and Zhendong Z. J Am Oil Chem Soc **2009**; 86,383–392.

[3] Kamila Pietrzak , Mikelis Kirpluks ,Ugis Cabulis , Joanna Ryszkowska .Polymer Degradation and Stability ,**2014**,1-11.

Hetero-functionalized Hyperbranched Polymers

Suresh Kumar Perala and S. Ramakrishnan
Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560012
e-mail:psurihcu@gmail.com

Hyperbranched polymers (HBPs) have seen extensive growth during the past two decades; this has also been accompanied by a recent upsurge in several interesting potential applications. The most important features of HBPs that make it very attractive are their compact molecular conformation and the relatively simple and scalable strategies for structural manipulations. During the past few years, we have developed some simple methodologies to access peripherally clickable HBPs that carry either propargyl/allyl terminal groups; it was also shown these groups can be readily modified quantitatively using the azide-yne or thiol-ene click reactions.[1]

Hetero-functionalized HBP is a term that could be used to describe HBPs whose periphery is decorated with two or more different types of segments; it was recently shown by us that if these segments are mutually immiscible, then self-segregation can lead to the formation of *Janus* and *Tripodal* molecular structures.[2] One aspect that has been largely unexplored is *tailored core-functionalization* to impart specific functions to HBPs;[3] in an effort to do so, we examine in this study general methods to prepare orthogonally functionalizable HBPs that bear two types of clickable functionalities – one type within the core region and the other at the periphery, as depicted in the scheme below. Such a general strategy would, in principle, permit the decoration of the periphery to impart the required solubility, while at the same time to install other types of functionality within the core to provide specific functions to the HBP; these could include sequestering analytes through specific binding, sensing, catalysis, etc. In this poster, different strategies to prepare such orthogonally clickable HBPs will be presented along with some initial results on imparting specific functions to these systems.

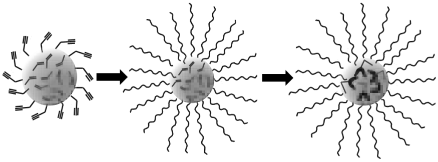


Figure-1: Schematic representation of orthogonally functionalized HBPs

References:

[1] a. Saha, A.; Ramakrishnan, S. Macromolecules **2009**, 42, 4956-4959.
b. Ramkumar, S. G.; Amala Rose, K. A.; Ramakrishnan, S. J. Polym. Sci. Chem. Ed. **2010**, 48, 3200-3208.
c. Rajkumar, R.; Ramakrishnan, S. J. Polym. Sci. Chem. Ed. **2011**, 49, 1735-1744.
d. Shree Varaprasad, N. S.; Venkhatesh, P.; Ramakrishnan, S. J. Appl. Polym. Sci. **2014**, 131, 40248.
[2] a. Ashok, Z. S.; Ramakrishnan. S. Macromolecules **2012**, 45, 2348-2358.
b. Ashok, Z. S.; Ramakrishnan, S. Langmuir **2013**, 29, 1245-1257.
[3] Rajkumar, R.; Ramkrishnan, S. J. Polym. Sci. Chem. Ed. **2013**, 51, 4125-4135.

Novel Aromatic Polyamides Containing Adamantane Substituted Triphenylamine for Gas Separation Application

Debaditya Bera[1], Susanta Banerjee[1*]
[1]Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
*susanta@matsc.iitkgp.ernet.in

Membrane based gas separation has already established as a highly efficient technique for the separation and purification of gases [1]. Aromatic polyamides due to their excellent mechanical and thermal properties can be used as a membrane materials in petrochemical industries for natural gas sweetening and also for the preparation of oxygen and nitrogen enriched air [2]. Considering the general tradeoff between gas permeability and permselectivity [3] a series of organo-soluble new aromatic polyamides were designed and synthesized from the new diamine containing pendant adamantane substituted triphenylamine (TPA) moiety and five different diacids. Incorporation of rigid propeller shaped TPA moiety yielded amorphous polyamides which were readily soluble and cast into flexible membranes (tensile strengths ~ 104 MPa). All the membranes showed high thermal stability (440 °C < T_{d10} in air). Basically, the effect of adamantane substituted TPA moiety on gas permeation and diffusion processes of four different gases (e.g., CH_4, N_2, O_2 and CO_2) were measured at 35 °C and at applied pressure of 3.5 bar. All these aromatic polyamides showed a favorable combination of permeability-selectivity ($P_{CO2} = 61.5$ and $P_{O2} = 14.2$ Barrer, $P_{CO2}/P_{CH4} = 63.00$ and $P_{O2}/P_{N2} = 11.67$) over many other reported polymers. The gas permeation properties of these PAs were correlated with their fractional free volume distribution.

References:

[1] Yampolskii, Y. Macromolecules.**2012**, 45, 3298-3311.
[2] Bera, D.;Bandyopadhyay, P.;Ghosh, S.; Banerjee, S. J. Membr. Sci. **2014**,453, 175-191.
[3] Robeson, L.M. J. Membr. Sci. **2008**,320, 390-400.

Design of Donor-Acceptor Type Low Band Gap Conjugated Copolymers for Solar Cell Applications

Bhavna Sharma and Josemon Jacob
Centre for Polymer Science and Engineering, Indian Institute of Delhi, New Delhi-16, India
sharma281004@gmail.com

Donor-Acceptor type low-band gap conjugated copolymers consisting of fluorene and cyclopentadithiophene as donors and various acceptor moieties were synthesized by Suzuki polycondensationand Directarylation coupling method in good yields. These polymers were characterized by ^{1}H NMR, UV-Vis absorption spectroscopy, thermo-gravimetric analysis and Cyclic Voltammetry. Optical properties of these polymers in solution as well as thin film were studied by UV-visible absorption and photoluminescence spectroscopy. All polymers showed strong absorption in UV-visible region in the range of 385- 665nm. Thermal properties were studied by thermo-gravimetric analysis, the thermal decomposition temperatures were found to be in the range of 250-350 °C. Electrochemical studies were done by Cyclic Voltammetry in 0.1M TBAP solution in acetonitrileby which HOMO-LUMO levels and electronic band gaps were calculated. The band gaps of the synthesized polymers were found to be in the range of 1.40-1.65 eV which is promisablefor use in polymer solar cells.

References

1. Roberto Grisorio, Giovanni Allegretta, PieroMastrorilli, and Gian Paolo Suranna, Macromolecules, **2011**, 44, 7977–7986.
2. ChakkoothVijayakumar, Akinori Saeki, and Shu Seki, Chem. Asian J. **2012**, 7, 1845 – 1852
3. Shu-Wei Chang, Huw Waters, Jeff Kettle, Masaki Horie, Organic Electronics, **2012**, 13, 2967–2974
4. QiangGuo, Jiaxing Dong, DanyangWan , Di Wu, Jingsong You, Macromol. Rapid Commun. **2013**, 34, 522–527
5. Wen-Ya Lee, Chien-Wei Chen, Chu-Chen Chueh, Chang-Chung Yang, and Wen-Chang Chen, Polymer Journal, **2008**, 40, 249–255.

Facile Synthesis and Characterization of Azo Linked Polymers

Savita Meena and Josemon Jacob
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New Delhi
savita.iitd@gmail.com

A precursor approach was used to readily synthesize dibromo functionalized azo containing monomers. These monomers were found to undergo Suzuki polycondensation with various co-monomers to generate a series of copolymers with azo group along the polymer backbone. Various donor-donor type and donor-acceptor type copolymers were synthesized by this approach. The synthesized polymers showed good solubility in common organic solvents and good thermal stability with initial degradation temperature in the range of 351-411 °C. These polymers were characterized by ^{1}H NMR, FT-IR, photoluminescence, cyclic voltammetry, gel permeation chromatography, thermo-gravimetric analysis and UV-Visible absorption spectroscopy. UV-Vis measurements in solution and film exhibited absorbance maxima in the range of 400-500 nm for the various polymers whereas the monomer exhibited an absorbance maximum of 315 nm. The optical band gap of the synthesized polymers was found in the range of 2.1-2.3 eV. Optical and electrochemical properties of the synthesized azo linked polymers indicate their suitability for potential electronic applications.

References:

[1] Izumi, A.; Teraguchi, M.; Nomura, R.; Masuda, T. Journal of Polymer Science Part A: Polymer Chemistry **2000**, 38, 1057-1063.

[2] Kuciauskas, D.; Porsch, M. J.; Pakalnis, S.; Lott, K. M.; Wright, M. E. The Journal of Physical Chemistry B **2003**, 107, 1559-1566.

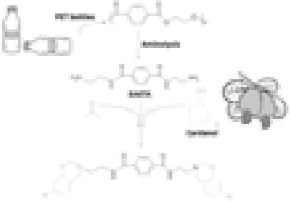
[3] Kinashi, K.; Kambe, Y.; Misaki, M.; Koshiba, Y.; Ishida, K.; Ueda, Y. Journal of Polymer Science Part A: Polymer Chemistry **2012**, 50, 5107-5114.

[4] Breukers, R. D.; Janssens, S.; Raymond, S. G.; Bhuiyan, M. D. H.; Kay, A. J. Dyes and Pigments **2015**, 112, 17-23.

Sustainable bis-benzoxazines derived from cardanol and recycled Poly (ethylene terephthalate)

Pratibha Sharma[1,2], Bimlesh Lochab[3], Devendra Kumar[2],
Prasun Kumar Roy[1]*,
[1]Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi-110054, India
[2]Department of Applied Chemistry and Polymer Technology,
Delhi Technological University, Delhi-110042 India
[3] Department of Chemistry, School of Natural Sciences,
Shiv Nadar University, UP 203207, India
pk_roy2000@yahoo.com

The aim of the present work is to reduce the curing temperature of thermally curable cardanol based benzoxazines by introducing multifunctionalisationinto the monomer. The amine fraction required for the synthesis of monomer is derived by tertiary recycling of PET bottle waste. Aminolysis of PET was carried out in the absence of catalyst to obtain Bis-(amino-ethyl)terepthalmide (BAETA) in high yields, which was employed as the difunctional amine for preparation of bis-benzoxazine. Complete aminolysisof PET could be achieved within 10 min under optimum reaction conditions.Cardanol: a byproduct of cashew nut industry, BAETA and formaldehyewere reacted in requisite amounts (2:1:4 molar ratio) to yield sustainable bis-benzoxazines, the structure of which was confirmed using FTIR and ^{1}H-NMR.The curingbehavior of the bis-benzoxazine wasstudied using non-isothermal Differential Scanning Calorimetry. The studies revealed that introduction of bifunctionalityled to a substantial reduction in the curing temperature, which decreased from an initial value of 240 °Cto 174°C. The pronounced reduction in the curing temperature could be attributed to the instability of the benzoxazines rings due to introduction of bulky amine functionality. The adhesive strength of prepared resin was determined from interlaminar shear strength studies.



References:

[1] R. K. Soni, K. Dutt, A. Jain, S. Soam and S. Singh, *J. Appl. Polym. Sci.*, 113, 1090-1096 (2009).

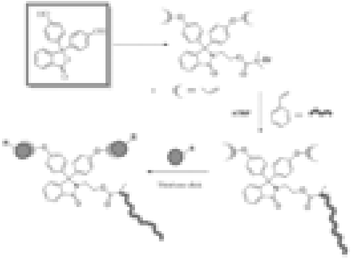
[2] S. Chaudhary, P. Surekha, D. Kumar, C. Rajagopal and P. K. Roy, *J. Appl. Polym. Sci.*, 129, 2779-2788 (2013).

[3] B. Lochab, I. Varma and J. Bijwe, *J Therm Anal Calorim*, 107, 661-668 (2012).

A New ATRP Initiator Based on Phenolphthalein for the Synthesis of Bis-allyloxy Functionalised Polystyrene Macromonomers

Sachin S. Patil,[a] Shamal K. Menon,[a] Prakash P. Wadgaonkar [a*]
[a*] Polymer Science and Engineering Division, CSIR-National Chemical Laboratory,
Dr. Homi Bhabha Road, Pashan, Pune- 411008, Maharashtra (India)
pp.wadgaonkar@ncl.res.in

A new atom transfer radical polymerization (ATRP) initiator, namely, 2-(1, 1-bis(4-(allyloxy)phenyl)-3-oxoisoindolin-2-yl)ethyl 2-bromo-2-methylpropanoate was synthesized starting from phenolphthalein- a commercially available, and an inexpensive chemical. Well- defined bis-allyloxy functionalised polystyrene macromonomers ($M_{n,GPC}$ 4,800-11,700 g mol^{-1}) with controlled molecular weight and narrow molecular weight distribution (1.05-1.09) were synthesized using ATRP by varying monomer to initiator feed ratio. The presence of allyloxy functionality on polystyrene was confirmed by FT-IR and ^{1}H-NMR spectroscopy. The kinetic study of polymerization revealed the pseudo-first order kinetics with respect to the monomer consumption. Initiator efficiency was found to be in the range 0.80-0.95. MALDI –TOF spectra showed narrow molecular weight distribution with control over molecular weight. The reactivity of allyloxy groups on polystyrene was successfully demonstrated by quantitative photochemical thiol-ene click reaction with benzyl mercaptan as a model thiol reagent. Furthermore, the thiol-ene click reaction was exploited to introduce other reactive functional groups such as hydroxyl and carboxyl by reaction of α,α′-bisallyloxy functionalised polystyrene with 2-mercaptoethanol and 3-mercaptopropionic acid, respectively.



References

[1] Sachin S. Patil, Shamal K. Menon and Prakash P. Wadgaonkar *Polym int (*2014) **DOI 10.1002/pi.4804**

[2] Jin Ran, Liang Wu, Zhenghui Zhang, Tongwen Xu *Progress in Polymer Science* **39** (2014) 124– 144.

[3] Krzysztof Matyjaszewski *Macromolecules* **45** (2012) 4015–4039.

[4] Mehmet A.Tasdelen, Muhammet U. Kahveci, Yusuf Yagci *Progress in Polymer Science* **36** (2011) 455–567.

Synthesis of 9-alkylated Fluorene-based poly(arylene ether) and their gas transport properties

Sipra Ghosh[1], Susanta Banerjee[1]*
[1]Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
*****_susanta@matsc.iitkgp.ernet.in_

Membrane based gas separation technology has got a special interest in both academia and industry [1-2]. Excellent thermal stability, chemical resistance, film forming ability, mechanical strength and versatile chemistry made poly(arylene ether)s (PAEs) promising materials for gas separation applications [3]. Accordingly, this work reports the synthesis of a new cardo bisfluoro monomer with branched aliphatic chain; 9, 9-bis (2-ethylhexyl) -2, 7-bis [4-fluoro-3-trifluoromethylphenyl] - 9H - fluorene and its polymerization with six different bishydroxy monomers namely 4, 4'- dihydroxybiphenyl, 4, 4'-isopropylidenediphenol (BPA), 2, 2 -bis (4-hydroxyphenyl) hexafluoropropane (6FBPA), 4,4'-(9-fluorenylidene)diphenol, 4,4'-cyclohexylidenebisphenol and N-phenyl-3,3-bis (4-hydroxyphenyl)phthalimidine. The monomer and the PAEs were characterized by elemental analysis, ^{1}H NMR, and FTIR techniques. The molecular weights of the PAEs were determined by GPC. Thermal and mechanical properties of the PAEs were also investigated. The polymers showed T_g up to 189 °C, 10 % degradation temperature up to 427 °C and 420 °C under nitrogen and air atmosphere respectively, tensile strength up to 64 MPa and dielectric constant (ϵ) as low as 2.33. The effect of cardo moiety together with branched aliphatic chain in the PAEs on gas transport properties were investigated at 35 °C using four different gases (e.g., CH_4, N_2, O_2 and CO_2). The PAEs showed high gas permeability and permselectivity in comparison with many other previously reported PAEs. The PAEs with two cardo moieties exceeded the upper boundary limit drawn by Robeson for O_2/N_2 gas pair and PAE containing phthalimidine moiety exhibited high permeability and permselectivity for CO_2/CH_4 (PCO_2=74.65 and PCO_2/PCH_4=61.69) gas pair which is very close to the present upper boundary limit drawn by L. M. Robeson.

References:

[1] Freeman, B.D. Macromolecules. **1999**, 32, 375-380.
[2] Robeson, L. M. J. Membr. Sci. **2008**, 320, 390-400.
[3] Ghosh, S.; Bera, D.; Bandyopadhyay, P.; Banerjee, S. Eur. Polym. J. 2014, 52, 207-217

1,2,3-Triazole Bridged Triptycene Alternate Polymers: Synthesis, Characterization and Host-Guest Chemistry with Explosive Nitroaromatic Compounds

Snehasish Mondal and Neeladri Das*
Department of Chemistry, IIT Patna
**neeladri@iitp.ac.in*

Triptycene, the simplest member in iptycene family, was first synthesized by Bartlett and co-workers in 1942.[1] In triptycene, three benzene rings are connected together by a [2.2.2]bicyclic ring in a paddle wheel configuration. Three dimensional (3D) rigid triptycene has been extensively used as a building block in supramolecular chemistry and polymer chemistry during last fifteen years.[2-4] Although Swager, Chen and others have reviewed progress in triptycene based polymers, there is still a lot of scope in the development of new polymers synthesized from triptycene monomers.

Herein, synthesis and characterization of a series of organosoluble 1,2,3-triazole linked alternate copolymers bearing triptycene motif will be discussed. The effect of temperature in regioselective formation of triazole units will be described. Some of the polymers were found to be fluorescent. Application of these triazole motif containing fluorescent triptycene based polymers in detection of nitroaromatic compounds (DNB, DNT, picric acid) will be discussed.

References:

1. Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.
2. Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301−3315.
3. Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1181−1189.
4. Chen, C.-F. *Chem. Commun*. **2011**, *47*, 1674−1688.

Synthesis of Linear Polyesters and Hyperbranched Poly(ester-urethanes) based on Natural L-Amino acids

Rajendra Aluri and Manickam Jayakannan*
Department of chemistry
Indian Institute of Science Education and Research (IISER),
Dr. Homi Bhabha road, Pune-411008, Maharashtra, INDIA

Hyperbranched polymers based on amino acids are important classes of materials for applications in biomedical industry. New classes hyperbranched poly (ester-urethanes) and linear poly(esters) have been synthesized by melt self-polycondensation from the same ABB' amino acid monomers. Structures of these polymers were established by ^{1}H, ^{13}C NMR and MALDI-TOF MS spectrometry. The ABB' monomer has one ester, carbamate and one hydroxyl group. At 120^{0}C in serine monomer only ester and hydroxyl group participate in the condensation to produce linear polyesters. At 150^{0}C both ester and carbamate functionalities undergoes reaction with hydroxyl group resulting in hyperbranched poly(ester-urethanes). Degree of branching which is a characteristic of hyperbranched polymers was calculated as 0.65 from its ^{1}H NMR spectrum. Further the molecular weights of the polymers were determined by GPC which are in the range of 15,000 to 20,000. These polymers were thermally stable up to 230^{0}C determined from TGA analysis. Secondary structures and optical activity of the polymers were characterized by CD and absorption spectroscopes. The linear polymers have given intense CD signal whereas in hyperbranched polymers did not show any CD signal due to the branching nature. FE-SEM and TEM images of hyperbranched and linear polymers showed particle and fibrous nature, respectively.

References:

1. Deepa.P.; Jayakannan, M. *J. Polym.sci., Polym. Chem.* **2008**, *46*, 2445
2. Anantharaj, S.; Jayakannan, M. *Biomacromolecules* **2012**, *13*, 2446

Amino acid based melt condensation approach for linear, functional polymer and oligomers

Sonashree saxena, Santhanaraj Anantharaj and Manickam Jayakannan*
Department of Chemistry
Indian Institute of Science Education and Research (IISER)
Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India

Polymers based on biological resources have gained significant interest due to their potential application in therapeutics, cosmetics, biodegradable, biocompatible engineering thermoplastics and so on. Among the natural resources, amino acids are important class of biological - monomers for producing well-defined macromolecular architectures. Design and development of new synthetic approaches provide excellent opportunities for new-generic amino acid based biodegradable and biocompatible plastics. Recently, we have developed unique dual ester-urethane condensation chemistry for amino acid monomers under solvent free eco-friendly melt process. In this new process, amino acids were readily converted into dual ester-urethane monomers and polycondensed with commercial diols to produce high molecular weight fibrous polymers. The new synthetic process was tested for more than half-dozen of amino acids: glycine, β-alanine, L-alanine, L-leucine, L-phenylalanine and L-valine along with variety of commercial diols. Further, the development of new temperature and catalystselective melt condensation chemistry for ester functional group offers amino acids monomers to make diverse polymer architectures such A-B diads and A-B-A triads, amine functionalized linear polyesters, and cross-linked thermo-sets in a single synthetic approach under solvent free eco-friendly conditions. The enantioselectivity of the new reaction is also tested for D- ad L-isomers. These new classes of functional polymers were self-assembled to produce helical polymer assemblies. Anticancer drug molecules were loaded in the polymer micellar assemblies and their release mechanism was investigated using pH and enzyme as enzymes.

References:

1. Anantharaj, S.; Jayakannan, M. *Biomacromolecules*, **2012**, *13*, 2446- 2455.
2. Deepa, P.; Jayakannan, M. *J. Polym. Sci. Part-A: Polym. Chem***. 2008**, *46*, 2445-2458.

Development of a Free Radical Initiator for the Polymerization of Alkyl Methacrylates: Synthesis of Different Polymeric Architectures

Atanu Kotal[1,2] and Tarun K Mandal*[2]
[1]Department of Chemistry, Techno India University, Salt Lake, Kolkata-91, W.B.
[2]Polymer Science Unit, IACS, Jadavpur, Kolkata-32, W.B. India
*psutkm@iacs.res.in

Development of new free radical initiator systems that are capable of producing polymers with controlled molecular weights and low polydispersity is an emerging area of research compared to the use of conventional radical initiators such as benzoyl peroxide and azobisisobutyronitrile as these system resulted polydisperse polymers (PDI > 2) in absence of any chain transfer agent. Moreover, synthesis of well defined polymeric architectures by conventional radical initiators is very rare. In this regard, we have developed a versatile initiator for alkyl methacrylates and successfully synthesize different polymeric architectures by proper design of different initiators.

N,N-Dimethylanilinium *p*-toluenesulfonate (PTSA-DMA) has been successfully used as a versatile initiator for the quasi-living free radical polymerization of several alkyl methacrylate monomers such as methyl, ethyl, *n*-butyl, *tert*-butyl, and benzyl methacrylates (MMA, EMA, *n*-BuMA, *t*-BuMA and BzMA respectively) at 60 °C in dry THF.[1] The produced poly(alkyl methacrylates) had narrow polydispersities (PDIs) (M_w/M_n = 1.16-1.45). EPR spectroscopic study showed that this polymerization proceeded through radical mechanism. Quasi-living nature of this polymerization system was established by the chain extension experiment as well as the successful synthesis of a block copolymer of poly(methyl methacrylate)-b-poly(methyl methacrylate-co-benzyl methacrylate), by the sequential addition of the respective monomers as confirmed through NMR, DSC and AFM.

After gaining the knowledge about PTSA-DMA polymerization system, we extend our strategy for the synthesis of different polymeric architectures utilizing different designed initiators based on leucomalachite green, leucocrystal violet and 4- ((4-(bis (4-(dimethylamino) phenyl) methyl) phenyl) (4-(dimethylamino) phenyl)methyl)-N, N-dimethylbenzenamine with p-toluenesulfonic acid.

Reference:

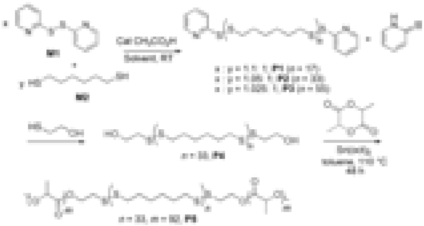
[1] Kotal, A.; Paira, T. K.; Banerjee, S.; Bhattacharya, C.; Mandal, T. K. Polym. Chem., 2010, 1(10), 1689-1695.

Telechelic Poly(disulfide)s and Related Block Copolymers

Dipankar Basak, and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Kolkata-700032, India
dip.basak@gmail.com

Polymers containing disulfide functionality exhibit sensitivity to redox stimuli and also to light owing to the labile nature of the S-S bond. Thus disulfide containing polymers have found applications in diverse fields including drug or gene delivery and self-healing materials. We envisioned a facile synthetic method that can produce structurally diverse poly(disulfide)s with tunable degree of polymerization and offers possibility of versatile end group modification and bioconjugation would have great utility as the existing methods based on oxidative polymerization require rather harsh reaction conditions and thus offer limited opportunities for functional group diversity. We have recently established a mild synthetic route for preparation of telechelic poly(disulfide)s by a step-growth polymerization between a dithiol monomer (for example 1,6-Hexanedithiol (**M2**)) and commercially available 2, 2' - Dithiodipyridine (**M1**) with stoichiometric imbalance (**M1** > **M2**)[1]. A series of telechelic polymers could be prepared with predictable molecular weight and reactive pyridyl-disulfide end groups by varying the **M1**/ **M2** ratio. Chain-end functionalization of the resulting poly(disulfide)s was possible by treating the parent polymer with R-SH where R contains functional group of choice such as hydroxyl, amine or carboxylic acid. The hydroxyl functionalized telechelic polymer was further used as a macroinitiator for ring opening polymerization of a cyclic lactide to produce an ABA triblock copolymer. This newly developed methodology for preparation of poly(disulfide)s and its implications in synthesis of stimuli-responsive functional polymers will be the focus of this presentation.

Scheme 1: Synthesis of telechelic poly(disulfide)s and block copolymers.



References:

[1] Basak, D.; Kumar, R.; Ghosh, S. *Macromol. Rapid Commun.* **2014,** *35*, 1340.

Nanoporous fluorinated co-poly(arylene ether) membranes withhigh thermal stability and low dielectric constant

Sayantani Saha, Ershad Ali Mistri, Debaditya Bera, and Susanta Banerjee*
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
**susanta@matsc.iitkgp.ernet.in*

High performance thermoplastics likepoly(arylene ether)s (PAE)s have found immense importance in microelectronic application as insulating materials owing to their low dielectric constant during these years. Three new semifluorinated co-PAEs containing cardofluorene moiety in the main chain have been synthesized by one pot high temperature polycondensation reaction using two bis-hydroxy compounds, 9,9-bis(3,5-dimethoxy-4-hydroxyphenyl)fluorene(DMHF), bisphenol A (BPA) and three different bis-fluoro monomers.The polymers exhibited good processabilitydue to the presence bulky $-CF_3$ groups and ether linkages.Flexible, transparent and mechanically strong membranes were obtained after solution casting from N,N-dimethylacetamide. Lower polymer concentration and lower cooling rate induced nanoporeswithin the membranes. Regular distribution of nano-pores was observed by FESEM analysis, whichconsiderably reducedthe dielectric constants (κ)of the membranes(~2.25 - 2.42 at 1 MHz). The presence of $-CF_3$ groups and cardo fluorine moiety also played an important role for such low k. The polymers exhibited reasonably high thermal stability (T_{d10}, 459-485°C) and high glass transition temperature (215-228 °C) with no crystallization peak suggesting amorphous nature of the polymers. Furthermore, membranes exhibited good mechanical properties with tensile strength in the range of 55.5-70.1 MPa and modulus value in the range 1.53-1.72 GPa. The membranes also revealed good optical transparency ($\lambda_{cut\text{-}off}$= 350-370 nm) along with very small water absorption (0.38-0.49 %) at saturation.

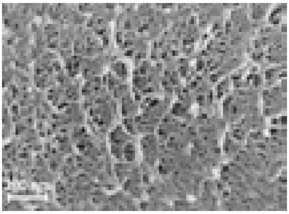


Figure 1: FESEM image on cross section

References:
[1] Maier, G.; Prog. Polym. Sci. **2001**, 26, 3 □ 65.
[2] Dhara,M.G.; Banerjee,S.Prog. Polym. Sci. **2010**, 35, 1022–1077.
[3] Wang, C.; Li,N.; Shin, D.W.; Lee,S.Y.; Kang, N.R.; Lee, Y.M.;Guiver, M.D. Macromolecules **2011**, 44, 7296 □ 7306.

A Combinatorial Approach to Develop Tailored Biodegradable Poly(xylitol dicarboxylate) Polyesters

Queeny Dasgupta[1], Kaushik Chatterjee[1,2], Giridhar Madras[3*]
[1]Bioengineering Program, [2]Department of Materials Engineering and [3]Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India
giridhar@chemeng.iisc.ernet.in

The objective of this work was to develop a versatile strategy for preparing biodegradable polymers with tunable properties for biomedical applications. A family of xylitol-based cross-linked polyesters was synthesized by melt condensation. The effect of systematic variation of chain length of the diacid, stoichiometric ratio and postpolymerization curing time on the physicochemical properties was characterized. The degradation rate decreased as the chain length of the di-acid increased. The polyesters synthesized by this approach possess a diverse spectrum of degradation (ranging from ~4 to 100 % degradation in 7 days), mechanical strength (from 0.5 to ~15 MPa) and controlled release properties. The degradation was a first-order process and the rate constant of degradation decreased linearly as the hydrophobicity of the polyester increased. In controlled release studies, the order of diffusion increased with chain length and curing time. The polymers were found to be cytocompatible and are thus suitable for possible use as biodegradable polymers. This work demonstrates that this particular combinatorial approach to polymer synthesis can be used to prepare biomaterials with independently tunable properties.

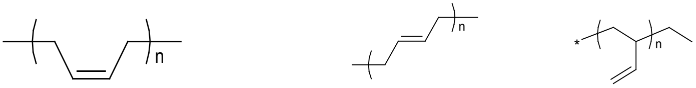
References:

[1] Bruggeman, J. P.; de Bruin, B.-J.; Bettinger, C. J.; Langer, R. Biodegradable poly (polyol sebacate) polymers. Biomaterials 2008, 29 (36), 4726-4735.
[2] Sathiskumar, P.; Madras, G. Synthesis, characterization, degradation of biodegradable castor oil based polyesters. Polymer Degradation and Stability 2011, 96 (9), 1695-1704.
[3] Bruggeman, J. P.; Bettinger, C. J.; Nijst, C. L.; Kohane, D. S.; Langer, R. Biodegradable Xylitol-Based Polymers. Advanced materials 2008, 20 (10),1922-1927.
[4] Bruggeman, J. P.; Bettinger, C. J.; Langer, R. Biodegradable xylitol-based elastomers: In vivo behavior and biocompatibility. Journal of Biomedical Materials Research Part A 2010, 95 (1), 92-104.

Effect of Microstructure on HTPB based polyurethane (HTPB-PU)

Abhijit Dey,[a*] Md Abdul Shafeeuulla Khan,[a] Javaid Athar,[a]
Arun Kanti Sikder[a] , Santanu Chattopadhyay[b]
[a]Energetic Materials Research Division, High Energy Materials Research Laboratory (Defence Research & Development Organization), Sutarwadi, Pune, India-411 021
[b] Rubber Technology Centre, Indian Institute of Technology, Kharagpur, West Bengal
E-mail: abhidey_bkn @yahoo.com

Effect of HTPB microstructure on HTPB based polyurethane network (HTPB-PU) were investigated. These evaluations were carried out by mean of several characterization like measurement of gel point, mechanical properties, hardness, cross link density measurement and thermal analysis like STA (TG-DTA). The variation of microstructures concentration (cis, trans and vinyl, See Fig. 1) were observed in different grades of HTPB. Its creates remarkable variation in PU properties with respect to mechanical, thermal properties and crosslink density. The results showed that polyurethane synthesized from HTPB prepolymer containing higher amount of cis and trans microstructure exibited better pot life, good mechanical properties and thermal stability with higher cross link density. Here, three different grades of HTPB were experimented. HTPB (Gr. 2) contains higher amount of cis and trans microstructure. The polyurethane synthesized from HTPB (Gr. 2) i.e. HTPB (Gr.2)-PU shows improved mechanical properties with better thermal stability and crosslink density as compared to other two polyurethane. Hence, HTPB (Gr.2) is relatively superior prepolymer than the other two grades for better HTPB-PU network formation.



(a) **(b)** **(c)**

Fig. 1: Microstructure of HTPB (a) cis, (b) trans (c) vinyl

References:

1. Daniel, M. A. Polyurethane Binder Systems for Polymer Bonded Explosives, Weapons Systems Division DSTO Defence Science and Technology Organisation, 2006.
2. Mathieu, J.; Stucki, H. Chimia **2004**, 58, 383-389
3. Gupta, T.; Pradhan, N.C.; Adhikari, B. Bull Material Science **2002**, 25, 533-536
4. Yang, J.M.; Lin, H.T.; *Journal of Membrane* Science **2001**, 187, 159-169.
5. Chen, S.H.; Yu, K.C.; Houng, S.L.; Lai, J.Y.; Journal of Membrane Science. **2000**, 173, 99-166.
6. Kuo, C.; Samuelson, L.A.; McCarthy, S.P.; Tripathy, S.K.; Kumar, J. J Macromolecular Science. Part A. Pure Applied Chemistry A, **2003**, 40, 1383-1396.

Synthesis and characterization of Energetic Nanocomposites based on GAP and PolyNIMMO

J. Athar*, Rashmi Wagh, Vineet Nangare, Abhijit Dey,
R R Soman and A K Sikder
High Energy Materials Research Laboratory, Pune, India-411021

Glycidyl Azide Polymers (GAP) and Poly Nitratomethyl methyl oxetane (PolyNIMMO) are promising candidates as energetic binder in futuristic advanced propellants and explosive compositions having positive heat of formation, minimum smoke and low sensitivity. Because of these properties, These energetic binders appear to be a promising replacement of Hydroxy terminated polybutadiene (HTPB) in propellant/explosive compositions. Formulations based on GAP and PolyNIMMO are often have low tensile strength and poor elongation which restrict them to be used as binder.

It is well reported that polyurethane nanocomposites based on montmorillonite clay are having better mechanical properties like tensile strength, better adhesion and flexibility. So, attempts have been made to prepare energetic nano composite based on GAP and PolyNIMMO. Organo modified montmorillonite clay was dispersed (2-3 wt%) in polymer matrix by high speed stirring at elevated temperature followed by ultrasonication to give exfoliation of silicate layers of organo clay. Then, this mixture is cured with calculated amount of Tri Methylol Ethane (TME) as a crosslinker and Desmodur N100 as a curator in presence of catalyst. Clay dispersion leading to exfoliation in polyurethane nanocomposites was investigated by X-ray diffraction analysis and its morphology was studied by Scanning Electron Microscope. Further, these composites were characterized by FTIR, DSC, Rheological and mechanical properties.

The thermal behavior of composite samples was investigated by DSC and found comparable with the control samples i.e. cured GAP without nano-clay. Glass transition temperature determined by DSC was also similar for nanocomposites and control samples. Almost 80% increase in tensile strength and 70% increase in E-modulus were found for GAP and PLN based nanocomposites where the clay dispersion was up to 3%. Rheological parameter like flow behavior, yield stress, shear velocity etc, after clay dispersion has also been investigated in order to see the solid loading in the binder before curing. These energetic nanocomposites were also found to be an ideal coating material for the desensitization of HEMs. HNF and CL-20, RDX etc. were successfully desensitized by coating with these energetic nanocomposites.

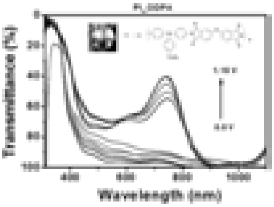
References

1. Mul J.A., Korting, P.A. and Schoyer, H.F.R. " A New Storable High Energy Propellants" ESA Journal, Vol. 14, 1990. 253-270.
2. Polymer, 43 (2002) 1017-1020 "Polymer/layered clay nanocomposites: 2 polyurethane nanocomposites" K. J. Yao, M. Song, D.J. Hourston, D.Z. Huo.

Triarylamine-Based Electroactive Polyimides Containing Pendant Pentadecyl Chains

Deepshikha Chatterjee, Chayanika Das and Prakash P. Wadgaonkar*
Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India.
Email: pp.wadgaonkar@ncl.res.in

A new triarylamine containing diamine possessing pendant pentadecyl chain, namely 4, 4'-diamino-4''pentadecyltriphrnylamine, was successfully synthesized starting from cashew nut shell liquid- a non-edible oil which is a by-product of cashew processing industry. 4, 4'-Diamino-4''pentadecyltriphrnylamine was polycondensed with commercially available aromatic dianhydrides, *viz. 4,4*'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA), 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-biphenyl diphthalic anhydride (BPDA) by single step high temperature polycondensation in *m*-cresol. Inherent viscosities and number average molecular weights were in the range of 0.4-0.55 dL/g and 12,000-33,000 respectively, indicating formation of reasonably high molecular weight polyimides. Polyimides were amorphous and easily soluble in organic solvents such as chloroform, *N*-Methyl-2-pyrrolidone, *N,N*-dimethylacetamide, etc, which could be attributed to the 'packing disruptive' effect of the pentadecyl chains. The polyimides could be cast into flexible and transparent films from their chloroform solution. Glass transition temperatures (Tg) of polyimides were in the range of 172°C-233°C and 10% weight loss (T_{10}) temperatures were in the range 415°C-440°C with char yields of 35%-45%, indicating their good thermal stability. Polyimides exhibited maximum UV-Vis absorption at 325 -336 nm in chloroform solution as well as in the form of thin films. The electrochromic properties of polyimides were studied by electrochemical and spectrochemical methods. Cyclic voltagrams of triarylamine containing polyimides showed half-wave potentials ($E_{1/2}$) at 0.68 V-0.75 V *vs*. Ag/AgCl in dry acetonitrile solution and exhibited a reversible colour change from neutral pale yellow to bright green or blue on switching the potential between 0 V and ~1.4 V.



References:

[1] Voirin ,C; Caillol ,S; Sadavarte, N. V; Tawade, B.V.; Boutevin, B; Wadgaonkar, P. P. *Polym. Chem.*, **2014**, *5*, 3142-3162.

[2] Yen, H; Guo, S; Yeh, J; Liou, G. *J. Polym. Sci, Part A: Polym. Chem.* **2011**, *49*, 3637-3646.

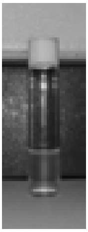
[3] Hsiao, S; Chang, Y; Chen, H; Liou, G. *J. Polym. Sci, Part A: Polym Chem.* **2006**, *44,* 4579-4592.

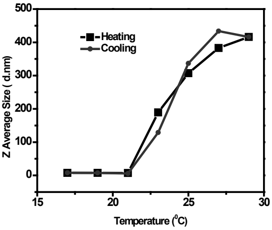
[4] Kung, Y; Liou, G; Hsiao, S. *J. Polym. Sci, Part A: Polym Chem.* **2009**, *47*, 1740-1755.

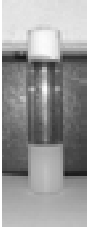
Thermosensitive Water-Soluble PVDF based Graft Copolymers

Atanu Kuila[1], Nabasmita Maity[1], Dhruba P. Chatterjee [2] and Arun K. Nandi[1]*
[1]Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India
[2]Dept. of Chemistry, Presidency University, Kolkata-700 073, India
*psuakn@iacs.res.in

Earlier we have reported a novel synthetic platform for grafting of various vinyl monomers [mainly (meth)acrylates][1]. The strategy involved Atom Transfer Radical Coupling(ATRC)[2] of 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl radical(4-Hydroy TEMPO) on PVDF backbone, followed by coupling of suitable acyl halide moieties to develop model initiating sites for Atom Transfer Radical Polymerization(ATRP) of vinyl monomers. Here in this report, we have prepared a water soluble PVDF grafted Polymethoxyethoxyethyl-methacrylate (PVDF-g-PMeO$_2$MA) by polymerization of MeO$_2$MA on PVDF backbone using atom transfer radical polymerization (ATRP) with copper based catalyst system at 60 ^{0}C. Characterisation of the synthesized polymer has been carried out using FTIR, NMR, GPC, DSC and XPS techniques. Dynamic light scattering study of PVDF-g-PMeO$_2$MA in water indicates a sharp increase of Z-average particle size for attaining lower critical solution temperature(LCST) at 24 ^{0}C and in the cooling cycle, it shows a complete reversibility.







References:

[1] **Kuila, A**.; Chatterjee, D.P.; Nandi, A.K. J. Polym. Sci. Part A: Polym. Chem. **2014**, 52 (7), 995 – 1008.

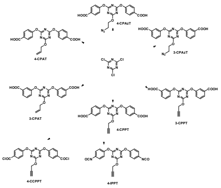
[2] Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z**.** Macromolecules **1998**, 31, 5955 –5957.

Synthesis of 1,3,5-Triazine Containing Difunctional Monomers Possessing Pendant Clickable Groups

Kavita Garg, Nilakshi V. Sadavarte and Prakash P. Wadgaonkar*
Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India.
Email: *pp.wadgaonkar@ncl.res.in*

High performance polymers such as aromatic polyesters and polyamides have received considerable attention due to their notably high impact on industry. These polymers find applications in various industries such as aero-space, automobiles, electronics, packagings, coatings, etc, due to their excellent mechanical and thermal properties, good chemical resistance and insulating properties. However, for more specific applications these polymers are limited in scope because of the lack of functionalities on the polymer backbone for further modifications and tailoring.[1-2]

A series of triazine containing diacids and diisocyanates, possessing pendant clickable groups, namely alkyne, azide or allyl were synthesized using cyanuric chloride as an inexpensive, commercially available starting material employing simple organic transformations. These monomers are potentially useful for the synthesis of a range of step growth polymers. Polyurethanes (PU) were synthesized by polycondensation of 2,4-bis(4-acylazidephenoxy)- 6-propargyloxy-*s*-triazine(4-APPT) with a diol. The acylazide group undergoes Curtius rearrangement to form corresponding diisocyanates which react with diol to form polyurethane containing pendant alkyne, azide or allyl group. Click reaction of azido terminated polyethylene glycol with polyurethane containing pendant alkyne groups was demonstrated.



References:
[1] 1) Williams, C. K. *Chem. Soc. Rev*. **2007,** *36*, 1573.
[2] 2) Lecomte, P.; Riva, R.; Jerome, C.; Jerome, R. *Macromol. Rapid. Commun*. **2008,** *12*, 982.
[3] 3) Deepa, P; Jayakannan, M. *J. Polym. Sci. Part A: Polym. Chem*. **2008**, *46*, 2445.

Phosphorylation of poly vinyl alcohol using phosphorus pentoxide

K. Rajalakshmi[1], P. Santhana Gopala Krishnan[1, 2*] and S. K. Nayak[1, 2]
[1]Department of Plastics Technology, Central Institute of Plastics Engineering and Technology (CIPET), Guindy, Chennai, India
[2]Department of Plastics Engineering, Central Institute of Plastics Engineering and Technology (CIPET), Patia, Bhubaneswar-751024 (India)
* *psgkrishnan@hotmail.com*

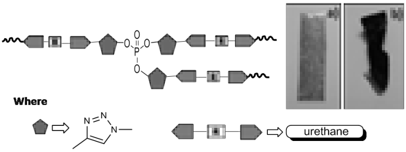
Polymeric materials find wide range of applications in our day-to-day life. The drawback of some of these materials is their limited flame resistance. Flame retardation of polymers can be achieved by physical incorporation of flame retardant additives or chemical modification with a flame retardant moiety. The commonly used halogen additives possess environmental hazard as they release toxic gases like hydrogen halide upon combustion. Further these additives leach out with time and so are less reliable. Chemical modification of polymers requires lesser amount of flame retardant, imparts permanent flame retardancy and has less influence on the physical and mechanical properties of the polymer, when compared to additive approach. A large number of compounds are available for the chemical modification of existing polymers. The use of phosphorus containing compounds as flame retardant agents has received much attention in the recent years.

In the present study, poly vinyl alcohol (PVOH) was phosphorylated with varying compositions of phosphorus pentoxide. Solution of phosphorus pentoxide in dimethyl sulfoxide (DMSO) was added to PVOH dissolved in DMSO. The reaction was carried out at 70 °C in nitrogen atmosphere. The reaction mixture was precipitated out in methanol and dried in vacuum. The samples were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and ^{31}P- NMR and the results confirmed the formation of phosphate linkage. Inductively coupled plasma atomic emission spectroscopy was done to determine the phosphorus content. WAXD studies were carried out to understand the crystalline nature of the samples. Glass transition temperature (T_g) of polymers was determined by differential scanning calorimetry. T_g of the phosphorylated samples were higher than pure PVOH. The thermal stability of polymers was analyzed using thermo gravimetric analysis in nitrogen atmosphere and the samples were found to be stable upto 200 °C and showed double stage decomposition.

Synthesis of novel phosphorous based flame retardant polymers via azide alkyne click chemistry

Kesavarao Sykam and Shailaja Donempudi*
Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Hyderabad- 500 007, India
*sdonempudi@iict.res.in

In recent times, due to the stringent regulations, a blanket ban was laid on halogenated flame retardant polymers (FRP) due to toxicology and environmental concerns. This has led to a major change to alternative FRP's that are halogen free but similar in performance[1]. Organo phosphorous compounds fully comply with the safety regulations and can be carefully matched with the type of polymer formulation with required end part properties that can be used as commodity polymers. However, they are accompanied with limitations in high temperature applications, due to the negative impact on mechanical properties as high loading is required for the FR activity. Therefore, in the present study, synthesis and characterization of novel phosphorous based monomer that can be used in FRP which has high thermal stability, low combustion heat release rate, yield in give high char formation and release minimum toxic fumes has been reported via azide-alkyne click chemistry. The novel monomer consists of triazole moiety and hydroxyl functionality such that the compounds have high C/H ratio resulting in less H_2 gas evolution on pyrolysis and release of non-combustible N_2 gas because of 1,2,3 triazoles, thus offering the synergistic benefits. The as synthesized phosphorous based monomer can be useful in development of fire retardant poly urethane coatings on reacting with diisocyanate and can be useful to develop in fire retardant poly ether coatings by epoxide opening reactions.



a), b) Polymeric films before and after exposure to fire respectively.

Fig 1: Representation of halogen free, phosphorous, triazole based poly urethane fire retardant coating.

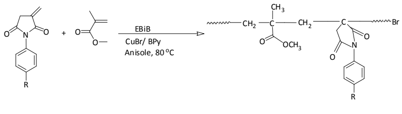
References:

[1] Alexander B. Morgan, Charles A. Wilkie-The Non-halogenated Flame Retardant Handbook-Wiley-Scrivener (**2014**)

Controlled Radical Copolymerization of *N*-aryl itaconimides with Methyl Methacrylate *via* Atom Transfer Radical Polymerization

Chetana Deoghare[1,$], Vishnu S. Nadkarni[2], N. N. Ghosh[1],
R. N. Behera[1] and Rashmi Chauhan[1,*]
[1]Department of Chemistry, Birla Institute of Technology & Science,
Pilani – K. K. Birla Goa Campus, Zuarinagar - 403726, Goa, India
[2]Department of Chemistry, Goa University, Taleigao Plateau – 403206, Goa, India
[$] *chetskm@gmail.com*

The incorporation of imides such as itaconimides in the polymer backbone is reported to enhance glass transition temperature and thermal stability of resulting polymers. The copolymerization of *N*-aryl itaconimides with methyl methacrylate (MMA) has been mostly done by conventional free radical polymerization which offers poor control over the molecular weight and architecture of the resulting polymers. Synthesis of these copolymers using atom transfer radical polymerization (ATRP) process, which is known to give polymers with known architecture and active chain ends, may be interesting. In this work, we report the copolymerization of various *N*-aryl itaconimide monomers [such as *N*-phenylitaconimide, *N*- (4-methylphenyl) itaconimide, *N*- (4-methoxyphenyl) itaconimide, *N*-(4-chlorophenyl) itaconimide] and MMA using CuBr/ Bpy as catalyst in anisole at 80 °C and ethyl-α-bromoisobutyrate (EBiB) as initiator, as shown in reaction Scheme 1. The structural characterization of obtained copolymers has been done using FT-IR, ^{1}H NMR spectroscopy and elemental analysis. The molecular and thermal characterization has been done using GPC and DSC/ TGA, respectively. The kinetic studies were done to investigate if the copolymerization proceeds under controlled radical polymerization condition. The linear first-order kinetics of monomers with time as well as linear evolution of the molecular weight with conversion confirms controlled polymerization.



Where R = –H, $-CH_3$, $-OCH_3$, and –Cl

Scheme 1. Reaction scheme for the synthesis of copolymer of *N*-aryl itaconimides and MMA *via* ATRP.

References:

[1] Solanki, A.; Anand, V.; Choudhary, V.; Varma, I.; *J. Macromol. Sci., Polym. Rev.* C41 (2001) 253.
[2] Chauhan, R.; Choudhary, V.; *J. Appl. Polym. Sci.* 112 (2009) 1088.
[3] Matyjaszewski, K.; *Macromolecules* 45 (2012) 4015.
[4] Matyjaszewski, K,; Tsarevsky, N. V.; *J. Am. Chem. Soc.* 136 (2014) 6513.

Effect of bulky group on gas transport properties of semifluorinated poly(ether amide)s

Soumendu Bisoi and Susanta Banerjee*
Materials science centre, Indian Institute of technology, Kharagpur 721302, India
*susanta@matsc.iitkgp.ernet.in

Polymer Membrane-based gas separation has established as an alternative separation technique over other conventional separation procedures like cryogenic distillation, adsorption due to its high energy efficiency [1,2].The advancement of the membrane based separation technology depends on the availability of the superior membrane materials with high gas permeability and gas selectivity. In this scenario aromatic polyamides (PAs) can be used as a membrane material. PAs have high melting or glass-transition temperatures (T_g) [2,3]. A series of new processable PA membranes containing polar pyridine units for gas separation were prepared from a newly synthesized acid 2,6-bis[3'-trifluoromethyl -4'(4''-carboxyphenoxy) benzyl] pyridine and previously reported four diamines monomer. The synthesized PAs showed high thermal stability (up to 468 °C in air, for 10% weight loss), high glass transition temperature (243–254 °C) and tensile strength up to 95 MPa. The permeability of four different gases CH_4, N_2, O_2 and CO_2 through these PA membranes was investigated at 35 °C under an applied upstream pressure of 3.5 bar. PAs showed high gas permeability (P_{CO2} up to 81 and P_{O2} up to 20 barrer) and high permselectivity (P_{CO2}/P_{CH4} up to 47.50 and P_{O2}/P_{N2} up to 6.9). The gas transport properties have been correlated with the polymer structures with respect to their fractional free volume (FFV) and density.

References:

[1] Yampolskii, Y. Macromolecules. **2012**,45, 3298-3311.
[2] Liu, P.; Liu, C.; Jian, X. Journal of Applied Polymer Science. **2007**,104, 2807-2811.
[3] Bandyopadhyay, P.; Bera, D.; Ghosh, S.; Banerjee, S. RSC Adv. **2014**, 4, 28078-28092.

POSS tethered amphiphilic graft copolymer based on poly(caprolactone)

Souvik Ata, Nikhil K Singha*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur

Inorganic-organic hybrid materials based on polyhedral oligomeric silsesquioxane (POSS) have interesting properties. POSS, the smallest silicone particles, consists of an inner inorganic framework of silicone and oxygen atoms and an outer shell of organic moieties. Due to biocompatibility, inertness, low inflammatory response, nontoxicity, cytocompatibility and ability to incorporate to any polymers, POSS has created a great importance also in the field of drug delivery. In this investigation, we report well defined synthesis of POSS tethered poly(caprolactone)-graft-poly(acrylic acid) (POSS-PCL-*graft*-PAA) polymer via grafting onto approach in combination with ATRP and click chemistry. Poly(^{t}butyl acrylate) was synthesized via ATRP whose Br- end group was replaced by azide group and then azide alkyne click (CuAAC) reaction was performed with alkyne functionalized PCL in presence of Cu(I) catalyst. Later hydrolysis of tert-butyl group to acid led to the POSS tethered PCL-*graft*-PAA polymer. This amphiphilic graft copolymer was characterized by GPC, NMR and FT-IR analyses. Morphology was characterized by high resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM). CMC value was determined by fluorescence spectroscopy using pyrene as a probe. This material can be a potential carrier for targeted drug delivery.

References:

[1] Tanaka, K.; Inafuku, K.; Naka, K.; Chujo, Y., Org. Biomol. Chem. **2008**, 6, 3899-3901.
[2] McCusker, C.; Carroll, J. B.; Rotello, V. M., Chem. Commun. (Cambridge, U. K.) **2005**, 996-998.
[3] Ghanbari, H.; de Mel, A.; Seifalian, A. M., Inter. J. Nanomedicine **2011**, 6, 775-86.
[4] Tanaka,K.; Chujo,Y.; J.Mater.Chem., **2012**, 22, 1733-1746.
[5] Tanaka,K.; Inafuku,K.; Adachi,S.; Chujo,Y.; Macromolecules, **2009**, 42, 3489-3492.
[6] Escude,N.C.; Chen,E.Y.X.; Chem. Mater, **2009**, 21, 5743-5753.
[7] Zhang,W.; Müller,A.H.E.; Polymer, **2010**, 51, 2133-2139.

Synthesis and characterization of bio-based building blocks from Renewable monomers

Somisetti Varaprasad, Ramanuj Narayan, K.V.S.N.Raju*
Polymers and functional materials division,
Indian institute of chemical technology, Hyderabad
*kvsnraju@iict.res.in

The main objective of our research is to develop new bio-based polyurethanes from renewable resources as the substitution of petroleum-based raw materials. We have synthesized novel tri-functional epoxide monomer through esterification of glycerol and 10-undecenoic acid followed by epoxidation. The synthesized building block was utilized for the preparation of three different hydroxy terminated polymers by reacting with methanol, water and glycerol. The chemical structure of these bio-based polyols and their intermediates were determined by different spectroscopic analyses.

The polyols were further reacted with different ratios of 4, 4′-methylenebis (phenyl isocyanate) to get isocyanate-terminated polyurethane prepolymers which were cured under atmospheric moisture to get the desired coating films. The final bio-based and moisture cured polyurethanes were characterized in detail by FT-IR studies, whereas the properties of these polymers were assessed by DSC, TGA, DMTA, and tensile test experiments. These films showed good coating properties, thermal stability and mechanical strength.

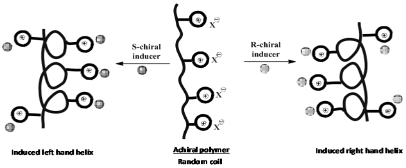
References:

[1] Ronda, J.C., Lligadas, G., Galia, M., Cadiz, V. Eur . J. Lipid Sci. Technol. 2011, 113, 46–58.
[2] Stéphanie, L.; Cédric, H.; Luc, A. Green Chem., 2014, 16, 3958.

Chiral Polymers: Synthesis, Characterization and their Applications in Enantioselective Synthesis

Nellepalli Pothanagandhi, Yenuganti Mahesh, Akella Sivaramakrishna,
Kari Vijayakrishna*
Organic Chemistry Division, School of Advanced Sciences,
VIT University, Vellore-632014, Tamil Nadu, India
** Kari Vijayakrishna@gmail.com*

Enantioselective synthesis is a key process in chemistry and is particularly important in the field of pharmaceuticals, as the different enantiomers or diastereomers of a molecule often have different biological activity. Poly ionic liquids (PILs) are finding increasing applications in the field of chemistry, biology and material science due to their unique properties [1, 2]. In our studies we synthesize three different proline based chiral poly ionic liquids (CPILs) by creating chirality on anionic site of imidazolium salts [3]. The synthesized chiral poly ionic liquids we used as catalysts for enantioselective Baylis Hillman reaction carried out between methyl vinyl ketone and arylaldehydes [4]. The CPILs shows better catalytic activity than proline and also we observe chiral switch (we can synthesize desire isomer as major) in the reaction catalyzed by CPILs. The hypothetical explanation for observation of chiral switch in Baylis Hillman reaction due to different helices of CPILs [5]. The CPIL catalyze Baylis Hillman reaction of methyl vinyl ketone and arylaldehydes gave moderate yield and enantioselectivity. All the results will be discussed during the presentation.



References

[1] (a) Prabhu Charan, K. T. Pothanagandhi, N. Sivaramakrishna, A. Mecerreyes, D. Sreedhar, B. Eur. Polym. J. **2014**, 60, 114-122; (b) Garcia, R. Vijayakrishna, K. Mecerreyes, D. React. Funct. Polym. **2014**, 79, 54-58.

[2] (a) Vijayakrishna, K. Mecerreyes, D. Gnanou, Y. Taton, D. Macromolecules. **2009**, 42, 5167-5174; (b) Vijayakrishna, K. Jewrajka, S. K. Ruiz, A. Marcilla, R. Pomposo, J. A. Mecerreyes, D.; Taton, D.; Gnanou, Y., Macromolecules. **2008**, 41, 6299-6308.

[3] Pothanagandhi, N. Vijayakrishna, K. Communicated Manuscript. **2014**.

[4] Goren, K. Portnoy, M. Chem. Commun. **2010**, 46, 1965-1967.

[5] Han, L. Hong, M. Inorg. Chem. Commun. **2005**, 8, 406-419.

Synthesis and characterization of difunctional benzoxazines based on ester containing aromatic diamines and their thermal behavior

Periyavaram Surendra, B. S. Rao*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad – 500 007, India
E mail: butti@iict.res.in

Thermosetting resins, for instance phenolic, epoxy, unsaturated polyester and bismaleimide resins are superb in terms of water, chemical and heat resistance, mechanical strength and reliability. Even though they have convinced disadvantages like generation of volatile by-products at the time of curing of phenolic resin, inferior flame retardance as far as polyester and epoxy resin are concerned and moreover, bismaleimide resin is extremely expensive. In order to overcome these drawbacks, a new type of phenolic resins called polybenzoxazines, which cure by ring opening polymerization were being developed. As promising thermosetting resins, polybenzoxazines have drawn attention in the past decade due to their unique physical and chemical properties. They are usually used as high performance materials in various fields, such as automotive, aerospace and construction industries, which require remarkable thermal stability in addition to flame retardance. We hereby report a series of difunctional benzoxazine monomers (M1-M4) and their thermosets (P_{M1-M4}) (see Scheme).

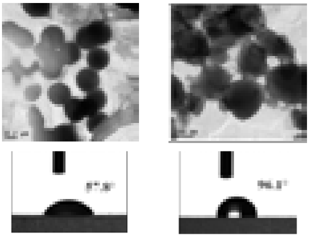
The structures of the synthesized monomers were confirmed by FT-IR, and ^{1}H- and ^{13}C-NMR spectroscopic techniques. Their high performance thermosets (P1-P4) were obtained by thermal curing (between 200 - 300 °C) of dibenzoxazines and studied their characteristics by DSC, TGA and DMTA. It was found that the developed polybenzoxazine from M1 showed good thermal stability compared to the polymers obtained from other monomers.

References:
[1] Ishida, H.; Sanders, D. P. J Polym. Sci.: Part B: Polym. Phys. **2000**, 38, 3289-3301.
[2] Lin, C. H.; Chang, S. L.; Hsieh, C. W.; Lee, H. H. Polymer **2008**, 49, 1220-1229.
[3] Wang, J.; He, X.-Y.; Liu, J.-T.; Liu, W.-B.; Yang, L. Macromol. Chem. Phys. **2013**, 214, 617-628.

NaMMT Stabilized Pickering Miniemulsion of Tailor-made Fluorinated Copolymers with Improved Hydrophobicity

Arindam Chakrabarty, Kinsuk Naskar, Nikhil K Singha*
Rubber Technology Centre, Indian Institute of Technology
Kharagpur Kharagpur - 721302, India
** nks@rtc.iitkgp.ernet.in*

This investigation reports the preparation of fluorinated copolymer latex by pickering miniemulsion polymerization using nanoclay (NaMMT) as sole stabilizer. In this case the copolymerization of Styrene (St), Butyl acrylate (BA) and 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) was carried out via Reversible Addition-Fragmentation chain Transfer (RAFT) process. Addition of 2-(acryloyloxy) ethyl trimethylammonium chloride (AETAC) as functional comonomer increased the rate of polymerization as well as conversion to a greater extent. AETAC, a cationic monomer was introduced to increase the polymer-clay interaction which has beneficial effect on the final properties of the copolymer. The copolymers had controlled molecular weights as well as narrow dispersity. Nanoclay armored morphology was observed by TEM and SEM analyses. The copolymer films had improved hydrophobicity as evidenced by the measurement of water contact angle (WCA).



WCA of copolymer with NaMMT

WCA of copolymer with NaMMT & 2 wt% AETAC

Figure: TEM images of NaMMT stabilized emulsion of fluorinated copolymers and their water resistance.

References

1. Bonnefond, A.; Paulis, M.; Bon, S.A.F.; Leiza, J.R.; Langmuir. 2013, 29, 2397-2407.
2. Zhang, J.; Chen, K.; Zhao, H.; J polym Sci Part A: Polym Chem. 2008, 46, 2632-2639.

Iron(II) catalyzed Atom Transfer Radical Polymerization of Ethylene and Butylmethacrylate

Somip Borphukan, Urmilla Baruah, Maitrayee Saikia,
Arvind Gautam and Shashi D. Baruah
Petroleum & Natural Gas Division, CSIR-North-East Institute of Science & Technology,
Jorhat 785006, Assam, India
E-mail: baruah_shashi@yahoo.co.in

Co-polymers of ethylene and functional monomers are high value polymer materials.[1,2] Controlling the co-polymerization of ethylene with polar monomers remains a very significant challenge.[3] Keeping in view of the demand, for olefin based copolymers with polar functionalities, poly(ethylene-co-butylmethacrylate) was synthesized by the incorporation of butylmethacrylate as the polar moiety into ethylene chain using atom transfer radical polymerization. The reaction was studied at a high pressure-high temperature reactor with iron(II) complex as catalyst in presence of aluminium trifluoromethanesulfonate as recyclable lewis acid. The copolymer was characterized by NMR, FT-IR, GPC and XRD analysis. It was found that the copolymer formed is of low molecular weight and it exhibited broad molecular weight distribution with amorphous behaviour. DSC result revealed that the thermal stability of the copolymer is improved with the increase concentration of ethylene in the feed. Thermal degradation parameters of the copolymers were evaluated from TGA and DSC analysis.

References:

1. Kermagoret, A.; Debuigne, A.; Jerome, C.; Detrembleur, C. Nature Chemistry, **2014,** *6*, 179.
2. Sugimoto, R.; Kaneko, H.; Saito, J.; Kawahara, N.; Matsuo, S.; Matsugi, T. Polym. Bull. **2014,** *71*, 1421.
3. Franssen, N. M. G.; Reek, J. N. H. Chem Soc. Rev. **2013,** *42*, 5809.

Synthesis of Novel Hyperbranched Polyaspartic-ester Polyol based Functional Polyurethane-urea and their Hybrids for High Performance

Rajnish Kumar, Ramanuj Narayan, KVSN Raju*
Polymers and Functional Materials Division,
Indian Institute of Chemical Technology, Hyderabad-500007, India

Hyperbranched polymers (HBP) play a key role in tuning the properties of one of the most versatile material, polyurethane (PU). Hyperbranched polyurethane-urea (HBPUU) exhibit excellent functional properties through core, end group and backbone modification of HBP and hybrid formation. Despite great potential and wide application of PU coatings and materials, there is some limitation such as slow film build up, solvent content, low UV resistance, mono and/or dual functionality, adhesion, application method etc. Polyaspartic- polyurethanes (ASP-PU) can meet those challenges as their characteristic properties include UV resistance, high gloss, high abrasion and chemical resistance, fast curing time and good film build-up in single coat. Polyaspartic polyols (PAP) contain a 'polyaspartic ester' group in their backbone and were first developed in the 1990s. These coatings can be used for both interior and external purposes and can be coated on wood, concrete, metal and plastics.

The synthesis of hyperbranched polyaspartic-ester polymers (HBPAP) was done with high atom economy by trimethylol propane (TMP) core following polycondensation reactions and Michael addition. The reactions were monitored based on acid values and equivalent mass was calculated based on hydroxy values. We developed high solid moisture cured polyaspartic-ester polyurethane urea (ASP-PUU) by reaction of HBPAP with H^{12}MDI in 1.6:1 ratio [NCO: reactive components (-OH,-NH)]. To improve flexibility, ASP-PU was further modified with hydroxylated soybean oil (HV = 230) in varying percentages to form various hybrid coatings (ASPSPUs). Structural confirmation was done by NMR, FTIR and mass spectrometry and characterization by TGA, DMTA, UTM, Abrasion, Corrosion, SEM, XRD, antimicrobial and gloss test at various angles. In comparison to other HBPUs, ASP-PU shows higher gloss, higher thermal stability and increased reaction time for urethane formation.

Fig1: Hyperbranched polyaspartic-ester polyurethane-urea

References:

[1] Kumar, Rajnish; Narayan, Ramanuj; Aminabhavi, T.M.; Raju, K.V.S.N. J. Polym. Res. **2014**, 21, 547 – 562.

[2] Campbell, M. T. Polyaspartic polyurethane application in composite industry **2011**, US Patent, 8003552B2.

Acetoacetylation of hydroxylated polyesters for the development of eco-friendly polyurethane coatings

Radhika K. R., Ramanuj Narayan and KVSN Raju*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India
**kvsnraju@iict.res.in*

The present work reports an easy method for the development of low viscous acetoacetylated polyester polyols for the development of eco-friendly polyurethane coatings. In the first step, a highly branched hydroxyl group terminated polyester polyol resin is prepared through one-pot polycondensation process using Neopentyl Glycol (NPG), Adipic Acid (AA), Isophthalic Acid (IPA) and Trimethylol propane (TMP). The introduction of trimethylolpropane into the polyester synthesis improves the number of branchings in the resin due to its trifunctionality. In the next step, the synthesized polyesters were treated with ethylacetoacetate in different precentages to develop acetoacetylated polyesters. It is observed that with increase of acetoacetylation the viscosity of the resin was reduced. This is due to the replacement of more polar OH group with the less polar and bulky β-ketoester group to a polymer backbone, which in turn results in chain separation as well as in reduction in auto-associative effect due to hydrogen bonding of HPs. For instance, the viscosity of the polyester polyol was reduced from 230 Pa.sec to 49 Pa.sec after 50% acetoacetylation. The synthesized acetoacetylated polyester resins were treated with a diisocyanate to get polyurethane coating films. All the coating films are showing good thermal and mechanical stabilities along with excellent corrosion resistance properties.

Scheme: Representative steps involved in the development of acetoacetylated polyester and their polyurethane coatings

References

1. F. D. Rector, W. W. Blount, D. R. Leonard, Journal Of Coating Technology (1989), vol 61, page 31.
2. Ramanuj Narayan, K.V.S.N. Raju, Progress in Organic Coatings (2002), vol 45, 59–67

Self-healing polymeric material via RAFT polymerization

Nabendu B Pramanik, Golok B Nando, Nikhil K Singha*
Rubber Technology Centre, Indian Institute of Technology Kharagpur,
Kharagpur- 721302, West Bengal, India
*nks@rtc.iitkgp.ernet.in

Tailor-made copolymers of furfuryl methacrylate (FMA) and butyl methacrylate (BMA) (PFMA-co-PBMA) were successfully synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization technique using 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTSP) as RAFT reagent. The copolymer PFMA-co-PBMA contained reactive furfuryl group from PFMA unit which was used as a diene in the Diels-Alder (DA) reaction. This PFMA undergoes gel formation during free radical polymerization but during RAFT polymerization the copolymer formed are all gel free and the reactive furfuryl group remains unaffected during RAFT polymerization. The thermoreversible network was successfully achieved by DA and retro-DA (rDA) reaction between the furfuryl groups of PFMA unit and a bifunctional maleimide cross-linker, bismaleimide as dienophile. This process was studied by NMR, FT-IR, differential scanning calorimetry (DSC) and nano-indentation analyses. The DA and rDA reactions were used to prepare self-healing polymer. Here PBMA unit was used to lower the T_g of this cross-linked materials and better flowability of the material towards the healing site thus lowers the rDA temperature. DSC analysis was used for determination of the endothermic rDA reaction. In this investigation self-healing property of the above cross-linked material was demonstrated by monitoring the repair of a scratch in the copolymer film upon heating and cooling. This was analyzed by scanning electron microscopy (SEM).

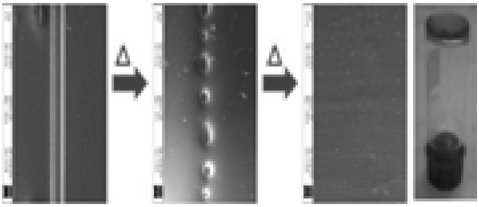


Fig 1: SEM photographs of self-healing experiments of copolymer/BM DA adduct.

References:

[1] Barthel MJ, Rudolph T, Teichler A, Paulus RM, Hoeppener JVS, Hager MD, Schacher FH, Schubert US. Adv Funct Mater 2013; 23: 4921-4932.

[2] Kavitha AA, Singha NK. ACS Appl Mater Interfaces 2009; 1: 1427–1436.

[3] Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, Sheran K, Wudl F. Science 2002; 295: 1698-1702.

[4] Goiti E, Huglin MB, Rego JM. Polymer 2001; 42: 10187-10193.

Facile synthesis of sulfur rich hyperbranched polymers using Thiol-yne click Chemistry for developing multifunctional Polythiourethane-urea coatings

I. Nagaraj Goud, B. Jagadeesh Yadav, Ramanuj Narayan, KVSN Raju*
Polymers and Functional Materials Division, IICT, Hyderabad-500007, India.
** drkvsnraju@gmail.com*

Catalyst free moisture cured multifunctional Poly (thiourethane-urethane)-urea (PTU-PU-urea) coatings were developed based on solvent free, one pot synthesis of sulfur rich hyperbranched polyester polyols (SRHBPs) and thiourethane containing –NCO terminated monomer. SRHBPs were synthesised via A_3+B_3 polycondensation approach and thiol-yne click chemistry. A sulfur core monomer (B_3) was synthesised at room temperature using thiol-yne click chemistry and condensed with acid terminated monomers (A_3). We developed catalyst free PTU-PU-urea coatings for these two SRHBPs by reacting with an isocyanate containing thiourethane units in 1:1.2 (OH: NCO) ratio. The structural characterisations were done by ^{1}H-NMR, ^{13}C-NMR, FT-IR, ESI-MS and MALDI-TOF techniques. The thermal and mechanical properties of the resulting coating films were carried out by TGA, DSC, DMTA and UTM techniques. Coatings showed good corrosion resistance property and remarkable bacterial and fungal resistance. Moreover, refractive index, transparency, adhesive properties were also determined for coatings.

References:

[1] Li, Q.; Zhou, H.; Wicks, D. A.; Hoyle, C. E.; Magers, D. H.; McAlexander, H. R. Macromolecules. **2009**, 42, 1824-1833.

[2] Chen, G.; Kumar, J.; Gregory, A.; Stenzel, M. H. Chem. Commun. **2009**, 41, 6291-6293.

[3] Hoyle, C. E.; Bowman, C. N. Angew. Chem. Int. Ed. **2010**, 49, 1540-1573.

Polybutadiene based binder with inbuilt burn rate catalyst for the use in propellants

Billa Narasimha Rao[1,2] and Tushar Jana[1,2*]
[1]School of Chemistry, [2]Advanced Centre of Research in High Energy Materials,
University of Hyderabad, Hyderabad, India
E-mail: tusharjana@uohyd.ac.in

Burn rate catalysis is very important for solid rocket propellants and missile applications. Binder helps the friendly processing of the energetic materials and provides the required mechanical strengths to the final composition of the propellant while burn rate catalysts increasesburning rate of propellant in turn the speed of rocket or missile. Simple ferrocene compoundsarecommonly employed as burn-rate (BR) catalysts in composite solid propellants (CSPs), mainlybecause of their general binder solubility, fluidity,combustion and the better ignitability of thepropellant compared to ones containing conventional inert solid catalysts such as ferric oxide(Fe_2O_3), copper chromite (CuCh), and so forth.However, loading of conventional catalysts beyond2 wt % significantly damages the mechanical properties of the propellant and its processingcharacteristics because of commonly encountered agglomeration, migration,and evaporation orsublimation loss during processing, and phase separation by crystallization in low-temperatureapplications or storage.

To overcome these problems,we have developed methods in which we substituted simple ferrocene compounds in the hydroxyl terminated Polybutadiene(HTPB) backbone and these approaches solved migration and evaporation or sublimation problems.The two approaches which we have persuaded very rigorously are (1)grafting of polyvinylferrocene(PVF) to HTPB and hydrosilylation of ferrocenylsilane at the pendant double bonds of HTPB and these can increase burning rate but viscosity drastically increased(semi solid/ resin) and(2) Attaching of ferrocene derivative at the terminal carbon atoms which do not alter any of the parent physicochemical properties of HTPB.

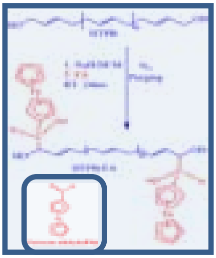


Figure: schematic diagram for the synthesis of HTPB-FA

References:

[1] Shankar, R. M.; Roy, T. K.; and Jana, T.J. Appl. Polym. Sci. **2009**, 144, 732-741.
[2] Shankar, R. M.; Roy, T. K.; Jana, T. Bull. Mater. Sci.**2011**, 34, 745– 754.
[3] Shankar, R. M.; Subhadeep, S.; Seeni, M. K.; Jana, T. Bull. Mater. Sci.**2009**, 32, 507– 514.
[4] Subramanyan, K.J. Polymer Sci. A **1999,**37, 4090-4099.
[5] Cho, B. S.; Noh, S. T. J. Appl. Polym. Sci. **2011**, 121, 3560-3568.
[6] Narasimha, R. B.; Jana, T. (Manuscript under preparation).

Synthesis and Characterization of Polydimethylsiloxane Alumina nano composite

Cross linked polysiloxane possess very poor mechanical properties and are very weak materials and must be reinforced before being used in any practical applications. Polydimethylsiloxane alumina nano composites have been prepared and characterized. Polydimethylsiloxane have been synthesized by In situ condensation and hydrosilyation curing method. Vinyl functional cross linker results in cures very slowly and cured at room temperature. Less cross linking causes the pure polymer to gain a yellowish tint. FTIR studies have been done for liquid samples before curing. It has shown the cross linking of Si-O bond.

Contact angle have been confirmed the hydrophobicity of PDMS. It has shown that angle increases as filler content increased and remains constant for more than 1 percent concentration. SEM and DSC study have been done.

References:

1. Polysiloxane layered silicate nano composites synthesis characterization and properties. Daniel Frederick Schmidt.
2. Modification of PES Fabric by Stimuli Responsive Micro gel Using Sol-gel Technology Brigita Tom!i
3. Supplementary material (ESI) for chemical communications journal is the royal society of chemistry 2003.
4. Surface and fouling release properties of silicon/organomodified MMT coatings.
5. Cyclic Siloxane compounds and making method US Patents Uehara et al.
6. Preparation and evolution of hydrophobic surfaces of polyacrylate polydimethylsiloxane co-polymers for anti-icing.
7. Dongrveil Yu, Yunhui Zhao Hui Li Hengzhi Qi Boli Xiaoyan Yuan
8. Preparation and characterization of polysiloxane polyacrylates composite lattices by two seeded emulsion polymerization and their film properties Mingxuan, Zou Qing Zhao Sun Nie Zhicheng Zhang.
9. Sol-gel concave micro-lens arrays fabricated by combining the replicated PDMS soft mold with UV-cured imprint process. Xuehua Zhang, Wenxiu Que, Jing Chen, Jiaxing Hu, Tianxi Gao, Weiguo Liu.

Surface modified Cellulose Nanoparticles with Silanes asReinforcement in Composites

Ramakrishnan Anju[1] and Raghavachari Dhamodharan [2]
Department of chemistry, IIT Madras
anjuanilroy@gmail.com

With increasing global concern over depletion of non-renewable fossil fuel and rising price for petroleum and petroleum derived products, present and future demands materials that are eco-friendly (with minimum waste disposal), having light weight, high durable with mechanical properties greater than or equal to those of traditional petroleum based materials. Natural cellulose based materials (wood, hemp, cotton, linen, etc.) have been used by our society as engineering materials for thousands of years, but cannot compete with high performance materials. By extracting cellulose at the nanoscale, the majority of the defects associated with the hierarchical structure can be removed, and a new cellulose based ‘’building block’’ (Cellulose nanoparticles (CNs)) can be obtained as the next generation of cellulose based composites. But one drawback is the hydrogen bonds present in CNs tend the fibres to agglomerate into bundles and unevenly distribute throughout the non-polar polymer matrix during compounding processing; resulting a weak interfacial adhesion. Therefore fiber treatment is beneficial towards improving the water resistance and wettability of the fiber surface by polymers and enhances interfacial adhesion. A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix. Mainly organosilanes are efficient coupling agents and they have been extensively used in composites. The hydroxyl groups present on the surface of the cellulose nanofibres is allowed to condense with the hydroxyl groups formed insitu during the hydrolysis of the silicates under alkaline or acidic pH conditions.

In this present work CNs were prepared from various sources like cotton, paper, baggase etc and in situ surface treatment with tetraethyl orthosilicate (TEOS) was also done. The properties of surface modified cellulose fibres are characterized by PXRD, SEM, TEM, TGA and FTIR. These reinforcement fillers were used in composites and the properties enhancement were studied.

References:

1) Robert, J. M.; Martini, A.; Nairn, J.; Simonsenf, J.; Youngblood, J. *Chem. Soc. Rev*., **2011**, *40*, 3941–3994.
2) Abdelmouleh, M.; Boufi, S.; Salah, A.; Belgacem, M. N.; Gandini, A. *Langmuir*, **2002**, *18*, 3203-3208.
3) Yanjun Xie, Callum A.S. Hill , Zefang Xiao , Holger Militz , Carsten Mai . Silane coupling agents used for natural fiber/polymer composites: A review *Composites*: Part A 41 (**2010**) 806–819

Effect Of Dechlorination And Ultrasonic Degradation On Various Grades of Polyvinyl Chloride

Arjit Gadgeel[1] and S. T. Mhaske[*]
[1]Department of Polymer and Surface Engineering, Mumbai
[*]Department of Polymer and Surface Engineering, Mumbai
*arjitga@gmail.com

This study examined the dechlorination of different grades of polyvinyl chloride (PVC) under alkaline solution. Dechlorination under atmospheric pressure is carried out NaOH/EG solution at 170^{0}C to 200^{0}C for 3 hrs. This dechlorinated PVC is then subjected to ultrasonic degradation. Measurements of infrared (IR) spectroscopy, SEM, GPC and DSC were used to indicate the changes in PVC structure and properties due to formation of polyvinyl alcohol (PVAc) sequences in the polymer chain.

Keywords: Polyvinyl chloride, Dechlorination, NaOH/EG solution, Polyvinyl alcohol.

Synthesis and Characterization of Model Amines for Corrosion Applications

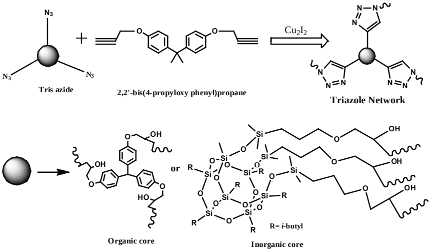
John Vergara, Dr. Giuseppe Palmese, Drexel University
jhv23@drexel.edu

Fundamental studies aimed at elucidating the key contributions to corrosion performance are needed to make progress toward effective and environmentally compliant corrosion control. Epoxy/amine systems are typically employed as barrier coatings for corrosion control. However, the hardening agents used for coating applications can be very complex, making fundamental studies of water and oxygen permeability challenging to carry out. Creating model building blocks for epoxy/amine coatings is the first step in carrying out these studies. We will demonstrate the synthesis and characterization of model amine building blocks from saturated fatty acids and simple amines such as diethylenetriamine (DETA) and Bis(3-aminopropyl)amine. The structure-property relationship of thermosets made from these model amines and Diglycidyl ether of bisphenol A (DGBEA) will be discussed.

Organic *vs.* Inorganic Core Shape Memory Polymers;Synthesis and Properties

Ragin Ramdas M., Santhosh Kumar K.S.*, Reghunadhan Nair C.P.
Polymers and Special Chemicals Division,
Vikram Sarabhai Space Centre, Thiruvananthapuram-22
E-mail: ragram53@gmail.com

Shape memory polymers (SMPs) are intelligent polymers (stimuli-responsive polymers) which can regain their permanent/original shape upon exposure to external stimuli. In this work, synthesis of novel SMPs from two different trifunctionalcores*viz.* organic and inorganic is presented. The SMPs are synthesised from azide functional polyhedral (silsesquioxane) (POSS) and aromatic trisphenyl core groups by copper catalysed azide-alkyne polycycloaddition. The inorganic core based SMP resulted in higher transition temperature (T_{trans}>150°C) whereas the organic one exhibits lower T_{trans} of 80 °C. The rigidity and crystallinity of POSS units enhance the shape recovery temperature in inorganic core SMP. The shape recoveries of both SMPs are > 95%and thermally stable up to 250°C.



Scheme1: Copper catalysed azide-alkyne cycloaddition reaction for the synthesis of inorganic and organic core SMPs**.**

References

1. A.Lendlein, S.Kelch, Angew.chem.Int.Ed.**2002**, 4l, 2034-2057.
2. Justin.R.K., StuartJ.R. J.Am .Chem. Soc. **2011**, 133,, 12866-12874.
3. K.S. Santhosh Kumar, R. Biju, C.P. Reghunadhan Nair Reactive & Functional Polymers 73(**2013**) 421-430.

Synthesis and Characterization of Novel pH Sensitive Polyketal-based Amphiphilic Block Copolymers *via* Click Chemistry

Kheyanath Mitra[1], Shikha Singh[1], Niraj Kumar Vishwakarma[1],
Kalyan Ramensh[1], Rajshree Singh[1], Partha Pratim Manna[2]
and Biswajit Ray[1]*
[1] Department of Chemistry, Faculty of Science, Banaras Hindu University,
Varanasi- 221005, India.
[2] Department of Zoology, Faculty of Science, Banaras Hindu University,
Varanasi- 221005, India.
*biswajitray2003@yahoo.co.in

Self-assembled block copolymer micelles, typically, with several tens of nanometers in diameter and relatively narrow size distribution have long been explored as nano-sized drug delivery system based on entrapment of drugs into core-shell architecture, owing to their simple, economic and versatile approach.1,2 Here in we report for the first time, the synthesis of alkyne-terminated polyketal3 copolymer and there after the synthesis of novel amphiphilic block copolymers via click chemistry4 with azide terminated poly(N-vinylpyrrolidone) (PNVP)5. The resulting polymers have been characterized by 1H NMR, FT-IR, and GPC studies. Critical meceller concentration (CMC) of the block copolymer has been determined by fluorescence spectroscopy.6 Anticancer drug doxorubicin has been successfully loaded in micelles and their release profiles in different pHs have been studied.

Key words: Amphiphilic block copolymer, Micelle, Drug delivery.

References:
1. Guo X., Shi C., Yang G., Wang. J, Cai Z., Zhou S. *Chem. Mater.*, 2014, **26**, 4405–4418.
2. Binauld S., Stenzel M. H. *Chem. Commun.*, 2013, **49**, 2082—2102.
3. Heffernan M. J., Murthy N. *Bioconjugate Chem.*, 2005, **16**, 1340-1342.
4. Tsarevsky N. V., Bencherif S. A., Matyjaszewski K. *Macromolecules*, 2007, 40, 4439-4445.
5. Patel V. K., Ph. D. thesis, Banaras Hindu University, 2013.
6. Mishra A. K., Patel V. K., Vishwakarma N. K., Biswas C. S., Raula M., Mishra A., et al. *Macromolecules,* 2011, **44**, 2465-2473.

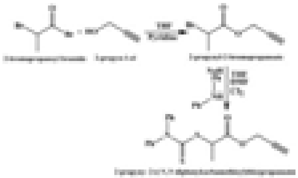
Synthesis and Characterization of Imide Containing Hybrid Epoxy Resin with Improved Mechanical and Thermal Properties

U. G. Rane, Chaitanya M Mundhe and V. V. Shertukde

Phosphorous containing amine, tripropyldiamine phosphine oxide (TPDAP), and hybrid monomer 4-(N-phthalimidophenyl) glycidylether (PPGE) were synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis (EDX). PPGE was incorporated in bisphenol A epoxy resin (BPA) in various concentrations (5% to 20%), based on a weight percentage of BPA resin. Curing was carried out with the stoichiometric amount of TPDAP and 1,3-propanediamine (PDA) to result in cross-link network. Various mechanical, chemical, thermal, and flame retardant properties of modified and unmodified epoxy resin were studied. The coatings obtained with the addition of PPGE were found to have improved properties as compared with those of the unmodified resin. Coatings with 15% loading of PPGE showed improved flame retardant and mechanical properties with stable thermal behaviour.

Synthesis of a Novel Alkyne-terminated RAFT Agent 2-Propynyl-2-((*N, N*-diphenylcarbamothioyl)thio) propanoate, and Its Uses for the RAFT Polymerization of *N*-Vinylpyrrolidone

Archana Kumari, Shikha Singh, Kheyanath Mitra, Niraj Kumar Vishwakarma, Sambhav Vishwakarma and Biswajit Ray*
Department of Chemistry,
Faculty of Science, Banaras Hindu University, Varanasi- 221005, India
biswajitray2003@yahoo.co.in



Reversible addition-fragmentation chain transfer (RAFT) polymerization allows the synthesis of polymers with well-defined molecular weight, polydispersity and architectures. The process is compatible with many kinds of monomers and applicable both in homogeneous and heterogeneous media. From last decade the RAFT polymerization and synthesis of suitably functionalized RAFT agents have drawn extensive attention in the field of polymer science.[1,2,3] Here in, we report the synthesis (Scheme below) and characterization of 2-propynyl-2-((*N,N*-diphenylcarbamothioyl)thio)propanoate, a novel alkyne terminated RAFT agent and its' use for the RAFT polymerization of *N*-vinylpyrrolidone (NVP) under different parameters like temperature, monomer concentration, time etc. Kinetic study, chain-end analysis and chain-extension experiments have also been carried out to check the livingness of the polymerization process. Resulting polymers have been characterized by GPC, ^{1}H-NMR, FTIR, TGA and DSC studies.

References:

[1] Mishra A. K., Patel V. K., Vishwakarma N. K., Biswas C. S., Raula M., Mishra A., et al. *Macromolecules* 2011, **44**, 2465-2473.

[2] Ramesh K., Mishra A. K., Patel V. K., Vishwakarma N. K., Biswas C. S., et. al. *Polymer,* 2012, **53**, 5743-5753 .

[3] Shin S. J., Yu Y. C., Seo J. D., Cho S. J., Youk J. H. *J. Polym. Sc.: Part A: Polym.Chem*, 2014, **52**, 1607–1613.

Novel, film forming polyhydroxy prepolymers: Synthesis, mechanical and adhesive properties

Satheesh Kumar B.*, Dona Mathew, C.P.Reghunadhan Nair
Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre
Thiruvananthapuram, Kerala, India-695022
*skbisro@gmail.com

A novel polyhydroxy compound was derived by reacting cycloaliphatic epoxy compound (3, 4-epoxycyclohexylmethyl-3′, 4′-epoxycyclohexane carboxylate) with bisphenol A. The polymer was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Hydroxyl value, Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). The synthesized polymer (BPC) of molecular weight (Mn) about 2500 exhibited hydroxyl value of 282 mg KOH/g. The polyhydroxy polymer was studied as melt -adhesive whose adhesive properties can be tuned by blending with another epoxy resin and curative. Thus the polymer was evaluated in various adhesive formulations also, in combination with different proportions of an epoxy novolac and cured using an amine based catalyst system. Cure behavior of these adhesive formulations were studied using FTIR, Differential Scanning Calorimetry (DSC) and Rheometry and cure conditions were optimized. The adhesive property of these systems were evaluated at different temperatures by measuring the lap shear strength(LSS) at low temperature(77°K), room temperature (25°C) and at high temperature (100°C) on aluminium substrates. The adhesives exhibited LSS in the range of 160 to 270kg/cm^2 at RT, 110 to 200 kg/cm^2 at 77°K and 20to 30 kg/cm^2 at 100°C. Structure-composition-adhesive property co relationships were derived, based on the LSS values. Films were also cast using blends of these prepolymer with an epoxy novolac cured using amine catalyst and their mechanical properties were correlated to the blend composition. The system finds application as high performance adhesive which can cater to the adhesive requirements under conditions ranging from LN2 temperature to 75°C.

TPP

120°C / 5 hrs.

Bisphenol A

Cycloaliphatic
epoxy resin

Prepolymer (BPC)

Scheme 1: Synthesis of Prepolymer (BPC)

Reference:

Bull. Mater. Sci., Vol. 32, No. 2, April 2009, pp. 199–204. © Indian Academy of Sciences

Interaction of Sodium Dodecyl Sulfate with Polyethyleneimine: a detailed thermodynamic study

Debolina Mitra
Department of Chemistry, Rishi Bankim Chandra College, Naihati
contact.debolinamitra@gmail.com

Polyethyleneimine (PEI) is a positively charged polyelectrolyte, existing both in linear and branched forms. It has wide use because of its unique property of facilitating strong attachments between biological cells and plates. Strong binding interaction of PEI (Molecular weight 600 & 1800) with an anionic surfactant sodium dodecylsulfate in aqueous medium reveals unique features of the polymer. Conductometry measurement was performed in order to monitor the charged nature of PEI-SDS complex. Enhanced surface adsorption at the air-water interface at low surfactant concentration with no appreciable changes on increasing surfactant concentration limits the use of tensiometric measurements. Electrostatic neutralization around the charge neutralization between the surfactant and the polyelectrolyte results in dense precipitation or coacervation. Turbidimetric studies reveal that at low surfactant concentration, the complex is stable in solution. Above a critical concentration, the system is an unstable colloid dispersion of the complex particles. Finally dissolution takes place at a particular concentration with the formation of a stable dispersion of PEI-SDS complex. The enthalpy change at each transition point is monitored from microcalorimetric measurements. Studies in aqueous-alcoholic medium reveal the effect of solvent polarity change on the PEI-SDS complex.

References:

[1] Meszaros, R.; Thompson, L.; Bos, M.; Varga, I.; Gilanyi, T. Langmuir **2003**, 19(3), 609-615.
[2] Batchelor, S. N.; Tucker, I. M.; Petkov, J. T.; Penfold, J.; Thomas, R. K. Langmuir **2014**, 30(32), 9761-9769.
[3] Heisig, S. E.; Merchan, M. D.; Velazquez, M. M. J. Colloid Sci. Biotech. **2012**, 1(1), 33-41.

Synthesis of polyamine curing agents from cardanol via thio-ene chemistry and their application in epoxy based coatings

Nikita Mhadeshwar, Mukesh Kathalewar, Anagha Sabnis*
Department of Polymer & Surface Engineering
Institute of Chemical Technology, Matunga, Mumbai, India
** as.sabnis@ictmumbai.edu.in*

Recent trend towards utilization of renewable feed stocks for development of functional materials that can be used as components for polymer systems has been considered as a step towards sustainable development. In the same line of work, we demonstrate a series of amine and amido-amine curing agents derived from carboxyl modified cardanol via thio-ene reaction. The curing agents structurally similar to phenalkamines were synthesized in our lab and characterized by functional analysis and FTIR, NMR spectroscopy techniques. These were then used as cross-linkers for epoxy based coatings. The cured coatings were evaluated for mechanical, chemical, thermal and anticorrosive properties. The study conducted showed that these biobased materials provide excellent coating performance with respect to mechanical and anticorrosive properties at par with the commercial curing agents.

References:
[1] Vorine, C. Poly. Chem. **2014**, 5, 3142-3162.
[2] Huang, K. Prog. Org. Coat. **2012**, 74, 240-247.
[3] Rao, B. S. J. App. Poly. Sci**. 2006**, 100, 3956-3965.
[4] Cheng C.W. Patent US 626148B1, **2001.**

Improvement in Flame Retardancy of Polyurethane Dispersions by Modifying with Flame Retardant Triol

Kunal Wazarkar[1], Anagha Sabnis[2]*
Department of Polymer and Surface Engineering,
Institute of Chemical Technology, Mumbai-400019
**as.sabnis@ictmumbai.edu.in*

Flame retardants are key components in reducing devastating effect of fires on property, people and environment. Flame retardants are compounds that inhibit or delay the burning of materials and are essential for protecting plastic products, electrical appliances, construction materials and textiles. Flame retardant coatings are designed for application over a range of combustible or non-combustible surfaces.

Following research work reveals the synthesis of trifunctional phosphorous based flame retardant and its incorporation in polyurethane backbone to yield flame retardant dispersions (FRPUDs). The structure of flame retardant monomer was confirmed by FTIR, ^{1}H-NMR and ^{31}P-NMR spectroscopy. The polyurethane prepolymer was modified with phosphorous containing triol in various amounts (30, 40 and 50% on equivalent basis) and FRPUDs were prepared. The performance of synthesized FRPUDs was evaluated by characterizing their mechanical, chemical, optical, thermal and flame retardant properties. It was observed that, the flame retardancy was greatly depending on the phosphorous content and increased with increase in phosphorous content. Moreover, nitrogen present in the polyurethane gave rise to synergistic system by acting along with phosphorous improving overall flame retardancy.

Keywords: reactive, trifunctional, flame retardants, synergistic, dispersion

References:

[1] Malshe V. C., Sikchi M. A., Basics of Paint Technology Part-I, Antar Prakash Centrefor Yoga, Uttarakhand, India, **2008**

[2] Chattopadhyay D. K., Raju K. V. S. N., Prog. Polym. Sci. 32 **(2007)** 352–418

[3] Qian L., Feng F., Tang S., Polymer 55 **(2014)** 95-101

[4] Songa L., Hu Y., Tang Y., Zhang R., Chen Z., Fan W., Polymer Degradation and Stability 87 **(2005)** 111-116

Adsorption and Desorption of CO_2 on Styrene-Divinyl Copolymers Containing Nanoclays

Smita S. Nande and B. Garnaik*
Polymer Science & Engineering Division,
CSIR-National Chemical Laboratory, Pune, India
b.garnaik@ncl.res.in

The removal and recovery of carbon dioxide from hot gas is becoming increasingly significant in the field of energy production. Large volumes of carbon dioxide are released to the environment by the combustion of fossil fuels, such as coal or natural gas, and this has become one of the most serious global environmental problems. Various modified nanoclays have been used as catalysts or adsorbents for several applications and they are suitable to carbon dioxide sequestration in gas phase. This is an important application to control the greenhouse effect because CO_2 is by far the most significant greenhouse gas produced as a result of human activities. The capacity of CO_2 removal using nanoclays is high at low and high temperature, but there is no consensus about its capacity is due to adsorption. In this work, we evaluate the adsorptive capacity of CO_2 removal at low temperatures, using St-DVB copolymers incorporating nanoclays and also amine compounds. Suspension polymerization of styrene and divinyl benzene (DVB) was carried out in presence of benzyl peroxide initiator using various suspending reagents in water at 80 ^{0}C under argon atmosphere to produce styrene- DVB copolymer beads. Experimental design methods were employed to investigate the influence of crosslinker content; nanoclays type, nanoclays and various amines level on the surface area, pore volume and pore diameter of the resins. These adsorbents incorporated in St-DVB copolymers were characterized using XRD, TGA and BET surface area. Carbon dioxide adsorption was conducted using adsorption unit in BET surface area analysis and the results showed an CO_2 adsorption at room temperature.

References:

(1) H. G. Yuan , G. Kalfas & W. H. Ray (1991) Journal of Macromolecular Science, Part C, 2006, 31:2-3, 215-299,.
(2) Muniyappan Rajiv Gandhi,† Natrayasamy Viswanathan,‡ and Sankaran Meenakshi*,†Ind. Eng. Chem. Res. 2012, 51, 5677−5684
(3) Tao Zhao†,‡ and Dong Qiu*,†Langmuir 2011, 27, 12771−12774
(4) Shaghayegh Hamzehlou, Yuri Reyes,† and Jose R. Leiza*Macromo

Synthesis of Polymer Supported Catalyst Containing Palladium metal for Heck reactions

Kavita K. Mohite, B.Garnaik*
Division of Polymer Science and Engineering,
CSIR-National Chemical Laboratory, Pune-411008, India
Email: b.garnaik@ncl.res.in

Spherical particulate Styrene-Divinyl benzene (St-DVB) copolymer resins have become ubiquitous support materials in solid phase synthesis, and also in the heterogenizing of homogenous catalyst. Recently macroporous species find increasing utility than highly crosslinked gel type species. We now report suspension copolymerization of St-DVB in presence of benzyl peroxide initiator using various suspending agents in water at 80 ^{0}C under argon atmosphere to produce St-DVB copolymer beads. The influence of crosslinker content; porogen type and porogen level on the surface area, pore volume and pore diameter of the resins were explored. From these results, it was observed that the porogen has a greater influence than the crosslinker. Variation of porogen type and level while keeping crosslinker level constant then to the maximization of each parameter of interest, resulting in set of crosslinked polymers with a wide range of values. The resulted crosslinked St-DVB beads were extracted with dichloromethane using Soxhlet apparatus to remove linear polymers. The purified polymer beads were characterized by TGA, BET, ESEM and XRD etc. Palladium Chloride was incorporated into the polymer beads during suspension polymerization and *in situ* reduction were carried out by using various reducing agents such as sodium borohydride, formaldehyde and hydrazine. The results of polymeric beads as well as palladium supported St-DVB copolymers in term of spherical beads size, pore volume, surface area and thermal stability will be discussed and application of the polymer supported catalyst in Heck reaction will be highlighted.

References:

1] Dahan, A.; Portnoy, M. J. Am. Chem. Soc. **2006**, 129, 5860-5869.
2] Heck, R. F.; Nolley, J. P. J. Org. Chem. **1972**, 37, 2320-2322.
3] Heck, R. F.; Org. React. **1982**, 27, 345-390.
4] Park, C. M.; Kwon, M. S.; Park, J. Synthesis. **2006**, 22, 3790-3794.
5] Liu, J.; Li, Y. Q.; Zheng, W. J. Monatsh Chem. **2009**, 140, 1425–1429

Polyesteramide-Poa Nanocomposite for Anticorrosive Coating From Pet Waste

Aarti P. More, Kunal V. Yeole, Pradnya C. Rane, Shashank T. Mhaske[1*]
*Department of Polymer and Surface Engineering, Institute Of Chemical Technology, Mumbai, Maharashtra, India

Poly(ethylene terephthalate) (PET) is engineering polymers having wide range of application area. Due to its non-biodegradable nature it starts accumulating hence create threat to the environment. Recycling of the PET is carried out to solve this problem.

In this studyaminolysis of PET is carried out and ethanolamine is used as depolymerizing agent. The monomer formed by this depolymerization is bis (2-hydroxyethyl) terephthalamide (BHETA).The product is characterized with FTIR, ^{1}H-NMR, and DSC.

As the coating industry is shifting towards eco-friendly, renewable and sustainable resources for resin synthesis. Here in BHETA, hydroxyl functionality is there along with amide groups in between its structure hence it is used as a monomer for polyesteramide resin synthesis. This is much more beneficial from coating industry point of view since here source is waste material. So the carboxyl terminated polyesteramide resin was synthesized and cured with epoxy. Poly (o-anisidine) (POA) is introduced in this coating composition at various concentrations. The coating was studied for its mechanical, chemical, thermal and anticorrosive properties. The anticorrosive performance was measured by salt spray and electrochemical impedance spectroscopy (EIS). It is observed due to amide linkage, aromatic structure of BHETA and curing with epoxy results to shows anticorrosive performance of the coatingwhich is further enhances by the addition of POA and hence anticorrosive coating is developed from the waste material.

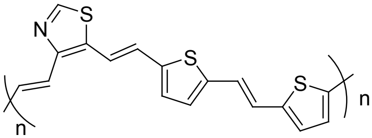
References:

[1] Tawfik ME, Ahmed NM, Eskander SB, J. Appl. Polym. Sci., **2011**, 120, 2842-55p.
[2] More AP, Kute RA, Mhaske ST,*Iran PolymJ*,**2014**, 23,59-67.
[3] PatilD., PatilP., SeoY-K., HwangY.K., *Sensor Actuat B-chem*;**2010**,148, 41.

Conjugated Polymer containing thiophene and thiazole: Synthesis and properties

K. Mahesh and S. Karpagam*
Organic Chemistry Division, School of Advanced Sciences,
VIT University, Vellore – 632014, Tamilnadu, India
**skarpagam80@yahoo.com*

Thiophene and thiazole substituted vinylene polymer was synthesised by Wittig polymerization route. Synthesized polymer was characterized by FT-IR, NMR and GC-MS spectral technique.An optical property wasalso carried out by UV and PL spectroscopy. The final polymer was showed excellent solubility in common organic solventssuch as dichloromethane, chloroform, 1,2dichloroethane, toluene and tetra hydro furan. The results of polymer suggest that this is useful as light emitting and photovoltaic material.



References

[1] Bingzhi. C,Youzhi.W, He. T, Eur. Polym. J,**2004,** 40, 1183-1191.

[2] Karpagam. S,Guhanathan.S, FiberPolym.,**2012**, 13, 1105-1112.

Effect of High energy radiations on glycolysis of waste PET under conventional and microwave conditions and preparation of ecofriendly coatings.

Vandana Jamdar[1], Mukesh Kathalewar[1], R. N. Jagtap[1],
Kumar Abhinav Dubey[2], Anagha Sabnis*[1]
[1] Department of Polymer & Surface Engineering, Institute of Chemical Technology
Nathalal Parekh Marg, Matunga (E), Mumbai-400019, India
[2] Radiation Technology Development Division, Bhabha Atomic Research Centre
Department of Atomic Energy, Government of India, Mumbai 400085, India

Polyethylene terephthalate (PET) is one of the extensively used plastic materials for range of applications and thus results in generation of large quantity of waste all over the world. Disposal of this waste is of global concern as it cannot decompose naturally. Therefore recycling of such polymer by different methods has been attempted. Among them, chemical recycling by glycolysis method is being successfully studied over the years with very good feasibility. However, the commercial implementation of this process has not yet received much attention due to high process cost and lower conversion of PET to its monomeric units such as bis (2-hydroxyethylterephthalate) (BHET).

In the present study, we report for the first time the effect of gamma irradiation on degradation of PET and its subsequent effect on glycolysis by using excess ethylene glycol (EG). The results showed an increase in the extent of depolymerization of PET proportional to the dose of gamma radiation as analyzed by molecular weight determination & Differential Scanning Calorimetry (DSC). The irradiated PET samples were further subjected to chemical recycling by glycolysis using conventional and microwave method in presence excess EG and zinc acetate (0.5%) as a catalyst. Depolymerization of the polymer by gamma radiation resulted in increased yield of BHET after variable time intervals. In addition, hydroxyl number, saponification number and molecular weights of the oligomeric products were also determined. The recycled material, BHET, was then used in combination with bio-based monomers to prepare a new ecofriendly polyester polyol which can be used as component for polyurethane coating formulations.

References

1. Guoxi Xi, Polym. Degradation and Stability , **2005**,87 , 117-120.
2. David E. Nikles, Macromol. Mater. Eng. ,**2005**, 290,13–30.
3. Buttafava A ,Polym Degradation and Stability, **2005** ,89,133-139.
4. Kaixiang Li, Journal of Applied Polym. Sci., **2008** , 109, 1294–1297.
5. Dimitris S. Achilias, Journal of Applied Polym. Sci. ,**2010**, Vol. 118, 3066–3073.

Beta hydroxy alkyl azides as potential low temperature curative for cyanate ester: a mechanistic investigation

[1]K Sunitha*, [2]Vijaya Lakshmi, [1]Dona Mathew, [1]C P Reghunadhan Nair
[1]Polymers and Special Chemicals Group
[2]Analytical, Spectroscopy and Ceramics Group,
Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India-695022
*sunitha.baburaj@gmail.com

The influence of β - hydroxyazide on polymerization of cyanate ester was evaluated through reaction between bis phenol A dicyanate and β-hydroxyazidopropyloxy novolac. Spectroscopic investigations showed the evidences for the formation of iminocarbonates rather than tetrazoles as in conventional nitrile-azide click chemistry. FT-IR studies using model compounds showed characteristic peaks at 3340cm-1 and 1680cm-1 due to iminocarbonate moieties. Cure mechanism operating in cyanate-azide reaction in presence of hydroxyl groups was studied theoretically using B3LYP/6-31G** level of density functional theory (DFT) on model compounds viz, biphenyl cyanate and 1-azido-3-phenoxypropan-2-ol. Activation energy calculated from DFT studies predicted the involvement of a cyclic transition state in β - hydroxyl alkyl azide mediated reaction of cyanate ester. The mechanism involves neighbouring group participation of azide groups in the seven membered transition state. These observations were corroborated by experimental evidences obtained from reaction between monofunctionalazide-cyanate-hydroxyl model compounds. Mechanism of anchimeric involvement of azide functions on cyanate-hydroxyl reaction favouringiminocarbonate formation was established. Thus a new room temperature curative for cyanate ester was introduced.

Scheme 1: Curing of bisphenol dicyanate through the formation of iminocarbonate network

Reference:

[1] Hamerton, Chemistry and Technology of Cyanate Ester Resins,Springer Science & Business Media, 1994.

High molecular weight Poly(L-Lactic acid)s and their copolymers by polycondensation: Is it Possible ?

Yogesh R. Nevare, Bhaskar B. Idage, Susheela B. Idage,
Swaminathan Sivaram
Polymer Science and Engineering Division,
National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411 008

Poly(L-lactic acid)s (PLLA) in the useful molecular weight range are best synthesised by ring opening polymerization (ROP) of L-Lactide. In spite of being the method of choice, both in the laboratory and in industrial processes, ROP has many limitations. The cyclic lactide is relatively expensive and is incompatible for copolymerization with many α,ω -hydroxy carboxylic acid esters. Consequently, only those monomers which can polymerize by ROP have been copolymerized with L-lactide [1].

It would be, therefore, useful to have a monomer for PLLA capable of undergoing linear polycondensation. L-lactic acid is available only as an aqueous solution and is difficult to polymerize. Methyl-L-lactate is available in a non-aqueous form [2]; however, its low boiling point precludes its utility as a co-monomer. Furthermore, linear polycondensation of poly(L-lactic acid)s by dehydrative polycondensation is beset with the problem of formation of cyclic oligomers [3].

To re-examine this question, we undertook the synthesis of a model dimer, namely, 1-methoxy-1-oxopropan-2-yl 2-hydroxy propionate, or methyl lactyllactate (MLL) by cross esterification of L-lactic acid with L-methyl lactate.

This dimer has no free acid group and can be obtained as a high boiling liquid (b.p. 252.5^{0}C at 760 mmHg). The synthesis of MLL, its structural and compositional characterization and its polymerization behaviour will be presented.

References:

[1] Rafael A. Auras, Loong-Tak Lim, Susan E. M. Selke, Hideto Tsuji ; Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications, John Wiley and Sons, USA, **2010**.

[2] Marques D, Gil M, Baptista C, J. Appl. Polym. Sci. **2012**, 125, 283.

[3] Shyamroy S, Garnaik B, Sivaram S, J. Polym. Science., Part A, Polymer Chemistry, **2005**, 43, 2164.

Synthesis of poly(ε-caprolactone-co-δ-valerolactone)s random copolymers and their use as an impact modifier for poly(L-lactide)

Megha D. Deokar, Bhaskar B. Idage, Susheela B. Idage,
Swaminathan Sivaram
Polymer Science & Engineering Division,
CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411 008

Poly (L-lactide)s (PLLA) and PLLA based blends as well as their copolymers are subjects of significant current research interest. PLLA has attracted considerable attention as it is obtained from renewable resources and has useful properties. PLLA's find wide use in biomedical, packaging, injection molded and extrusion coated products in view of their desirable properties such as, biodegradability and biocompatibility [1-3]. PLLA obtained from ring opening polymerization (ROP) of L-lactide is semi-crystalline in nature; however, PLLA's are brittle material with poor elongation at break which limits its applications. Therefore, substantial improvements in mechanical and thermal properties are required.

In this work we first synthesized PLLA with a composition of 96% L-LA: 4% D-LA. The tensile strength of PLLA is 17.6±1.3 MPa and is very low for many applications. We reasoned that the mechanical properties of PLLA can be improved by blending with aliphatic polyesters containing longer carbon chains in the backbone.

Accordingly, we synthesized random copolymers of poly(ε-caprolactone-co-δ-valerolactone)s by ROP of ε-caprolactone (CL) with δ-valerolactone (VL) using stannous octoate as catalyst. The copolymers were characterized by FTIR, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC) and DSC. Morphology of fractured surface was studied by scanning electron microscopy (SEM). The synthesized random copolymers were melt blended with PLLA using a twin screw micro compounder and extruded. Tensile properties of compression molded blends were investigated as a function of composition and molar masses of the two components in the blend. It was shown that copolyesters with a composition 47:53 mol% (CL: VL) results in significant increase in tensile strength of compression molded PLLA.

References:

1. R. Auras, L-T. Lim, S. E. M. Selke and H. Tsuji, Poly(Lactic acid): Synthesis, structures, properties, processing and applications, **2010**.
2. D. E. Cutright, E. E. Hunsuck, J. Oral Surg., **1971**, 31, 134-139.
3. C.K.Williams and M.A. Hillmyer, Polymers from renewable resources, Polymer Rev., **2008**, 48, 1-10.

Synthesis and Characterization of Soluble Aromatic Polyamides Containing 1,2,4-Triazole and Pentadecyl units.

Aslam B.Tamboli, Shivaji D. Ghodke, Basavraj S. Kalshetti,
Rajesh G. Borkhade, Noormahmad N. Maldar*,
School of Chemical Science , Solapur University, Solapur-413255 (India)
maldar_nn@rediffmail.com

A New series of aromatic polyamides containing 1,2,4-triazole in the main chain and pendant long aliphatic pentadecyl unit, was synthesized by low temperature solution polycondensation of novel aromatic diamine namely 3,5-Bis (4′-amino phenyl)-4-(4″-methoxy-2′′-pentadecyl phenyl) 1,2,4,triazole (İ) with aromatic diacid chlorides, namely isophthaloyl chloride (IPC) and terphthaloyl chloride (TPC). Coplyamides were also synthesized by employing various mole proportion of IPC and TPC with diamine (İ). Inherent viscosities of these polyamides were in the range 0.50-0.65 dL/g as determined in DMAc, indicating formation of moderate to high molecular weight of polymers.The diamine (İ) was characterized by FT-IR, NMR (^{1}H , ^{13}C), Mass etc. These polyamides showed good solubility in polar aprotic solvents such as N,N,Dimethyl acetamide (DMAc), N-Methyl 2-Pyrrolidone (NMP), N,N,Dimethyl formamide (DMF), and Dimethyl sulphoxide (DMSO), which may be due to incorporation of bulky pendant pentadecyl units leading to amorphous polyamides as evidenced by XRD. These polyamides had lower glass transition temperature compared to conventional aromatic polyamides probably due to internal plasticization effect by pentadecyl group as determined by DSC. Polymers showed good thermal stability, with initial decomposition temperatures above 300 ^{0}c.

References:

1. Imai Y., Maldar N. N. and Kakimoto M., J. Polymer Sci. Polym. Chem. Ed., 23, 1797 and 2077, (1985).
2. Pal R.R., Patil P.S., Salunkhe M.M., Maldar N.N., and Wadgaonkar P. P., J. Polymer International, 54: 569 (2005).
3. Kun-Li Wang,Yi-lang, I-Hao Shih, Koon-Gee Neoh and En-Tang Kang J. Polymer Science Part A: Polymer Chemistry 48., 24. 5790 (2010).

Polymeric Emulsion latex of N-(2 Amino benzothiazole)methacryamide and evaluation of its antimicrobial properties

Gunawant Lokhande and R. N. Jagtap*
Department of Polymer and Surface Engineering,Institute of Chemical Technology,
Matunga (E), Mumbai-400019,India
gunawant103@gmail.com

Monomer with thiazole moiety was synthesized and copolymerized with Butyl acrylate and methyl methacrylate by RAFT emulsion polymerization and their antimicrobial activity was investigated. The molecular weight of copolymer were fixed and monomer concentration was changed. The monomer was incorporated up to 3, 5 and 7 wt % in emulsion system and its effect was studied. The monomer and its copolymers were employed to screen an antimicrobial activity against E.coli, B.subtilis, C.albicans and Aspergilus niger.The Antimicrobial activity was checked by using optical density method. The synthesized monomer and RAFT agent was characterized by Mass spectroscopy, FT-IR, ^{1}HNMR and block copolymers were characterized by Gel permeation chromatography(GPC) and differential scanning calorimetry (DSC).The emulsions were evaluated for particle size analysis and zeta potential for their stability.

References:

[1] Stuart W. Prescott, Mathew J. Ballard, EzioRizzardo and Robert G. Gilbert, Macromolecules **2002,** 35, 5417-5425.
[2] Patel, M. B.; Patel, S. A.; Ray, A.; Patel, R. M. J. Appl. Polym. Sci., **2003**, 89, 895-900.
[3] Woong-Sig Moon, Kyoo-Hyun Chung, Du JinSeol, Eun-Soo Park, Jae-Hun Shim, Mal-Nam Kim, Jin-San Yoon, Journal of Applied Polymer Science, **2003**, Vol. 90, 2933–2937.
[4] Marty Ward, Melissa Sanchez, Mohamed O. Elasri, Andrew B. Lowe1, Journal of Applied Polymer Science, **2006**, Vol. 101, 1036–1041.
[5] Woong-Sig Moon,Kyoo-Hyun Chung, Du JinSeol, Eun-Soo Park, Jae-Hun Shim,Mal-Nam Kim,3 Jin-San Yoon, Journal of Applied Polymer Science, **2003**, Vol. 90, 2933–2937.
[6] Roshan T. A. Mayadunne, EzioRizzardo, John Chiefari, Yen KwongChong,GraemeMoad, and San H. Thang Macromolecules, **1999**, 32, 6977-6980.

Oleic Acid based Polymeric Flow Improvers for Langhnaj (North Gujarat, India) Crude Oil

Mayur R. Patel [a], Pranav S. Chitte [a], D. P.Bharambe [a*]
[a] Applied Chemistry Department, Faculty of Technology & Engineering,
The Maharaja Sayajirao University of Baroda, Vadodara-390 001, India

This research article investigates the effect of Polymeric Flow Improvers (FI) as pour point depressants (PPD) and rheological properties improvers of waxy crude oil for Langhnaj, North Gujarat (India), since application of FI is a more economically viable option for crude oil transportation. Three new comb-shaped copolymers of Maleic Anhydride and n-alkyl Oleate were synthesized by free radical solution polymerization, which were consequently reacted with Hexadecyl Amine to get poly (hexyl oleate-co-hexadecyl maleimide-co-n-alkyl oleate). Synthesized polymers were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Gel Permeation Chromatography (GPC). These FI were further evaluated for its pour point depression property and rheology modifier with and without additive using Fann Viscometer. The prepared FI act as effective pour point depressant as well as Viscosity Index Improvers.

Synergistic effect of incorporated imine functionality and grafted nano zinc oxide particles on Antimicrobial activity synthesized by RAFT Polymerization

Sachin Chambahre and R. N. Jagtap*
Department of Polymer and Surface Engineering,Institute of Chemical Technology,
Matunga (E), Mumbai-400019,India
sachinchambhare16@gmail.com

Block copolymers of butylacrylate with varying concentration of glycidyl methacrylate i.e. 3%, 5%, 10% and12% were synthesized by xanthate mediated RAFT polymerization. Further these copolymers were modified by reacting with dicyandiamide to incorporate imine functionality in polymer backbone. The end group functionality of block copolymers were utilized for grafting nano zinc oxide particles in various concentrations (Wt%) i.e.0.15,0.30 and0.45.These modified copolymers were screened for antimicrobial properties against *E.coli* and *B.subtilis* strain by well diffusion method. Synthesized xanthate RAFT agent was successfully characterized by FT-IR, 1HNMR and GC-MS analysis for structural elucidation. Block copolymers were characterized by GPC and epoxy equivalent analysis. The grafting nano ZnO particles were confirmed by TEM analysis.

References:

[1] Stuart W. Prescott, Mathew J. Ballard, EzioRizzardo and Robert G. Gilbert, Macromolecules **2002,** 35, 5417-5425.

[2] Patel, M. B.; Patel, S. A.; Ray, A.; Patel, R. M. J. Appl. Polym. Sci., **2003**, 89, 895-900.

[3] Woong-Sig Moon, Kyoo-Hyun Chung, Du JinSeol, Eun-Soo Park, Jae-Hun Shim, Mal-Nam Kim, Jin-San Yoon, Journal of Applied Polymer Science, **2003**, Vol. 90, 2933–2937.

[4] Marty Ward, Melissa Sanchez, Mohamed O. Elasri, Andrew B. Lowe1, Journal of Applied Polymer Science, **2006**, Vol. 101, 1036–1041.

[5] Woong-Sig Moon,Kyoo-Hyun Chung, Du JinSeol, Eun-Soo Park, Jae-Hun Shim,Mal-Nam Kim,3 Jin-San Yoon, Journal of Applied Polymer Science, **2003**, Vol. 90, 2933–2937.

[6] Roshan T. A. Mayadunne, EzioRizzardo, John Chiefari, Yen KwongChong,GraemeMoad, and San H. Thang Macromolecules, **1999**, 32, 6977-6980.

Synthesis and Characterization of Imide Containing HybridEpoxy Resin with Improved Mechanical and Thermal Properties

U. G. Rane, Chaitanya Mundhe, A. A. Sabnis[1] and V. V. Shertukde[1]
[1]Department of Polymer and Surface Engineering, ICT, Mumbai
ulka.rane@gmail.com, *chaitanyamundhe@gmail.com*

Phosphorous containing amine, tripropyldiamine phosphine oxide (TPDAP), and hybrid monomer 4-(N-phthalimidophenyl) glycidylether (PPGE) were synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis (EDX). PPGE was incorporated in bisphenolA epoxy resin (BPA) in various concentrations (5% to 20%), based on a weight percentage of BPA resin. Curing was carried out with the stoichiometric amount of TPDAP and 1,3-propanediamine (PDA) to result in cross-link network. Various mechanical, chemical, thermal, and flame retardant properties of modified and unmodified epoxy resin were studied. The coatings obtained with the addition of PPGE were found to have improved properties as compared with those of the unmodified resin. Coatings with 15% loading of PPGE showed improved flame retardant and mechanical properties with stable thermal behaviour.

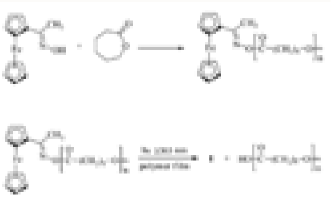
References:

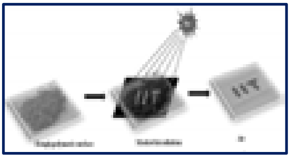
[1] S. Ghorabi, L. Rajabi, S. S. Madaeni, S. Zinadini, and A. A.Derakhshan, "Effects of three surfactant types of anionic, cationic and non-ionic on tensile properties and fracture surface morphology of epoxy/MWCNT nanocomposites,"IranianPolymer Journal,vol.21,no.2,pp.121–130,2012.
[2] C. Gerard, G. Fontaine, and S. Bourbigot, "New trends in reaction and resistance to fire of fire-retardant epoxies,"Materials,vol. 3, no. 8, pp. 4476–4499, 2010.
[3] D. Derouet, F. Morvan, and J. C. Brosse, "Chemical modification of epoxy resins by dialkyl(or aryl) phosphates: Evaluation of fire behavior and thermal stability,"Journal of Applied Polymer Science, vol. 62, no. 11, pp. 1855–1868, 1996.
[4] G. Camino, G. Martinasso, and L. Costa, "Thermal degradation of pentaerythritol diphosphate, model compound for fire retardant intumescent systems: part I—overall thermal degradation,"Polymer Degradation and Stability,vol.27,no.3, pp. 285–296, 1990.
[5] Y.L.Liu,Y.C.Chiu,andC.S.Wu,"Preparationofsilicon-/phosphorous-containing epoxy resins from the fusion processto bring a synergistic effect on improving the resins' thermalstability and flame retardancy,"Journal of Applied Polymer Science,vol.87,no.3,pp.404–411,2003.

Development of Photoacid Generators (PAGs) and their Application in Photoresponsive Polymer Surfaces

Rakesh Banerjee, Md. Iqbal, N D Pradeep Singh* and Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur,
West Bengal 721302 India
*Email: dibakar@chem.iitkgp.ernet.in

Over the past few decades, photoacid generators (PAGs) have gained enormous interest due to their immense applications in microlithographic industry. PAGs are the key material used in the field of photoresists for semiconductor fabrication. On photoirradiation of polymer film containing a PAG, results in generation of acid, which catalyzes certain important chemical transformations within the polymer film such as deprotection of functional groups, initiation of polymerization or cross linking process. We have synthesized four different classes of photoresponsivehomopolymers and their copolymers with methyl methacrylate, styrene, ethyl acrylate, etc. using the well-known free radical polymerization techniques. After completion of the polymerization the resulting polymers were characterized by IR, ^{1}HNMR and GPC. To investigate the polymers as PAG, polymers was spin coated onto silicon wafers using a headway research spinner. The FT-IR spectra indicated photodecomposition of polymer films on irradiation. The hydrophobicity of the surface was tested by measuring water contact angle. One of the schematic presentations of synthesized polymer and their application for the development of photoresponsive polymer surfaces is given below. The details of the other polymers and their synthetic procedures will be presented.





References:

[1] Ikbal,M.;Jana, A.;Singh, N.D. P.;Banerjee, R.;Dhara, D. *Tetrahedron***2011**, *67*, 3733-3742.
[2] Ikbal, M.;Banerjee, R.;Atta, S.;Dhara, D.;Anoop, A.;Singh, N. D. P. *J. Org. Chem.* **2012**, *77*, 10557-10567.
[3] Ikbal, M.;Banerjee, R.;Atta, S.;Jana, A.;Dhara, D.;Anoop,A.;Singh, N. D. P.*Chem. Eur. J.***2012**, *18*, 11968 - 11975.
[4] Ikbal, M.;Banerjee, R.;Barman, S.;Atta, S.;Dhara,D.;Singh, N. D. P*J. Mater. Chem. C***2014**, *2*, 4622-4630.

Synthesis of New Block Copolymers for Highly Selective and Sensitive Detection of Cu^{2+} Ions in Aqueous Medium

Rakesh Banerjee, Chiranjit Maiti, Tanay Deb Barman,
Deep Sankar Pal, Dibakar Dhara*
Department of Chemistry, Indian institute of Technology Kharagpur,
West Bengal 721302, India
Email: dibakar@chem.iitkgp.ernet.in

Development of new chemosensors that are selective and sensitive to Cu^{2+}ions, especially in aqueous media, is of tremendous importance. We report synthesis of two new block copolymers that are capable of highly selective and sensitive detection of Cu^{2+} in aqueous medium. In the first case, poly (t-butylacrylate)-block-poly (3-bromopropylacrylate) was prepared using RAFT polymerization technique. The said block copolymer was reacted with 2, 4-dihydroxybenzaldehyde followed by reaction with rhodamine B hydrazide for successful incorporation of the desired rhodamine units in the block copolymer structure. The second polymer was synthesized from poly(2-pyrrolidinemethyl acrylate) using RAFT polymerization technique. The pyrrolidine nitrogen group of polymer was subjected to aza-Michael type addition with ethyl acrylate. Then rhodamine is attached to the polymer. Cu^{2+} induced opening of the spirolactam ring of the rhodamine units resulted in rapid and easily noticeable color change, thus enabling a highly selective detection of Cu^{2+} ions in aqueous medium for concentrations as low as 2 μM. We have further demonstrated that this Cu^{2+} bound polymer complex can further act as a selective and sensitive sensing platform for CN^- in aqueous medium with concentrations < 1 μM (0.06 ppm). Moreover, the polymer can also be used to remove Cu^{2+} from the aqueous medium.The ability of these polymeric systems to detect copper in aqueous media, in comparison to the previous reports of using organic solvents to make such a polymer soluble, opens a new window for application of these systems in detection of copper in biological systems.

References:

[1] Rakesh Banerjee, Deep Sankar Pal and Dibakar Dhara *Polymer international* ,**2014,** *63*, 1974–1981
[2] Chiranjit Maiti, Rakesh Banerjee, Tanay Deb Barman, Deep Sankar Pal, Dibakar Dhara *Communicated*
[3] Maiti, C.; Dey, D.; Mandal, S.; Dhara, D. *J. Phys. Chem. B.* **2014,***118*, 2274-2283
[4] Maiti, C.; Banerjee, R, D.; Maiti, S.; Dhara, D. *Communicated*

Arm First Approach Towards the Synthesis of Core Cross-Linked Star Polymer with Hydrophobic Corona via Metal-free, Environment Friendly "[PhI(OAc)$_2$]" Click Chemistry

Saikat Maiti, Rakesh Banerjee, Gargi Biswas, Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur,
West Bengal 721302 India
**Email: dibakar@chem.iitkgp.ernet.in*

Instead of the conventional copper-based reagents for the development of star-branched polymers, we have established a novel and environmentally benign method, whereby a 1,3-dipolar cycloaddition reaction has been applied using a non-toxic reagent, Iodosobenzenediacetate [PhI(OAc)$_2$]. We have demonstrated the synthesis of core cross-linked star (CCS) polymers via the formation of isoxazoline ring using 'click reaction' between acrylate functionalities in a polymer chain and in situ generated nitrile oxide groups from a cross-linker added externally. In the initial step, a well-defined styrenic block copolymer with acrylate-functionalized middle-block was synthesized by reversible addition fragmentation chain transfer polymerization (RAFT)α,α′ using -xylyl-bis(dithiobenzoate) as a chain transfer agent using 4-vinyl benzyl chloride and styrene as co-monomers. Thereafter, the chlorobenzyl groups were converted into acrylate by reacting with acrylic acid. In the following step, core cross-linked star (CCS) polymers were synthesized by reacting the above block copolymer and oxime-functionalized cross-linkers (bi- and tetra-functional) using [PhI(OAc)$_2$] 'click chemistry'.This approach has been drawn a step further via its introduction in polymer-polymer system where both the oxime and acrylate has been dangled from linear polymeric chains and have been reacted towards the formation of CCS polymers. In aqueous medium these CCS polymers produced polymeric nanoparticles (NPs), which could potentially serve as a carrier of hydrophobic drug molecules. Their drug loading capacity was investigated using coumarin dyes through steady state and time resolved spectroscopy studies.

References:

[1] Banerjee, R.; Maiti, S.; Dhara, D. Green Chem. 2014, 16, 1365-1373.
[2] Maiti, S.; Biswas, G.; Banerjee, R.; Dhara, D. Communicated.

Synthesis and Characterization of $(AB)_n$ type Polymer Via Anionic Thiol-Ene Click Reaction of Vinyl and Allyl Silanes

Ranajit Pal*, Ashna Vargese, Suraj S
Polymers and Special Chemicals Division
Vikram Sarabhai Space Centre, Thiruvananthapuram - 695 022
*ranajitp@gmail.com

The thiol-ene reaction is a clean and effective method for the introduction of the thioether functionality into unsaturated compounds. It appears to be perfectly suited to create multifunctional polymer structures and proceeds via radical/anionic path. “Ene” reactivity falls with decreasing electron cloud over the double bond [1]. Thiol-ene reaction also may be an essential route to fabricate $(AB)_n$ type of polymeric backbone. Compounds formed by thiol-ene chemistry have more regular structure than those formed by standard free radical polymerization. Hydrothiolations of alkenes are accomplished under mild base or nucleophilic catalysis via anionic path [2]. The use of weak base catalysts, e.g. triethylamine, is known to catalyze the process due to readily accessible pK_a of most thiols yielding *anti-Markonikoff* product.

In this work, we report synthesis of chain polymer from bisallyl and bis vinyl silane systems of bisphenol-A via thiol-ene reaction with a dithiol compound (Scheme 1). To carry out this work, diene parts were synthesized and characterized (FTIR, ^1H NMR, GC-MS, and CHNS). The polymers were characterized by FTIR, GPC and ^1H NMR. GPC indicated that the conversion is more for allylsilane compared to vinylsilane. The Difference in reactivity is attributed to the electron density of the double bond.

Scheme 1: Schematics of chain polymer

References:

[1] Hoyle, C. E.; Lee, T.Y.;Roper, T. J. Polym. Sci. Part A: Polym. Chem. **2004**, 42, 5301-5338.

[2] Andrew, B. L. Polym. Chem. **2010**, 1, 17-36.

Synthesis and Aggregation of Peptide/Polypeptide-based Polymer Bio-conjugates

Anupam Saha, Somdeb Jana, Mrinmoy Biswas and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700032, India.
** E-mail: psutkm@iacs.res.in*

In recent decades, Peptide/protein-polymer conjugate are an important class of biomaterials with a wide range of applications in biotechnology, tissue engineering and therapeutics.[1,2] These biomaterials are typically prepared by "*grafting from*" or *"grafting to"* methods.[3,4] In this context, the synthesis and aggregation behavior of poly(methyl methacrylate)-*block*-polytyrosine (PMMA-*b*-Ptyr) and poly(methacrylic acid)-*block*-peptide (PMA-*b*-Peptide) bio-conjugates are described. PMMA-*b*-Ptyr is prepared by combination of ATRP, *"click"* chemistry and ROP of tyrosine N-carboxyanhydride using designed dual initiator. PMA-*b*-Peptide is prepared via ATRP of *tert*-butyl methacrylate using sequence-defined peptide based macroinitor followed by successful hydrolysis of acid-labile *tert*-butyl-group. These two as-synthesized conjugates are characterized by NMR, FTIR and GPC analyses. The PMMA-*b*-Ptyr conjugate shows the formation of mostly helical conformation as studied by FTIR and CD spectroscopy. On the other hand, PMA-*b*-Peptide conjugate shows the formation of β-sheet conformation in water. The PMMA-*b*-Ptyr undergoes self-assembly to form composite micelles in DMF, but PMA-*b*-Peptide self-assembles in alkaline water (pH~6) to form well-dispersed spherical micelles as confirmed from FESEM analysis.

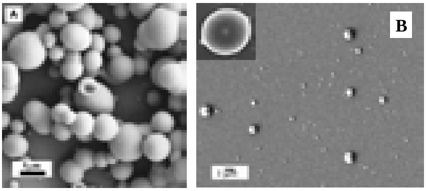


Figure: FESEM images of composite micelles of PMMA-*b*-Ptyr conjugate in DMF (A) and spherical micelles of PMA-*b*-peptide conjugate in alkaline water (B).

References:

[1] Harris, J. M.; Chess, R. B. *Nat Rev Drug Discov* **2003**, *2*, 214-221.

[2] Averick, S. E.; Paredes, E.; Grahacharya, D.; Woodman, B. F.; Miyake-Stoner, S. J.; Mehl, R. A.; Matyjaszewski, K.; Das, S. R. *Langmuir* **2012**, *28*, 1954-1958.

[3] Lutz, J.-F.-o.; Borner, H. G. *Prog. Polym. Sci.* **2008**, *33*, 1-39.

[4] Averick, S.; Simakova, A.; Park, S.; Konkolewicz, D.; Magenau, A. J. D.; Mehl, R. A.; Matyjaszewski, K. *ACS Macro Letters* **2012**, *1*, 6-10.

Recent Developments and Dynamic Modelling of Dynamics of Solid State Polymerization of PET

Durgesh Tripathi[1], Santosh Kumar Gupta[1]
[1]Department of Chemical Engineering, UPES, Dehradun
durgeshtrp@gmail.com

It is economically more advantageous to complete the polymerization of PET by a "solid stating" process than to continue the melt polymerization for a substantial extra number of hours in order to bring the intrinsic viscosity of the final product from about 0.7 dL/g to around 1.0 dL/g. Firstly, the amorphous chips enter a fluidized pre-crystallizer where they are crystallized at ~170 degree C with vigorous agitation to prevent sticking. The amorphous transparent chips turn opaque because of the formation of spherulites. The chips are further crystallized at higher temperature ranges (~ 190 degree C) in a rotary crystallizer, which consists of a heated vessel with a rotating stirring element (a screw or a shaft with paddles) which pushes the chips forward. Air or nitrogen may be used during the crystallization. The chips leaving the rotary crystallizer have a density of 1.3845g/cubic cm (having a crystallinity of 30%).PET crystallization is advisable for the design of the crystallizers.The moving bed, or gravity-flow continuous SSP reactor,essentially consists of a long tube where a bed or column of polymerizing chips moves by gravity downwards while an inert gas is passed through the moving bed in a counter-current direction at a velocity which is insufficient to raise or fluidize the bed but sufficient to remove the volatile reaction products such as EG and AA. The height of the moving resin column is essentially constant by the continuous addition of the crystallized low I.V. resin at the top of the column and withdrawal of the high I.V. material at the bottom.The reactor provides plug flow so that the chips experience close to uniform residence time.The gas-to-solids ratio in the reactor and the temperature setting are used to control the rate of the reaction. The final chips reach an I.V. of 0.70-0.85dL/g, depending on the intended application, and a density of ~ 1.400 g/cubic cm.

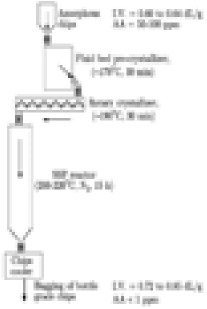


Figure 1 : Rough draft of SSP Reactor

References:

1. Handbook of Thermoplastic Polymers: Homopolymers, Copolymers, Blends, and Composites. Edited by StoykoFakirov.
2. http://nptel.ac.in/courses/116102010/40
3. Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters. Edited by J. Scheirs and T. E. Long.
4. Polymer Reaction Engineering. Edited by José M. Asua
5. Chemical Reactor Design, Optimization, and Scaleup. Second Edition. E. Bruce Nauman. Rensselaer Polytechnic Institute.
6. Polymer Reaction Engineering. Edited by José M. Asua. Institute for Polymer Materials (POLYMAT).The University of the Basque Country, Spain.
7. Continuous Solid-state Polycondensation of Polyesters .143. Brent Culbert and Andreas Christel. Modern Polyesters:Chemistry and Technology of Polyesters and Copolyesters. Ed. John Scheirs and Timothy E. Long.
8. A Molecular Model for Solid-state Polymerization of Nylon 6. A. KAUSHIK and S. K. Gupta. Department of Chem. Engg. IIT Kanpur.(1986)

ATRP of MMA using a novel Initiator: Acetyl chloride

Prachi Shah, Pavan Karkare, C. N. Murthy*
Applied Chemistry Department, Faculty of Technology & Engineering, PO Box 51,
Kalabhavan, The M. S. University of Baroda, Vadodara-390001,
chivukula_mn@yahoo.com

The atom transfer radical polymerization technique has been growing with new range of choices of different initiating systems to the controlled molecular structures and functional polymers. The emulsion atom transfer radical polymerization (ATRP) was successfully applied to methyl methacrylate initiated by novel acetyl chloride using Brij 98 surfactant. The conventional initiators like alkyl halides which involves quick and easily removable halogen groups that are actually transferred. Use of acetyl chloride groups as initiating systems is a totally new concept as RCO—Cl bond is highly reactive and dissociates readily to form radicals and thus producing halogen radical for further transfer reactions. The effects of surfactant concentration, temperature, and monomer/initiator ratio on the system livingness, polymer molecular weight control were examined in detail. It was found that the polymerization system with Brij 98 as surfactants at 28^0C gave good product yield (91 – 94%) with high reaction rates. The polymer samples prepared under these conditions had narrow molecular weight distributions (Mw/Mn=1.1-1.2). The polymer characterization was done using Fourier-Transform Infrared spectroscopy (FT-IR), nuclear magnetic resonance (^{13}C-NMR), Thermo gravimetric analysis (TGA), Scanning Electron Microscope (SEM) and Gel Permeation Chromatography (GPC). The result has encouraged the successful use of acetyl chloride as effective ATRP initiator.

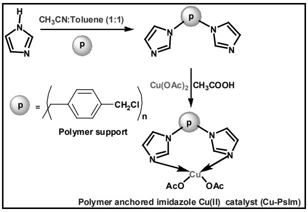
References:

1. Percec V, Barboiu B, Neumann A, Ronda JC, Zhao M, Macromolecules, 29:3665–3668, 1996.
2. Percec V, Barboiu B, Macromolecules, 28:7970–7972, 1995.
3. Dnyaneshwar V. Palaskar, Prakash S. Sane, Prakash P. Wadgaonkar, Reactive and Functional Polymers, 70:931-937,2010.
4. Ying Feng, Jinhua Feng, Jiruo Zhao, Yuling Wang, Polymer, 48:1581-1585, 2007.
5. Haddleton DM, Jasieczek CB, Hannon MJ, Shooter AJ, Macromolecules, 30:2190–2193, 1997.
6. Haddleton DM, Crossman MC, Dana BH, Duncalf DJ, Heming AM, Kukulj D, Shooter AJ, Macromolecules, 32:2110–2119, 1999.
7. Moineau G, Granel C, Dubois P, Jerome R, Teyssie P, Macromolecules 31:542–544, 1998.

An efficient and recyclable polymer anchored Cu(II) catalyst for the one-pot synthesis of 1,4 disubstituted 1,2,3-triazoles starting from anilines in water

Susmita Roy, Md. Mominul Islam, Mita Halder,
Usha Mandi, Sk. Manirul Islam*
Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India
Email: manir65@rediffmail.com

We have developed an efficient procedure for the one pot synthesis of 1,4-disubstituted 1,2,3-triazole derivatives by the 'click' reaction of azides generated in situ from anilines or amines and terminal acetylenes catalyzed by polymer anchored Cu(II) catalyst in water without using any additives. The polymer anchored Cu(II) catalyst was synthesized and its catalytic activity was evaluated in the Huisgen [3+2] cycloaddition reaction for the first time. This protocol offers several advantages like low catalyst loading, high yields, clean reaction, recyclability of the catalyst, reaction in water, no use of hazardous organic solvents for the purification of product, one pot synthesis of triazoles from anilines or amines [1-5].



References:

1. (a) C. Girard, E. Onen, M. Aufort, S. Beauviere, E. Samson and J. Herscovici, *Org. Lett.*, 2006, **8**, 1689; (b) S. Chassaing, M. Kumarraja, A. S. S. Sido, P. Pale and J. Sommer, *Org. Lett.*, 2007, **9**, 883.
2. (a) N.Mukherjee, S. Ahmmed, S. Bhadra and B. C. Ranu, *Green Chem.* 2013, **15**, 389; (b) R. B. N. Baig and R. S. Varma, *Green Chem.*, 2012, **14**, 625, (c) H. Sharghi, R. Khalifeh and M. M. Doroodmand *Adv. Synth. Catal.*, 2009, **351**, 207.
3. S. Roy, T. Chatterjee and S. M. Islam, *Green Chem.*, 2013, **15**, 2532.
4. S. M. Islam, A. S. Roy, P. Mondal, N. Salam, J. Mol. Catal A: Chem. 358 (2012) 38.

New Possibilities in Post-Polymerization Modifications: Teaching an old dog new tricks!

Anindita Das and Patrick Theato*
Institute for Technical and Macromolecular Chemistry, University of Hamburg,
Bundesstrasse 45, D-20146 Hamburg, Germany
**E-mail: theato@chemie.uni-hamburg.de*

Designing a polymer usually involves the incorporation of multiple functional units into a polymer chain. By combining various functional units, a myriad of polymer properties can be fine-tuned. For example, various stimuli-responsive polymers can easily be synthesized from well-defined reactive pre-polymers. This route enables us to incorporate multiple functionalities, which render the obtained polymer responsive to multiple stimuli. Stimuli of interest are: temperature, light and redox.

Post-polymerization modifications are as old as the discipline of polymer science itself. As a matter of fact, the first polymer products were prepared by modifying natural polymers. Ever since, efficient chemistries – nowadays called "click chemistry" – have been utilized in post-polymerization modifications. In the present study, particular focus will be laid on recent developments in post-polymerization modifications utilizing modern multicomponent reactions as well as sequential conversions. These allow the synthesis of complex functionalities in facile synthetic steps. Various approaches will be presented to provide an overview of the possibilities of modern polymer synthesis when it comes to precision synthesis. For example, we could demonstrate the direct conjugation of amines onto polymers featuring alkyne units with the aid of tosylazides under copper(I) catalysis.[1] But also the polymerization of vinylcyclopropanes has been revisited with idea to use the respective polymers for post-polymerization modifications.[2] In conclusion, these and other examples document the valuable contributions synthetic polymer chemistry can make to the future of highly specialized functional polymers.

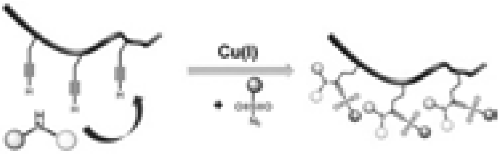


Figure 1: Example of a multi-component reaction that allows the direct conjugation of amines onto polymers featuring alkyne units [1]

References:

[1] R. Kakuchi, P. Theato, *ACS Macro Letters* **2013**, *2*, 419-422.

[2] D. Seuyep, G. A. Luinstra, P. Theato, *Polymer Chemistry* **2013**, *4*, 2724-2730.

Ratchet rectification effect on the translocation of a flexible polyelectrolyte chain induced by spatial asymmetry of the channel

Debasish Mondal
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA

We report a three dimensional Langevin dynamics simulation of a uniformly charged flexible polyelectrolyte, translocating through a asymmetric narrow channel with periodically varying cross-sections under the influence of a periodic external electric field. When reflection symmetry of the channel is broken, rectification effect is observed with a favored direction for the chain translocation. For a given volume of the channel unit and polymer length, the rectification occurs only after a threshold frequency of the external periodic driving. We also observe that the extent of the rectification depends on the length of the polyelectrolyte, geometric parameters of the channel governing the spatial asymmetry and the strength of the external periodic driving field. The observed rectification process is interpreted in terms of an effective asymmetric periodic potential along the direction of the polymer translocation.

Development of Polyurethane Coatings from 1,2,3-Triazole and Azo-Functionalized Cotton seed Oil based Polyols

Rajnish Kumar, Ram Kumar C.B, Ramanuj Narayan, KVSN Raju*
Polymers & Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad
**kvsnraju@iict.res.in*

Compounds that change their optical, magnetic, and electrical properties as a function of external stimuli, is an exciting area of study in materials science. Hyperbranched polymers with azo moiety are well known photo-responsive material (smart material). The photo-orientation of the azo moieties through *trans-cis-trans* isomerization induced by irradiation with polarized light in the absorption region of azobenzene (visible and UV) results in photo-induced optical anisotropy that makes this kind of polymers interesting functional materials for different applications. Also, presence of1,2,3-Triazole ring in polymer architecture induces anti-microbial properties.

In the present work, we have designed a polyurethane coating from cotton seed oil based hyperbranched polyol which consists of azo moiety as well as 1,2,3-Triazole ring. Further, the polyol was treated with 4,4'-methylenedicyclohexyl diisocyanate (H^{12} MDI) in a predetermined ratio. The resulting NCO-terminated prepolymer was cured under atmospheric moisture to get hyperbranched polyurethane-urea. The obtained PU was characterised by ^{1}H NMR, ^{13}C NMR, Fourier transform infrared spectroscopy (FTIR), ESI-Mass spectroscopy, X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV-vis absorption spectra, Thermogravimetric analysis (TGA) ,and Differential scanning calorimetry (DSC).

References:

[1] Bakhshi H.; Yeganeh H.; Ataei S.M.; Solouk A.; Irani S. Macromolecules **2013**, 46, 7777–7788.

[2] Li Z.; Qin A.; Lam J.W.Y.; Dong Y.; Ye C.; Williams L.D.; Tang B.Z. Macromolecules **2006**, 39, 1436-1442.

[3] Pandey S.; Kolli B.; Mishra S.P.; Samui A.B.; J. Polym. Sci. Part A: Polym. Chem. **2012**, 50, 1205–1215.

Various Functionalization of Polysulfone through Chloro Substitution Route

Sandip Ghosh & Virendrakumar Gupta*
Polymer R & D, Reliance Industries Limited, Navi Mumbai
Sandip.M.Ghosh@ril.com

Polysulfones are high performance engineering thermoplastic withexcellent chemical and thermal stability, excellent strengthand flexibility, transparency, as well as a high glass transitiontemperature and good film forming properties. Owing to theseproperties, polysulfones are used in the fields ofmaterials science,biology and polymer science and have been the basis of numerousapplications. Despite tremendous progress in their synthesisand applications, the materials have some limitations related tostress cracking with certain solvents, poor tracking resistance andweathering properties. The introduction of functional groups intothe polysulfones not only overcomes these limitations but alsoextends the range of potential applications like as membranes with special functions, nanocomposites, biofilm formation, fuel cells etc. and thusprovides a wider scope. Introduction of functionality to polysulfoneshas been accomplished by the post-functionalization process of polysulfone.

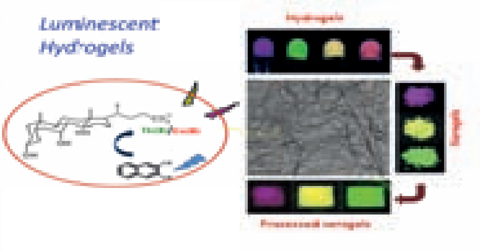
Chloro substitution of polysulfone is an important intermediate to functionalize various groups via grafting, crosslinking in the polysulfone backbone which expands the possibility of various applications.

References:
[1] Olabisi O, Handbook of Thermoplastics, Marcel Dekker, New York, **1997**.
[2] Rao, V. L.,J. Macromol. Sci. Rev. Macromol. Chem. Phys. **1999**, C39: 655–711.
[3] Kerres, J., W. Zhang, W. Cui, J. Polym. Sci.: Part A: Polymer Chemistry **1998**, 36, 1441.
[4] Yu, J., C. Dong, J. Liu, C. Li, J. Fang, R. Guan., J. Mater. Sci.**2010**, 45, 1017.

Functional Soft Matter – Design and Applications

Sandip Bhowmik, Arkajyoti Chakrabarti, Tumpa Gorai,
Mitasree Maity and Uday Maitra*
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India
*maitra@orgchem.iisc.ernet.in

Functional molecular gels are being increasingly investigated owing to their potential applications in various fields such as biomaterials, sensing, optoelectronics etc. Among many known gelators, bile acid derivatives are known to form self-assembled fibrillar networks (SAFINs), eventually leading to the immobilization of solvent molecules around them. We have recently developed a variety of metallogels using bile salts. The use of these novel soft materials for the design of nanostructured materials, luminescent hydrogels and enzyme sensors will be presented in this lecture.



References:

[1] Maity, M., Maitra, U. *J. Mater. Chem. A*, **2014**, *2*, 18952-18958; Bhowmik, S., Gorai, T., Maitra, U. *J. Mater. Chem. C.* **2014**, *2*, 1597-1600; Kandanelli, R., Sarkar, A., Maitra, U. *Dalton Trans.* **2013**, *42*, 15381-15386; Bhowmik, S., Maitra, U. *Chem. Commun.* **2012**, *48*, 4624-4626; Banerjee, S., Kandanelli, R., Bhowmik, S., Maitra, U. *Soft Matter* **2011**, *7*, 8207-8215; Bhowmik, S., Banerjee, S., Maitra, U. *Chem. Commun.* **2010**, *46*, 8642-8644.

[2] Chakraborty, A.; Maitra, U., Das, A.D. *J. Mater. Chem.* **2012**, *22*, 18268.

[3] Banerjee, S., Das, R.K., Maitra, U. *J. Mater. Chem.* **2009**, *19*, 6649-6687.

Functional Core-shell Cylindrical Brushes from Self-assembled Block Copolymer Structures

Bhanu Nandan
Department of Textile Technology, Indian Institute of Technology Delhi,
New Delhi 110016, India

Fabrication of core-shell polymer brushes with well-defined shape has been a subject of immense interest in polymer chemistry for more than two decades now. Different approaches such as those involving synthesis (grafting approaches) and block copolymer self-assembly (solution as well as bulk) have been used for the preparation of such polymer brushes. Of these approaches that involving bulk self-assembled structures of block copolymers have been of special interest because of the simplicity and range of shape and structures possible. Here, we intend to demonstrate the fabrication of cylindrical brushes via block copolymer self-assembly. The self-assembled cylindrical domains formed by a cylinder forming block copolymer in bulk is isolated by selective swelling of the matrix in a solvent. The cylindrical domains so isolated have a hairy or brush-like shell composed of matrix forming blocks. Furthermore, the different chemistry of the cylinder and matrix forming blocks could be utilized judiciously to impart targeted functionalities either in the core or shell of such cylindrical brushes. This could further be extended to the case where two different functionalities loaded in core and shell is combined in the same cylindrical nanoobject leading to nanomaterial with multifunctional properties.

References:

[1] Pal, J.; Sanwaria, S.; Srivastava, R.; Nandan,B.; Horechyy, A.; Stamm, M. Journal of Materials Chemistry. **2012**, 22, 25102-25107

[2] Sanwaria, S.; Pal, J.; Srivastava, R.; Formanek, P.; Stamm, M.; Horechyy, A.; Nandan, B. RSC Adv.**2013**, 3, 24009–24012

[3] Sanwaria, S.; Horechyy, A.; Wolf, D.; Chu, C.-Y.; Chen, H.-L.; Formanek, P.; Stamm, M.; Srivastava, R.; Nandan, B. Angew. Chemie. Int. Ed. **2014**, 53, 9090–9093.

Reactive Solution Blending Approach for Helical Self-Assembly of Semiconducting Materials

S. K. Asha
Polymer Science and Engineering Division, PAML, National Chemical Laboratory
Dr. Homi Bhabha Road, Pune-411008 India

Fabrication of π-conjugated chromophores, whether n-type or p-type into 1D-nanostructures with optimal optoelectronic properties is considered to be very promising as they may find application in future nanoelectronic devices. We report a simple, high temperature solution blending approach, whereby suitably designed donor and acceptor small molecules based on perylenebisimides (PBI; acceptor) and oligo(p-phenylenevinylene) (OPV; donor) could be incorporated into the backbone of insulating engineering thermoplastic polymer like [poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate)] (PCCD) or a chiral semicrystalline aliphatic polyester like Poly(L-lactic acid) (PLLA). Incorporation of p-type π-conjugated chromophores based on oligo(*p*-phenylenevinylene) (OPV) into the back-bone of chiral poly(L-lactic acid) (PLLA) via high temperature solution blending resulted in the transfer of chirality of the PLLA segments to the achiral OPV segments resulting in right-handed helical self-assembly of OPV chromophore in the solid state. The PLLA-OPV polyesters exhibited intense red shifted OPV aggregate emission in the powder form.

Nanofibers constructed from random copolyester incorporating both oligo(*p*-pheneylenevinylene) (OPV) and PBI chromophores using electrospinning technique exhibited blue, green and red emission upon excitation at different wavelengths. This is an easy approach to fabricate 1D nanostructures having strong fluorescence emission from π-conjugated chromophores, with scope of application in nanoscale optoelectronics, biological devices as well as sensing.

References

[1] Nisha, S. K.; Asha, S. K. ACS Appl. Mater. Interfaces **2014**, 6, 12457–12466.
[2] Nisha, S. K.; Asha, S. K. J. Mater. Chem C. **2014,** 2, 2051-2060.
[3] Nisha, S. K.; Asha, S. K. J. Phys. Chem. B **2013**, 117, 13710–13722.
[4] Nisha, S. K.; Asha, S. K. J. Polym. Sci. Polym. Chem. **2012**, 51, 509-524.

Drug Delivery Vehicles using Self-Assembling Polymer for Stable Noncovalent Encapsulation

Ja-Hyoung Ryu*, L. Palanikumar, Eun Seong Choi, and Boram Bae
[1]Department of Chemistry, Ulsan National Institute of
Science and Technology, Ulsan, South Korea
*jhryu@unist.ac.kr

Nanoscopic delivery vehicles capable of encapsulating drug molecules and releasing them in response to external stimuli are of great interest due to implications in therapeutic applications. Micellar assemblies are promising scaffolds to overcome many of the problems faced with traditional chemotherapies because of their capacity for non-covalent, hydrophobic guest molecule binding. However, the stability of encapsulation with such self-assembled systems is limited during blood circulation because of a requisite concentration for assembly formation. Thus, deliberate molecular design for stable encapsulation, targeting and triggered release is required. For this purpose, we have developed a facile synthetic method for highly stable, polymeric nanogels or polymer-caged hollow nanoparticles using a simple intra/inter-chain crosslinking reaction. We show a simple method for the preparation of biocompatible nanovehicles that provides the ability to encapsulate hydrophobic or hydrophilic drug molecules. We can control the size of the nano-carriers and release kinetics depending on crosslinking in responsive to stimuli. Nano-carriers showed great stability to encapsulate drug molecules and drugs were only released inside cell. In addition, we can use surface modified nano-carriers for target delivery system. Hence, the stimuli responsive nano-carrier formation using self-crosslinking polymers and the corresponding method of surface modification are a promising platform for creating polymer nanogels for a range of biomedical applications, from drug delivery to biosensing.

References:

[1] Ryu, J.-H.; Chacko, R. T.; Jiwpanich, S.; Bickerton, S.; Babu, R. P.; Thayumanavan, S. J. Am. Chem. Soc. **2010**, 132, 17227-17235.
[2] Ryu, J.-H.; Bickerton, S.; J. Zhuang; Thayumanavan, S. Biomaromolecules**2012**, 13, 1515-1522.
[3] Kim, K.; Bae, B.; Kang, Y. J.; Nam, J.-M.; Kang, S.; Ryu, J.-H.Biomacromolecules**2013**, 14, 3515-3522.

Functional Soft-Nanocomposites: En Route to Mechanical Rigidity and Biomedicine

Prasanta Kumar Das
Department of Biological Chemistry, Indian Association for the
Cultivation of Science Jadavpur, Kolkata-700032, India
E-mail: bcpkd@iacs.res.in

Investigations on bridging the functionality of the supramolecular self-assemblies and nanomaterials have emerged with huge promise for task specific application of soft-nanocomposite. Carbon nanotubes (CNTs) have emerged as a fascinating nanomaterial in the recent past owing to their versatile potentials in all domain of science. However the prime hurdle of exploiting CNTs is their insolubility, hence solubilization of this nanomaterial is the key challenge. This barrier was overcome by complementary fusion between self-assembled amphiphiles and nanotubes. We utilized this nanomaterial to develop supramolecular nanohybrids where single walled carbon nanotube (SWNT) has been incorporated within self-assemblies of amphiphiles leading to the development of soft-nanocomposite with superior viscoelastic properties. Peptide based hydrogelators were amalgamated with CNTs within self-assembled fibrillar network (SAFIN) of hydrogel without compromising the gelation efficacy.[1,2,3] Importantly, the inclusion of SWNTs within the hydrogel matrix resulted in a remarkable modulation in the mechanical rigidity of the soft nanocomposites which would find notable significance in biomedicine particularly in tissue engineering. In the continuation of our pursuit for developing superior soft-nanocomposite, we aim to develop new hybrid systems integrated with materials having fitting dimensions. To this end, we included silver nanoparticle (AgNP) into the SWNT incorporated self-assemblies. This supramolecular network was used for in situ synthesis of AgNPs without any external additives.[4,5] Rheology of the resulting soft-nanocomposite showed significant mechanical strength and thixotropic self-recovery properties, which made the composite suitable for use as a syringe-injectable hydrogel. These soft nanocomposites exhibited excellent antibacterial activity against both Gram-positive and Gram-negative bacteria. They showed low haemolytic activity and high biocompatibility to mammalian cells.

References:

[1] S. K. Mandal, T. Kar, and P. K. Das, Chem. Eur. J. **2013**, 19, 12486.
[2] D. Mandal, T. Kar, P. K. Das, Chem. Eur. J. **2014**, 20, 1349.
[3] [3] T. Kar, S. K. Mandal, and P. K. Das, Chem. Comm. **2012**, 48, 8389.
[4] [4] S. K. Mandal, S. Brahmachari, and P. K. Das, ChemPlusChem. DOI: **2014**, 10.1002/cplu.201402269.
[5] [5] S. Brahmachari, S. K. Mandal and P. K. Das, PloS ONE **2014**, 9(9), e106775.

Polymergel + organogel materials

J.M. Guenet
Institut Charles Sadron, UPR22
CNRS- Université de Strasbourg, Strasbourg, France
Jean-michel.guenet@ics-cnrs.unistra.fr

Mixing covalent polymers and supramolecular polymers by going through the gel state is of interest both from the fundamental aspect and for potential applications in functional materials [1]. Unlike blends of covalent polymers, for which phase separation may occur due to entropic effects, homogeneous solutions of these two kinds of polymers can easily be prepared by heating thanks to the disaggregation of the supramolecular polymer into its basic constituents. Toying with temperature and concentration allows one to prepare thermoreversible gels with enhanced properties (strength, functionality…).Here two types of self-assembling systems will be discussed. OPV molecules (fig.1) will be shown to form intermingled gels with *isotactic* and *syndiotactic* polystyrenes [2]. BHPB molecules, together with its fluorinated counterpart will be shown to sheathe polymer fibrils and so alter their surface [3].
The molecular structures of these gels will be presented and their properties reported.

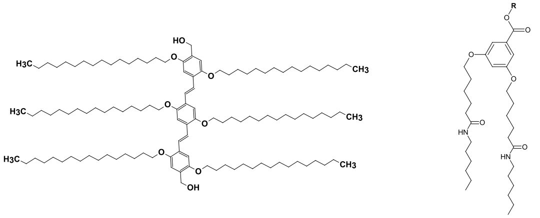


Fig.1: **left** OPV molecule used; **right** BHPB molecules with R= $C_{10}H_{21}$ or R= $C_{10}H_4F_{17}$

References:
[1] Lopez, D. ; Guenet, J.M. Eur. Phys.J B **1999**, B12, 405
[2] Dasgupta, D.; Srinivasan, S.; Rochas, C.; Ajayaghosh, A.; Guenet, J.M. Langmuir **2009**, 25, 8593
[3] Dasgupta, D.; Kamar, Z.; Rochas, C.; Dahmani, M.; Mesini, P.J.; Guenet, J. M. Soft Matter**2010**, 6, 3573

Tuning the architecture of DNA-amphiphile complexes withcounterions

A. V. Radhakrishnan[1], S. K. Ghosh[1], G. Pabst[2],
A. K. Sood[3] and V. A. Raghunathan[1]*
[1]Raman Research Institute, Bangalore
[2]Institute of Biophysics and Nanosystems Research,Graz
[3]Department of Physics, IISc, Bangalore
*varaghu@rri.res.in

Oppositely charged macroions form complexes in aqueous solutions by releasing the counterions that are condensed on them. Ordered macroion complexes of DNA and cationic amphiphiles, which form macroions via self-assembly, have been widely investigated due to their potential biomedical applications and their interesting electrostatics. We have observed structural polymorphism exhibited by two-dimensional crystals of single-chain amphiphile--DNA complexes. Their structures have been determined from a detailed analysis of small-angle x-ray scattering data. It is found that the presence of a strongly binding counterion, which competes with DNA to bind to the amphiphile micelle, can be used to tune the structure of these complexes.

References:

[1] Radhakrishnan, A. V.; Ghosh, S. K.; Pabst, G.; Raghunathan, V. A.; Sood, A. K. Proc. Natl. Acad. Sci. USA **2012**, 109, 6394 – 6398.

Self-assembled diamides : structural studies and functional materials

P. Mesini*
Institut Charles Sadron, 23 rue du Loess – BP 84047, 67034 Strasbourg Cedex 2, France
*mesini@ics-cnrs.unistra.fr

We have developed a series of bis-amides that self-assemble in non-polar solvent and form nanotubes with lengths of several micrometers and diameters of a few tens of nm with a narrow distribution.[1,2] We will present the thermal and spectroscopic properties of these self-assemblies, then we will discuss the determination of their shape and size by two techniques: electron microscopy on freeze fractured samples (Fig. 1 Left) and small angle scattering techniques (Fig. 1 Right). We show that these nanotubes can be used as templates to form large mesopores in organic resins by a “molding” process:[3,4] the tubes are formed in a mixture of monomer/crosslinkers, which yields a thermoreversible gel. Photopolymerization of this gel yields a resin containing the nanotubes. When the nanotubes are leached out with a dissociating solvent, they leave cylindrical pores. The morphology and size corresponds closely to those of the templating tubes, as shown by TEM and porosimetry. Basic treatment of the mesoporous resin can be used to functionalize the pores and synthesize mesoporous catalysts.[4] The resulting materials were tested as catalysts for a model reaction and showed an activity similar the one of alkaline-substituted mesoporous silica. We will also discuss the possibility to functionalize the nanotubes under their self-assembled state in gels[5] and to transform them into reactive aerogels.

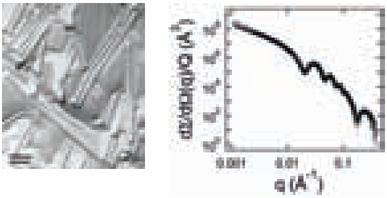


Fig. 1. Left : freeze-fracture TEM of self-assembled nanotubes from diamides.
Right : SANS, intensities scattered by the nanotubes.

References:

[1] Simon, F.-X.; Nguyen, T. T. T.; Díaz, N.; Schmutz, M.; Demé, B.; Jestin, J.; Combet, J.; Mésini, P. J. *Soft Matter* **2013**, *9*, 8483–8493.

[2] N. Diaz, F. X. Simon, M. Schmutz, M. Rawiso, G. Decher, J. Jestin, P. J. Mésini, *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 3260-3264.

[3] F. X.Simon, N. S. Khelfallah, M. Schmutz, N. Diaz, P. J. Mesini, *J. Am. Chem. Soc.* **2007**, *129*, 3788-3789.

[4] T. T. T. Nguyen, F. X. Simon, N. S. Khelfallah, M. Schmutz, P. J. Mésini, *J. Mater. Chem.* **2010**, *20*, 3831-3833.

[5] Nguyen, T.-T.-T.; Simon, F.-X.; Khan, N. A.; Schmutz, M.; Mésini, P. J. *J. Mater. Chem.* **2012**, *22*, 7712–7714.

Bioactive Polymersomes and Nanorods via Self-assembly of Amphiphilic Glycopolypeptides

Soumen Das[1], Debasis Pati[1], Dharmendra Kumar Sharma[2],
Arindam Chowdhury[2] and Sayam Sen Gupta[1]*
[1]Chemical Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road,
Pune 411008, India, [2]Department of Chemistry, Indian Institute of Technology,
Bombay, Powai, Mumbai 400076, India
ss.sengupta@ncl.res.in

Glycopolypeptide based polymersomes and nanorods can have promising applications as vehicles for targeted drug delivery since they are capable of encapsulating different pharmaceuticals of diverse polarity as well as interact with specific cell surfaces due to their hollow structural morphology and bioactive surfaces. We have synthesized glycopolypeptide-b-poly(propylene oxide) and glycopolypeptide-b-PCL by ROP of glyco-N-carboxyanhydride (NCA). These block co-polymera are composed of a biodegradable FDA-approved PPO/PCL hydrophobic block in conjugation with hydrophilic glycopolypeptides which are expected to be biocompatible. We demonstrate the formation of glycopolypeptide based polymersomes and nanorods from the self-assembly of these amphiphilic glycopolypeptides in which the presence of ordered helical glycopolypeptide segment is required for their self-assembly into spherical nanoscale polymersomes (~50-100 nm). The polymersomes were characterized in detail using a variety of techniques TEM, AFM, Light Scattering and fluorescence correlation spectroscopy measurements. As a model for drugs, both hydrophobic (RBOE) and hydrophilic (Calcein) have been incorporated within the polymersomes and nanorods from solution. To substantiate simultaneous entrapment of the two dyes, spectrally-resolved fluorescence microscopy was performed on the glycopeptide polymersomes/nanorods cast on a glass substrate. We show that it is possible to visualize individual nanoscale polymersomes/nanorods and effectively probe the dyes' colocalization and energy transfer behaviours therein, as well as investigate the variation in dual-dye encapsulation over a large number of single polymersomoes/nanorods. The uptake of these glycopolypeptide based polymerosomes into cells will also be discussed.

Supramolecular Polymers as Dynamic Functional Materials

Nicolas Giuseppone*
University of Strasbourg and Institut Universitaire de France, Institut Charles Sadron CNRS
23 rue du Loess, BP 84047, 67034 Strasbourg Cedex 2, France
* *giuseppone@unistra.fr*

The confluence of dynamic conformational and constitutional features related to supramolecular polymers and self-assemblies has recently opened a series of very intriguing possibilities in chemical science.[1] For instance, within this framework, emerging lines of investigations have been directed towards the development of dynamic combinatorial materials and devices.[2] These ones can be defined as multi-component chemical systems which, thanks to the reversibility of their interconnections within networks of competing reactions, and to their sensitivity to environmental parameters, aim at performing modular functional tasks by responding to external stimuli. The behavior of such dynamic materials is by essence more complex than the one produced by their static or single-component counterparts and as such, they hold higher potentialities in terms of information processing and functionality tuning. We will discuss some of our works concerning such responsive systems along these lines and, more particularly, we will focus on electroactive supramolecular polymers[3] and on equilibrium and non-equilibrium polymer-motor conjugates.[4]

References:

[1] (a) Moulin, E., Giuseppone, N. – Encyclopedia of Supramolecular Chemistry – From molecules to nanomaterials - Reactions in Dynamic Assemblies, John Wiley & Sons, Ltd., **2012**, *4*, 1543; (b) Busseron, E., Ruff, Y., Moulin, E., Giuseppone, N., *Nanoscale* **2013**, *5*, 7098.

[2] (a) Moulin, E., Cormos, G., Giuseppone, N., *Chem. Soc. Rev*. **2012**, *41*, 1031; (b) Giuseppone, N., *Acc. Chem. Res*. **2012**, *45*, 2178.

[3] (a) Moulin, E., Niess, F., Maaloum, M., Buhler, E., Nyrkova, I., Giuseppone, N., *Angew. Chem. Int. Ed.* **2010**, *49*, 6974; (b) Faramarzi, V., Niess, F., Moulin, E., Maaloum, M., Dayen, J.-F., Beaufrand, S. Zanettini, J.-B., Doudin, B., Giuseppone, N., *Nat. Chem*. **2012**, *4*, 485; (c) Moulin, E., Cid-Martin, J., Giuseppone N., *Adv. Mat*. **2013**, *25*, 477; (d) Armao, J. J., Maaloum, M., Ellis, T., Fuks, G., Rawiso, M., Moulin, E., Giuseppone, N. *J. Am. Chem. Soc*. **2014**, *136*, 11382; (e) Nyrkova, I., Moulin, E., Armao, J. J., Maaloum, M., Heinrich, B., Rawiso, M., Niess, F., Cid J.-J., Jouault, N., Buhler, E., Semenov, A., Giuseppone N., *ACS Nano* **2014**, 8, 10111.

[4] Du, G., Moulin, E., Jouault, N., Buhler, E., Giuseppone, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 12504.

Block Copolymers for sub-10 nm Assembly

Padma Gopalan[1]*
[1]Department of Materials Science and Engineering and the Department of Chemistry
University of Wisconsin-Madison, Madison, WI
*pgopalan@wisc.edu

In the last decade, the number of studies on various aspects of block copolymer assembly and their applications in microelectronics has exponentially increased. This involves a number of aspects, from synthesis of new block copolymers with high chi, chemistry and physics to enable their thin-film assembly, and technology to multiply the density of features. Some of the ongoing work in our group has focused on two of these aspects namely synthetic routes for potentially high chi block copolymers and the development of non-preferential surface chemistry to enable thin-film assembly. We have developed a versatile chemistry for fabricating nanopatterned polymer brushes. Our approach combines neutral brush chemistry for controlling block copolymer domain orientation with inimer chemistry to grow dense periodic arrays of patterned brushes. This is a large area approach which overcomes many of the limitations of other approaches based on patterning a self-assembled monolayer of initiators by serial top-down lithographic techniques. There is also a need to develop block copolymers which have all the required characteristics for sub 10 nm patterning, such as high chi, high etch selectivity between the two blocks, right thermal characteristics, ability to self-assemble in thin-films, and efficient pattern transfer to the underlying substrate. We will present synthesis and characterization of the newer block copolymers recently developed by us to meet these challenges.

References:

[1] Rational Design of a Block Copolymer with a High Interaction Parameter. Sweat, D.P; Kim, M.; Larson, S.R.; Choi, J.W.; Choo, Y.; Osuji, C.O.; Gopalan, P.; Macromolecules **2014,** 47(19), 6687-6696
[2] Phase Behavior of Poly(4-hydroxystyrene-block-styrene) Synthesized by Living Anionic Polymerization of an Acetal Protected Monomer. Sweat, D.P; Kim, M.; Schmitt, A.K.; Perroni, D.V.; Fry, C.F.; Mahanthappa, M.K.; Gopalan, P.; Macromolecules **2014,** 47(18), 6302-6310

Polymers as Probes: Synthesis and Design of Polymer Probes for Fresh Water Applications

Thomas Swift[1], Linda Swanson[1], Stephen Rimmer[1]*
[1]Department of Chemistry, University of Sheffield, United Kingdom
* *s.rimmer@sheffield.ac.uk*

Due to the vast worldwide usage of synthetic polymers in industrial applications (such as wastewater treatment, oil recovery, erosion control and ore processing) concerns have been raised regarding the impact of the release of polymer particles on aquatic life forms 1. Current methods of tracking the spread of water soluble polymers through the environment however have the drawback of being chemically involved or liable to struggle with contaminants found in fresh water. Here a new detection method is outlined for the detection of specific polymer contaminants in fresh water systems using interpolymer complexation with a specifically synthesised fluorescent polymer probe [2]. Further advances utilising fluorescence labelling can reveal important information about the complex solution behaviour of both linear and branched polymer systems [3].

This detection method was tested in a variety of fresh water situations and found to be robust against a range of contaminants. This method is remarkably fast and requires little sample modification compared to existing fluorescence methods of detection.

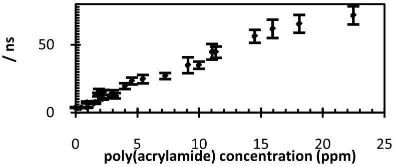


Figure 1: The restricted rotation of the polymer probe (measured in nanoseconds) shows a clear linear response to the presence of poly(acrylamide) at ppm concentrations. The lower limit of detection is dependent on the concentration of polymer probe (PAA conc. 0.3 mg ml^{-1})

References:

[1] Harford, A.J. et al. Water Research. **2011**, 45, 6393-6402.

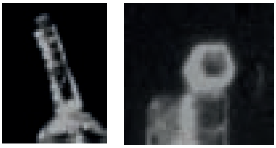
[2] Carter, S. R. et al. Macromolecular. Bioscience. **2007**, 7, 975-986.

[3] Swanson, L. Photochemistry and Photophysics of Polymer Materials, 2010, John Wiley and Sons, 689

Supramolecular Gel-Mimics for Controlling the Crystal Growth of Anticancer Drugs

Arnab Dawn and Jonathan W. Steed
Department of Chemistry, Durham University, Durham, United Kingdom
arnab.dawn@durham.ac.uk

Polymorph screening of the solid form of drug substances is a key issue to the pharmaceutical industries; drawing huge intellectual and financial investments. Different crystal forms have different bioavailability and solubility, and the crystal morphology significantly affects processing and tabletting behaviour. Our research aims to develop a novel method for identifying, isolation and screening, of new drug solid forms, particularly the production of previously unknown polymorphs by use of chemically and physically tunable supramolecular gels. A gel fiber represents on the local scale an ordered and controllable array of chemical functionality suitable to act as a heteronucleating surface and hence influence the structure of a growing crystal nucleus of a drug polymorph. In well-designed cases the drug will bind to the gel in such a way that the short-range periodicity within a gel fibril can match up with a complementary face of a precritical nucleus of a particular solid form and hence stabilize that nucleus relative to homogeneous nucleation. Such 'active' gels are expected to catalyse the formation of otherwise unstable or hard-to-nucleate solid forms. In a recent study, our group demonstrated that the high quality carbamazepine crystals could be grown in supramolecular gels. In a much more targeted approach, now, we aim to develop a series of platinum-based metallo gelators by mimicking the functional groups of platinum-based drug molecules. The platinum drugs are clinically important because of their anti-cancer activity. Cisplatin is oldest in this category; however, only two pure forms have been reported to date. Also, a recent study shows a hint of polymorphism for oxaliplatin, although only a single form has been authenticated. Thus in one way the current research can stimulate the general academic interest and at the same time it has the potential to address a crucial issue in pharmaceutical industry.



Cisplatin crystals with variable morphologies grown on the gel surface

References:

[1] Foster, J. A.;Piepenbrock, M.-O. M.; Lloyd, G. O.; Clarke, N.; Howard,J. A. K.; Steed, J. W. Nature Chem.**2010**, 2, 1037.

A New Family of Thermo-responsive Main-chain Acid Degradable Polymers with Unique Temperature Response and Neutral Degradation Products

Sanjoy Samanta and Jeffrey T. Koberstein*
Department of Chemical Engineering, Columbia University,
500 West 120th Street, New York, NY 10027, USA
**jk1191@columbia.edu*

This report includes the development of a remarkable new family of stimuli-responsive biocompatible polymers that, in a word, have the potential to revolutionize the field of stimuli-responsive polymers and bio-medical engineering. 'Acetal chemistry'-based "click" reactions are applied for rapid (within 2 hrs) synthesizing these water-soluble polymers that not only respond to pH, but show unique temperature response; their Lower Critical Solution Temperatures (LCSTs) can be predicted and tuned precisely to any demandable temperature within a range of about 7-80°C by simply adjusting the number of carbon and/or oxygen atoms in the repeat units, which is a perfect example of materials genome. Unlike majority of other degradable polymers which degrade into acidic byproducts resulting inflammation, these newly invented polymers degrade into neutral small-molecular degradation products under mildly acidic environment (pH 5-6.5) indicating the potential ability to be used in bio-medical field, particularly for cancer therapy due to the similar acidic environment (pH 5-6.5) of cancer cells. These recently invented polymers are one of few polymer systems that are intrinsically dual-responsive in nature, and to our knowledge, there is no other polymer that can match their chemical versatility and unique temperature responsive behavior.

Förster's Resonance Energy Transfer (FRET) as a tool to study the aggregation phenomenon of amphiphilic polymers

Priya Rajdev,* Dipankar Basak and Suhrit Ghosh*
Polymer Science Unit, Indian Institute of Science, Jadavpur, Kolkata – 700032
psupr2@iacs.res.in

Amphiphilic polymers have been a topic of immense interest in recent past owing to their biologically relevant versatile nano-structured assemblies. One of the parameters that is highly important for biomedical application is the dynamics of these aggregates. In the recent past, we have studied [1] aggregation of a family of amphiphilic random copolymers with different hydrophobic/ hydrophilic balance. The dynamics of aggregation were compared in this series of polymers by FRET among non-covalently encapsulated lipophilic donor (D) and acceptor (A) dyes in the hydrophobic pocket of aggregates. The pair of dyes, when in close proximity in the core of aggregates gave rise to FRET, which was monitored over time for probing aggregation properties as a function of solvent composition and polymer structure which revealed very slow dynamics for all polymers. Comparative studies with a structurally related small molecule surfactant confirmed this. More recently, we have synthesized a pair of block copolymers, again from a single parent polymer, where D or A chromophores are covalently attached to the hydrophobic block in a random fashion, via the post polymerization modification. Detail investigation on co-mixed aggregates of D- and A- functionalized block copolymers showed remarkably slow dynamics, high thermal stability and low critical aggregation concentration for the micellar aggregates, all desired properties for biological application e.g. drug delivery. To rationalize these intriguing observation, polymer structures were analyzed which revealed presence of unreacted pendant –OH groups in the hydrophobic block which were not fully consumed during post polymerization dye incorporation reaction. FT-IR and experiments with control polymers lacking such -OH groups, concluded that H-bonding among these OH groups supramolecularly cross-linked the micellar core, which was responsible for such astonishingly slow dynamics. Pros and cons of FRET in context of studying dynamics of amphiphilic polymer aggregates and insights into the unprecedented non-covalent core cross-linking of micelles will be the focus of this presentation.

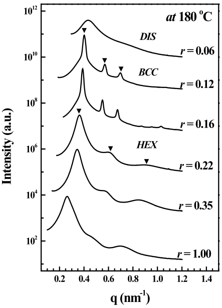
References:

[1] K. Dan, P. Rajdev,* J. Deb, S. S. Jana and S. Ghosh*. *J. Pol. Sc. Part A: Pol. Chem.;* **2013,** *51*, 4932.

Screening of Phase Transition and Interaction Parameter in Block Copolymer Mixtures

Sudhakar Naidu Neppalli[1*] and Dyu Yeol Ryu[2]
[1]Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India
[2]Department of Chemical and Biomolecular Engineering,
Yonsei University, Seoul, South Korea
*s.naidu@ncl.res.in

Morphological transitions in an asymmetric, disordered poly (styrene-*b*-(2-vinylpyridine) block copolymer (BCP) were investigated by quarternizing the poly (2-vinylpyridine) block with a super acid. The phase transitions of quarternized BCP from disorder-to-sphere-to-hexagonally packed cylindrical microphases were characterized using*in-situ* small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). The effective interaction parameter (χ_{eff}) between two block components was evaluated using Leibler theory based on the incompressible random phase approximation (RPA)for quarternized BCP in a disordered state.D-spacing was used to estimate effective interaction parameter χ_{eff}) of block componentsin weak and strong segregation regimesof ordered phase. Thermal stability of the polyelectrolytes was also examined using thermo gravimetric analysis (TGA) and observed that acid shows prominent effect on thermal stability of BCP.



References:

[1] Naidu, S.; Ahn, H.; Gong, J.; Kim, B.; Ryu, D. Y. *Macromolecules* **2011,** 44 (15), 6085-6093.

[2] Kim, J. K.; Suda, Y. *Macromolecules* **1999,** 32, (20), 6707-6717.

[3] Schmidt, K.; Schoberth, H. G.; Boker, A. *Nat Mater* **2008,** 7, (2), 142-145.

[4] Alexander A. Teran; Nitash P. Balsara*J. Phys. Chem. B* 2014, 118, 4-17.

[5] Carrasco, P.M.; Ruiz Luzuriaga, A.; Garcia, I.*Macromolecules* **2011,** 44, (12), 4936-4941.

Stimuli-Responsive Amphiphiles for Protein Manipulation

Nabanita Sadhukhan[1*], S. N. Jaisankar[1], A. B. Mandal[1,2*]
Takahiro Muraoka[3], Mihoko Ui[3], Kazushi Kinbara[3*]
[1]Polymer Division, CSIR-Central Leather Research Laboratory, Adyar, Chennai–600020
[2]Chemical Laboratory, CSIR-Central Leather Research Laboratory, Adyar, Chennai – 600 020
[3]IMRAM, Tohoku University, Aoba-ku, Sendai – 980 8577, Japan
nnsadhukhan@gmail.com

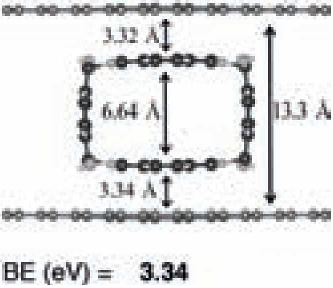
Polyethylene glycols (PEGs) are low toxic, neutral linear polyethers. PEGs have been widely utilized in the field of biology and pharmaceutical chemistry. A stimuli-responsive PEG amphiphiles will undergo conformational change in response to the external stimulus. The stimulus induced conformational change gives rise to hydrophilicity/hydrophobicity switching to the PEG amphiphiles. On the other hand, a protein becomes hydrophobic upon denaturation. A denatured protein often forms aggregates during protein manipulation. A hydrophobic PEG compound can inhibit such protein aggregation by interacting at the hydrophobic protein surfaces.

Utilizing such strategy, amphiphilic PEGs were successfully employed for suppression of protein aggregation. We have synthesized monodisperse PEG amphiphiles. Attaching a hydrophobic unit to the PEG backbone yielded monodisperse amphiphilic PEG macromonomer. Stimulus induced conformational change brought about varying degree of hydration property into the PEG amphiphiles, which in turn induced altering biochemical property to the PEG amphiphiles. The synthetic methodology of the monodispersed amphiphilic PEG molecules, their distinctive stimuli-responsive physicochemical properties and an extensive research relating to amphiphilic PEG assisted protein manipulation are discussed in the presentation.

Supramolecular Hybrid Gels based on Cyclophanes and Graphene Oxide

Srinivasan Sampath[1,2]*, Sang Hyun Je[2], Seoin Back[2], Gokhan Barin[2],
Onur Buyukcakir[2], Ruslan Guliyev[2], Yousung Jung[2],
Ali Coskun[2]*, Asit B. Mandal[1]
[1]Polymer Division, CSIR-Central Leather Research Institute (CLRI), Chennai, India
[2]Envinronment, Water and Sustainability (EEWS),
Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea
*sampathsrinivasan@yahoo.com

Graphene oxide (GO) is a one atom thick, two-dimensional carbon-based macromolecule incorporating several reactive oxygen functionalities, which are usually introduced during its preparation from natural graphite. Rich surface chemistry of GO has been investigated by several researchers in order to create 3D nanoarchitectures. Non-covalent functionalization of GO sheets with charged or neutral macromolecules lead to the formation various functional three-dimensional (3D) supramolecular gels, which have already found applications in several different areas, including drug delivery, catalysis, sensors, energy storage, and optoelectronics. Although, there are several reports in the literature related to the formation of supramolecular gels by dispersing GO sheets with various gelators, such as polymers, carbohydrates, peptides and DNA, none of these supramolecular gels form ordered structures. The work on the assembly of GO into well-ordered supramolecular assemblies is still limited, therefore the development of mild assembly strategies for the preparation of multifunctional 3D GO nanoarchitectures is important. We have developed a new strategy for the formation of ordered graphene oxide supramolecular gels using rigid tetracationic cyclophanes incorporating diazapyrenium units. That by varying the constitution of the cyclophane, one could, in principle, control the spacing between the GO layers. It is important to note that these ordered gels are formed under mild conditions and stabilized by series of non-covalent donor–acceptor, π–π stacking and cation-π–interaction. Details of the formation and characterization of GO supramolecular gels in the presence of rigid cationic macrocycles as gelators will be presented.



References:

[1] Srinivasan, S.; Je, S. H.; Back, S.; Barin, G.; Buyukcakir, O.; Guliyev, R.; Jung, Y.; and Coskun, A. Adv. Mater. **2014**, 26, 2725–2729.

Living Supramolecular Polymerization

Swarup Manna[1], Soichiro Ogi[2], Kazunori Sugiyasu[2]*,
Masayuki Takeuchi[2]*
[1]Department of Chemistry, BKC College, Kolkata
[2] Polymer Materials Unit, NIMS, Tsukuba, Japan
*takeuchi.masayuki@nims.go.jp

The fields of supramolecular polymers and in particular supramolecular polymerization have been developed extensively in the last decade.[1,2,3] Despite the good understanding of the polymerization mechanism it has remained a challenge to establish a system that undergoes living supramolecular polymerization. To achieve this, self organization occurring far from thermodynamic equilibrium – ubiquitously observed in nature – must take place. Through a delicate interplay of the self assembly phenomenon using isodesmic and cooperative models,[4,5,6] a living supramolecular polymerization of the porphyrin based monomers have been designed. The mechanism behind this process is similar to that of conventional living polymerization and for the first time supramolecular polymers were synthesized with controlled length and narrow polydispersity.

References:

[1] Brunsveld, L., Folmer, B. J. B., Meijer, E. W., Sijbesma, R. P. Chem. Rev. **2001**, 101, 4071–4097.
[2] Aida, T., Meijer, E. W., Stupp, S. I. Science **2012**, 335, 813–817.
[3] Hoeben, F. J. M., Jonkheijm, P., Meijer, E. W., Schenning, A. P. H. J. Chem. Rev. **2005**, 105, 1491–1546.
[4] Martin, R. B. Chem. Rev. **1996**, 96, 3043–3064.
[5] Zhao, D., Moore, J. S. Org. Biomol. Chem. **2003**, 1, 3471–3491.
[6] De Greef, T. F. A. et al. Chem. Rev. **2009**, 109, 5687–5754.

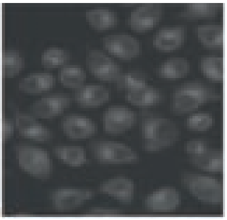
Amphiphilic block copolymer based biocompatible micelles for delivery of chemotherapeutic drugs: Synthesis & *In vitro* evaluation

Dipti Kakkar Thukral[1], Anant N Bhatt[a],
Sebastien Lecommandoux[b], Anil K Mishra[a]
[1]Institute of Nuclear Medicine and Allied Sciences, Defence Research and Development Organization, Brig S K Mazumdar Road, Timarpur, Delhi-110054, India
[2]Laboratoire de Chimie des PolymèresOrganiques, UMR 5629, Université Bordeaux 1/CNRS 16, Avenue Pey-Berland 33607 Pessac Cedex, France

Amphiphilic block copolymers of poly(ethylene glycol) (PEG) as the hydrophilic block and poly(γ-benzyl-L-glutamate) (PBLG) as the hydrophobic block were synthesized in the form of PEG-PBLG diblock and PBLG-PEG-PBLG triblock copolymers by the *click chemistry* approach. Alkyne functionalized poly-γ-benzyl-L-glutamate was synthesized by ring opening polymerization and then copolymerized with azide terminated polyethylene glycol by Cu(I) catalyzed click cycloaddition reaction to prepare the diblock and triblock copolymers. The synthesised block copolymers were evaluated by spectroscopic, thermal and chromatographic techniques: NMR (^{1}H and ^{13}C), IR, SEC and DSC.

These amphiphillicdiblock and triblock copolymers were then self assembled into polymeric micelles (<100nm) and loaded with the anti-cancer drug, doxorubicin (DOX), in order to validate their efficacy to deliver chemotherapeutic drugs. Drug loading studies were carried out at neutral as well as at basic pH.

In vitro cytotoxicity studies were carried out on the three DOX loaded polymeric micelles in KB cell lines with the help of MTT assay upto 72h and compared with that of free doxorubicin. Cellular uptake of doxorubicin was also studied in the KB cells by fluorescence microscopy and flow cytometry. The drug loaded polymeric micelles showed good cellular uptake of doxorubicin as shown by the bright fluorescence microscopic images as well as by the high fluorescence intensity values obtained from flow cytometry. The DOX-loaded micelles were also assessed for stability of the drug against degradation and its release at physiological pH of 7.4 and at acidic pH of 5.5. These developed PEG-PBLG polymeric systems are potential micellar drug carriers to improve drug accumulation at the tumour site thereby improving the therapeutic response to chemotherapy thus reducing the reported side effects due to non-specific distribution of anticancer drugs.



Flourescence microscopy image of cellular uptake of DOX loaded polymeric micelles.

Structure and thermodynamic properties of symmetric poly (styrene-*block*-acrylicacid) (PS-*b*-PAA) polyelectrolyte block copolymer micelle in salt-free aqueous solutions by atomistic molecular dynamics (MD) simulations with explicit solvent.

Rajalakshmi Chockalingam and Upendra Natarajan
Macromolecular Modeling and Simulation Lab, Dept. of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036.
rajic.lingam@gmail.com; unatarajan@iitm.ac.in.

The structure and thermodynamic properties of micelle formed by symmetric poly(styrene-*b*-acrylicacid) (PS-*b*-PAA) copolymer chains in salt-free aqueous solution as a function of degree-of-ionization (*f*) of PAA block (0 – 100 %) was studied by molecular dynamics (MD) simulations. To our knowledge, this is the first atomistic molecular dynamic study of a polyelectrolyte-neutral block copolymer micelle in aqueous solution. Our simulations are able to capture micelle formation using very different starting configurations. Insoluble PS blocks form the inner core and the soluble PAA block form the corona. Micelle size increases with *f,* in agreement with the experimental observations in literature,[1] due to the extended conformations adopted by PAA chains driven by repulsive dispersion interactions between PS and PAA units. With increase in *f*, the micelle attains spherical shape accompanied by decrease in core surface area. Pair correlation functions (RDF) of core and corona units with water oxygens and Na^+, as well as contribution of various species to solvation enthalpy show that core block interactions are insensitive to changes in *f* values. PAA-Water Hydrogen-bonds increases with ionization (i.e. charge density on the chain). Various aspects of the hydration behavior will be presented. Radial atom density profiles for corona and Na^+ ions as well as contributions of PAA-Na^+ and Water-Na^+ pairs to solvation enthalpy confirm the existence of the micelle in the "osmotic regime", in agreement with neutron scattering experiments and mean-field theory.[1,2]

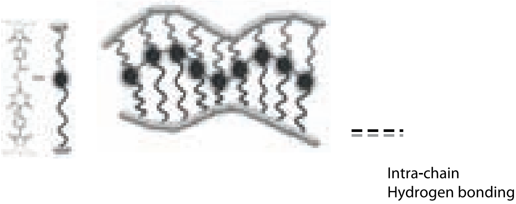
References:

[1] Groenewegen, W.,; Egelhaaf, S. U.; Lapp, A.; Van Der Maarel, J. R. C. *Macromolecules* **2000,** *33*, 3283-3293.
[2] Shusharina, N. P.; Linse, P.; Khokhlov, A. R. *Macromolecules* **2000,** *33*, 3892-3901.

A New Class of Amphiphilic Copolymer for Self-Assembled Superstructures under Aqueous Conditions

Ashlin Sathyan, Shivshankar R. Mane, Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata (IISERK), India
*sraja@iiserkol.ac.in

Two homopolymers with norbornene backbone were prepared using ring opening metathesis polymerization (ROMP), assisted by Grubbs catalyst (G2), and followed by their coupling to get the desired new class of amphiphilic copolymer. The copolymer was characterized through ^{1}H &^{13}C NMR, GPC and FT-IR spectroscopy. The formation of supramolecular self-assembly was primarily revealed from determination of critical aggregation concentration (CAC), dynamic light scattering (DLS) and atomic force microscopy (AFM). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the rod like superstructures with a size of 200 nm. Two transitions were observed in the circular Dichroism (CD) spectrum. This could be the result of cotton effect by $n \rightarrow \pi^*$ transition at 193 nm by carbonyl chromophore and $\pi_1 \rightarrow \pi^*$ transition at 197.5 nm of amide chromophore. The intra chain hydrogen bonding between the amine and carbonyl group of amide bond could be the driving force for the one handed helix like structures. We also demonstrated the drug release study of anticancer drug doxorubicin (DOX) by dialysis method.



References:

[1] Seo, H.S.; Chang, J.Y.; Tew, G. N. Angew. Chem. Int. Ed. **2006**, 45, 7526 –7530
[2] Mane, S.R.; Shunmugam, R. ACS Macro Lett.**2014**, 3, 44-50.
[3] Zhang, A.; Aleman, C.; Schluter, A. D. et al. Chem. Eur. J. **2008**, 14, 6924-6934
[4] Mane, S.R.; Dinda, H.; Sathyan, A.; Shunmugam, R. ACS Appl. Mater. Interfaces. **2014**, in press.

Bioactive self assembled nanostructures from Glycopolypeptides and Arginine mimics

Bhawana Pandey, Soumen Das, Sayam Sen Gupta
National Chemical Laboratory, Pune
bs.pandey@ncl.res.in

Glycopolypeptides, synthetic polypeptides featuring pendant carbohydrate moieties, have been of particular interest to the field of tissue engineering and drug delivery. This interest is derived from the complex roles that carbohydrates play in vivo, particularly in bimolecular recognition events such as cellular recognition, adhesion, cell growth regulation, cancer cell metastasis, and inflammation. For these glycopolypeptides to be used as delivery vehicles and as biomaterials, it would be advantageous if these could be assembled into supramolecular nanostructures that can be tuned to appropriately display their carbohydrate moieties. Thus, amphiphilic block copolymers containing glycopolypeptides as one of their blocks were attempted. We have demonstrated that self-assembled nanostructures can be generated from the amphiphilic glycopolypeptide conjugates. By changing the hydrophilic-lipophilic balance of the amphiphilic glycopolypeptides, we were able to self-assemble them into nanostructures with different morphologies. Herein we have prepared PICsomes (polyionic complex vesicles) by simple mixing of water-soluble and oppositely charged glycopolypeptide block catiomer and PEG block aniomer in aqueous medium. This nanostructure is a new member of the polymerosome family consisting of a polyionic complex (PIC) membrane sandwiched between outer and inner (PEG and glycopolypeptide) shell layers. In another approach I will discuss the formation of nanostructured biomaterials via dynamic self-assembly of poly-arginine based polypeptide for biomedical applications.

References:

[1] Antonietti, M and Forster, S Adv. Mater., 2003, 15, 1323–1333. Minton, A. P. J. Biol. Chem. **2001**, 276, 10577.
[2] Dong,W.; Kishimura,A.; Anraku,Y.; Chuanoi,S; and Kataoka,K. J. AM. CHEM. SOC. **2009**,131, 3805
[3] Koide,A.; Kishimura,A.; Osada,K.; Jang,W.; Yamasaki,Y and Kataoka,K. J. AM. CHEM. SOC**. 2006**,128, 5988
[4] Olli Ikkala and Gerrit ten Brinke .Science .**2002**,295, 2407

Interaction and Assembly of Improvised Amino Acids with Biomacromolecules: structure and function

Debasish Haldar,* Apurba Pramanik and Krishnendu Maji
[1]Department of Chemical Sciences, Indian Institute of Science Education and Research
Kolkata, Mohanpur, West Bengal -741252, India
*deba_h76@iiserkol.ac.in

Many synthetic organic small molecules are capable to recognize and interact with biomacromolecules such as proteins and DNA even by altering structures.[1] But most of them exhibit side effects when used as therapeutic agents.[2] Hence, it is challenging to develop designer small molecules having maximum DNA-binding or protein-binding activity, enhanced cellular and nuclear transport activity but less harmful for normal cells. In this report we will discuss the structure of improvised amino acids and their interactions with biomacromolecules like proteins and DNA. We report on the synthesis of 2-Acetyl amino-3-[4-(2-amino-5-sulfo-phenylazo)-phenyl]-propionic acid from phenylalanine as HEWL amyloid inhibitor (Figure 1).[3] The compound arrests the monomers and exhibits anti-aggregating activity. We have designed and synthesized 6-amino coumarine-3-carboxylic acid starting from coumarine. The compound has excellent emission at 450 nm and readily interacts with DNA. The confocal microscopy shows that the improvised amino acid can transport to nucleus of Hela cells and bind with DNA. We have also designed and synthesized an amino acid using click chemistry. We will discuss its structure and interaction with DNA in details.

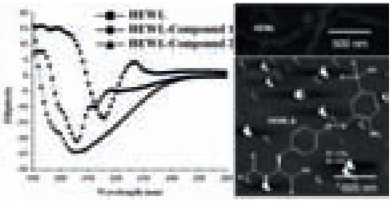


Figure1. Anti-aggregating activity of 2-Acetyl amino-3-[4-(2-amino-5-sulfo-phenylazo)-phenyl]-propionic acid against in vitro amyloid fibrillogenesis of HEWL model system by CD spectroscopy (left) and AFM (right).

References:

[1] Thompson, L. A.; Ellman, J. A. *Chem. Rev.*, **1996**, *96*, 555-600.

[2] Paul, A.; Bhattacharya, S. *Current Science*, **2012**, *102*, 212-231.

[3] Maity, S.; Kumar, R.; Maity, S. K.; Jana, P.; Bera, S.; Haldar, D. *Med. Chem. Commun.*, **2013**, *4*, 530-536.

High Mobility and Low Operating Voltage Field Effect Transistor Based on Doped Lamellae of Perylene Diimide

Bhanprakash Jain, Arulraj Arulkashmir,
Kothandam Krishnamoorthy*
Polymers and Advanced Materials Laboratory and Centre of Excellence in Surface Science,
CSIR-National Chemical Laboratory and CSIR-Network Institute of Solar Energy,
Dr. Homi Bhabha Road, Pashan, Pune 411008 (India)

In n-doping, electrons are injected into the lowest unoccupied molecular orbitals of the semiconductor from the dopant, hence the energy level of the dopant is much higher than the oxygen energy level (-5.2 eV). Thus, the dopant is unstable, which complicates the fabrication of n-doped devices. However, in few instances, it has been shown that successful n-doping improves the conductivity as well as air stability of organic electronic devices. Herein, we demonstrate that an air stable dopant can be used to inject electrons to perylene diimides and generate air stable radical anions. We noticed that the radical anion formation disrupts the self assembled nanowires of the perylene diimides. Structural integrity was imparted to the nanostructure by the reaction of carboxylic acid moieties of the perylene diimides with zinc ions. The field effect transistors fabricated using the zinc reacted and doped semiconductor exhibit charge carrier mobility as high as 13 cm^2/Vs with a threshold voltage of -0.1 V and a sub threshold slope of 0.16 V. The voltage required to operate the device is very low (1 V). It is necessary to note that the device fabrication and measurements were carried out under ambient conditions. Using ultra violet photoelectron spectroscopy, we corroborate the position of molecular orbital energy levels and explain the mechanism of electron transfer and transport.

References:

[1] Arulkashmir, A.; Jain, B.; Roy, K.; John, J. C. ; Krishnamoorthy, K. Chem. Commun. **2014**, 50, 326-328.

Bioactive Polymersomes Self-assembled from Amphiphilic Glycopolypeptides: Synthesis and Characterization, and Dual-Dye Encapsulation

Soumen Das[a], Dharmendra Kumar Sharma,[b]Arindam Chowdhury[b]*
Sayam Sen Gupta[a]*
[a]Chemical Engineering Division, CSIR-National Chemical Laboratory,
Dr. HomiBhabha Road, Pune – 411 008, India
[b]Department of Chemistry, Indian Institute of Technology
*Bombay*ss.sengupta@ncl.res.in*

Glycopolypeptide (GP) based polymersomes can have promising applications as vehicles for targeted drug delivery since they are capable of encapsulating different pharmaceuticals of diverse polarity as well as interact with specific cell surfaces due to their bioactive surfaces. We have synthesized GP-b-poly(propylene oxide) by ROP of glyco-N-carboxyanhydride (NCA) using the hydrophobic amine terminated poly-propylene oxide (PPO) as the initiator. This block co-polymer is composed of a biodegradable FDA-approved PPO hydrophobic block in conjugation with hydrophilic GP which are expected to be biocompatible. We demonstrate the formation of GP based polymersomes from the self-assembly of GP-b-PPO in which the presence of ordered helical GP segment is required for their self-assembly into spherical nanoscale polymersomes (~50-100 nm). The polymersomes were characterized in detail using a variety of techniques TEM, AFM, Light Scattering and fluorescence correlation spectroscopy measurements. As a model for drugs, both hydrophobic (RBOE) and hydrophilic (Calcein) have been incorporated within the polymersomes from solution. To substantiate simultaneous entrapment of the two dyes, spectrally-resolved fluorescence microscopy was performed on the GP polymersomes cast on a glass substrate. We show that it is possible to visualize individual nanoscale polymersomes and effectively probe the dyes' colocalization and energy transfer behaviors therein, as well as investigate the variation in dual-dye encapsulation over a large number of single polymersomes.This could potentially be very useful in understanding the interaction of these dye loaded polymersomes with cell surface receptors leading to its endocytosis. Finally, we show that the galactose moieties present on surface can specifically recognize lectin RCA120, which reveals that polymersomes' surface is indeed biologically active.

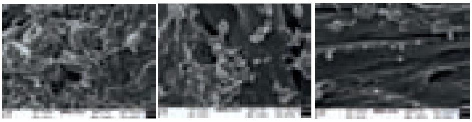
References:

[1] Discher, D. E.; Eisenberg, A. Science.**2002**, 297, 967–973.
[2] Pati, D.; Kalva, N.; Das, S.; Kumaraswamy, G.; Sen Gupta, S.; Ambade, A. V. J. Am. Chem. Soc. **2012**, 134, 7796–7802.

Anion Induced Gelation in Polyvinyl Alcohol: A Probe for Metal Ion Speciation Studies

Pallabi Samaddar and Kamalika Sen *
Department of Chemistry, University of Calcutta,92 APC Road, Kolkata - 700009, India
*kamalchem.roy@gmail.com

Polyvinyl alcohol (PVA) hydrogel is one of the most useful polymeric gels that is extensively used in numerous biomedical applications, for example as implants [1], artificial organs, contact lenses, drug delivery devices and wound dressings [2, 3]. Salt solutions of certain anions viz., sulphate, phosphate and citrate are reported herein to form hydrogels in PVA solutions for the first time. We have made PVA hydrogel without using any type of toxic or acidic materials which leads to a greener prospect of the material [4, 5]. Gelation phenomenon is observed only with those salts which have reported salting out behavior. Hydrogels in sulphate medium have very high viscoelastic property and higher porosity than the hydrogels obtained with phosphate or citrate as can be seen from the SEM images.



(a) (b) (c)

SEM Images of hydrogels obtained from (a) sulphate (b) citrate (c) phosphate

An attempt to find a chemical application of these gels in the field of elemental speciation reveals that smaller cations have lesser tendency to get adsorbed on the hydrogel surface. Fe(II), Fe(III), Mn(II) have either very less or no adsorption possibility. Mn(VII) undergoes species transformation to Mn(II) in the hydrogel and shows similar behavior as Mn(II) itself. Cr(III) has a certain adsorption in the sulphate hydrogel owing to some specific interactions. Cr(VI) remains in its anionic form and hence is not adsorbed. Fe(II) and Fe(III) however can be adsorbed upon suitable complexation in the hydrogel. Phosphate hydrogel serves as the better adsorber in these two cases. All the adsorptions follow Freundlich isotherm very nicely and the results are explained on the basis of the K value arising out of the isotherm equation. The hydrogels are thus eligible probes for species dependent metal adsorption studies.

References:

[1] Juang, J. H; Bonner, W. S; Ogawa, Y. J; Vacanti, P; Weir, G. C .Transplantation **1996** 61, 1557–61.

[2] Chen, D. H; Leu, J.C; Huang, T. C. J. Chem. Technol. Biotechnol., **1994,** 61, 351–7.

[3] Li, J .K; Wang, N; Wu, X. S. J Control Rel, **1998**, 56, 117–26.

[4] Hassan, C. M; Peppas, N. Adv. Polym. Sci., **2000,** 153, 37-65.

[5] Mansur, H. S; Sadahira, C. M ; Souza, A. N; Mansur, A. A. P. Mat. Sci. Eng. C, **2008**, 28, 539–548.

Synthesis of amphiphilic poly(N-vinylcaprolactam) using ATRP protocol and antibacterial study of its silver nanocomposite

Ashok Kumar[1], Deepak[1], Pooja Singh[1], Rajesh Kumar*[1] and Arti Srivastava[2]
[1] Department of Chemistry, Centre of Advance Studies in Chemistry, Faculty of Science,
Banaras Hindu University,Varanasi-221005, UP, India
[2]Department of Chemistry, School of Physical Sciences,
Guru Ghasidas Vishwavidyalaya, Bilaspur-495009 (CG), India
*E-mail: *rkr_bhu@yahoo.com*

Atom transfer radical polymerization of N-vinylcaprolactam (NVCL) was studied by employing ethyl-2-bromoisobutyrate as initiator in 1,4-dioxane. It led to controlled radical polymerization of NVCL, with the molecular weight increased along with the conversion of monomer and a relatively narrow molecular weight distribution could be obtained, as determined by GPC. The living nature of the ATRP for NVCL was confirmed by the experiments of PVCL chain extension.Self-assembling of the amphiphilic PVCL leads to the formation of their micellar aggregates in aqueous media which was confirmed by TEM. The critical micelle concentration value was calculated by UV absorption studies and was found to be 0.0320 mg/ml. The polymer nanocomposite was synthesized and found to possess strong antibacterial activity against *Enterococcus faecalis* with minimum inhibitory concentration value of 32 μg/ml.

Synthesis of Novel Polymeric Filled IPN Membranes For Dehydration of Acetic Acid by Pervaporation

Sunil Baran Kuila[1*], Samit Kumar Ray[2]
[1]Department of Chemical Engineering, Haldia Institute of Technology, Haldia, WB
[2]Department of Polymer Science and Technology, Rajabazar Science College,C.U.
*sunilbarankuila@gmail.com

Polyvinyl alcohol (PVOH) was chemically modified by crosslink copolymerization of acrylic acid (AA) and acrylamide (AM) in aqueous solution of PVOH and finally crosslinking the copolymer (PAAAM) with methylene bis acrylamide(MBA) and PVOH with glutaraldehyde to produce a full interpenetrating network(FIPN) membrane. Accordingly, a membrane containing PVOH:copolymer of 1:0.5 designated as FIPN500 was synthesized. This FIPN500 membrane was further filled with highly hydrophilic aluminosilicate filler to produce three filled membranes i.e. FIPN502, FIPN505 and FIPN5010 containing 2, 5 and 10 mass% (of total polymer) filler. PVOH membrane cosslinked with 2 mass% glutaraldehyde, PAAAM copolymer modified PVOH membrane i.e. FIPN500 and the three filled FIPN membranes i.e. FIPN502, FIPN505 and FIPN510 were used for pervaporative dehydration of acetic acid. The performances of the membranes were evaluated in terms of sorption and pervaporative dehydration of acetic acid. The filled IPN membranes were found to show higher flux and water selectivity than the unfilled FIPN membranes. Flux and water selectivity of these filled membranes were found to increase with increasing amount of filler in PVOH matrix. However, among the three membranes, FIPN510 were found to show the highest flux and water selectivity (6.612 kgm^{2}hr^{-1}μm flux and 325.53 water selectivity at0.953 mass% water in feed). Interaction parameters, intrinsic membrane properties like permeability and membrane selectivity, concentration average diffusion coefficients for all the membranes were also evaluated.

Key word: Pervaporation, acetic acid, crosslink copolymer, IPN, interaction parameter, partial permeability, diffusion coefficient

References:

[1] Kuila,S.B.; Ray,S.K.; Das,P.; Singha,N.R. Chem. Eng. & Proc. **2011,** 50, 391-403.

[2] Devi,D. A.;Smitha, B.; Sridhar, S.; Aminabhavi,T.M. J. Membr. Sci. **2006**, 280, 45–53.

[3] Kuila ,S.B.; Ray,S.K. Sep.& Purif. Tech. **2011**, 81, 295–306.

Synthesis of Metal Oxide NanostructuresTemplated by Core-Shell Hairy Polymer Nanoobjects

Sajan Singh[1], Sunita Sanwaria[1], Jit Pal[1], Rajiv Srivastava[1],
Andriy Horechyy[2], Manfred Stamm[2,3], Bhanu Nandan[1*]
[1]Department of Textile Technology, Indian Institute of Technology Delhi,
HauzKhas, New Delhi 110016, India
[2]Leibniz Institute of Polymer Research Dresden, HoheStrasse 6, Dresden 01069, Germany
[3]Technische Universität Dresden, Physical Chemistry of Polymer Materials,
Dresden 01062,Germany
*Email: *nandan@textile.iitd.ac.in*

Recently, a lot of interest has been shown for the synthesis of functionalnano-objects decorated with different functionalities has immense potential in a number of applications like in sensors, drug-delivery, tissue engineering etc. However, the approaches for fabricating such nanoobjects are few and most of them are tedious. Here, we present a simple approach for fabricating functionalnano-objects which involves self-assembly of block copolymer. The self-assembled structures formed via block copolymer self-assembly are isolated using a selective-swelling approach which then could be used as template for loading the desired functionality.In the present work, we demonstrate this concept using a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer. The isolated cylindrical nano-objects have their shell composed of P4VP chains which has the potential to host suitable functional additives. In the present study, we performed sol-gel chemistry on these nanoobjects for depositing metal oxides such as silica and titania. The resulting silica/polymer and titania/polymer hybrid nanobjects after the calcination step was converted to hollow silica and titaniananobjects,respectively. The method is versatile and could be carried out either on the polymer nanoobjects in the solution or in dry state where the nanoobjects are immobilized on a substrate.

Keywords: Nano-objects, block copolymers, self-assembly

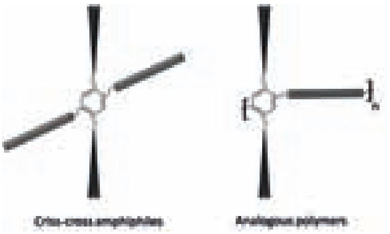
Reference:

1) Pal J, Sanwaria S, Srivastava R, Nandan B, Horechyy A, Stamm M, et al. Hairy polymer nanofibers via self-assembly of block copolymers. *Journal of Materials Chemistry***2012**, 22,25102-25107
2) Sanwaria S, Pal J, Srivastava R, Formanek P, Stamm M, Horechyy A and Nandan B,et al. Synthesis of hollow silica nanostructures using functional hairy polymer nanofibers as templates.*RSC Adv*.**2013**, 3, 24009–24012

Criss-cross amphiphiles and analogous polymers

Saheli Chakraborty and S. Ramakrishnan
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore 560012

Amphiphiles are an interesting class of molecules that generate a wide range of phase-separated morphologies depending on the spatial distribution of the two (or more) immiscible segments. Tschierske and co-workers have examined the wide range of morphologies that these interesting class of polyphiles can adopt.[1] In the most extensively investigated class of such polyphiles, the immiscible segments are placed around a calamitic mesogenic unit, and typically the hydrophilic segment carries a diol unit; capable of hydrogen bonding. Depending on the relative positions and volume-fractions of the two immiscible segments the organization of the two segments could change significantly. Recently, we have been interested in designing polymers wherein the immiscibility of two segments forces the polymer chain to self-segregate by folding or by conformational reorganization to generate zigzag folded single chains[2] or Janus structures;[3] by careful choice of segments we have utilized the crystallization of one or both the segments to stabilize the self-segregated conformation. In the present study, we have examined a different type of amphiphilic system, namely criss-cross amphiphiles; here we placed mutually immiscible segments, namely mPEG, alkyl (HC) and perfluoroalkyl (FC) on a phenyl ring such that the diametrically opposite segments are of the same type, as shown in the figure. Similarly, polymeric analogues of these structures have also been prepared; the objective is to examine the type of morphological characteristics that such criss-cross systems exhibit, both in bulk and in thin films and further to develop approaches to exploit such morphologies to create novel nanostructured polymeric systems.



References:

[1] Lui, F.; Keiffer, R.;Zeng, X.; Pelz, K.; Prehm, M.; Ungar, G.; Tschierske, C. Nat. Commun. **2012**, 3, 1104.
[2] Mandal, J.; Prasad, K. S.; Rao, D. S. S.; Ramakrishnan, S. J. Am. Chem. Soc. **2014**, 136, 2538.
[3] Samuel, A. Z.; Ramakrishnan, S. Macromolecules. **2012**, 45, 2348.

Molecular weightof polystyrene segment as a strategy to vesicle size control in self- assembling hybrid systems

Asha Susan Chacko, R. Lakshmi and V. S. Prasad*
CSIR- National Institute for Interdisciplinary Science and Technology
Thiruvananthapuram 695019
*vsprasad@niist.res.in

Self assembling organic-inorganicpolymer clay hybrid systems (PCH) which can assemble into macro or nano morphologies such as vesicles, tubes etc. are of great importance for the possible applications as advanced functional materials in controlled delivery of drugs or cosmetics due to the rigidity and higher thermal stability compared to liposomes. In the present work exfoliation of montmorillonite clay was studied using polyhedral oligomericsilsesquioxane (POSS) synthesised by acid activated process through *in situ* modification and characterised. The results indicated the increased exfoliation of MMT in the case of acid activated POSS compared to that synthesised by aging process. The PCH was further synthesied with POSS-modified MMT and styrene by *in situ* polymerization at various conditions and characterised for its molecular weight to study the effect of molecular weight and polydispersityon the self- assembly of these PCHs in solutions. It was observed that as the molecular weight increases and polydispersity becoming more near to unity, the self-assembly into uniform vesicles become more prominent, whereas in the case of PCH with lower molecular weights, spherical micelles were only formed in excess. The results indicated the possible strategy for the synthesis of uniform microvesicles which can have applications in drug delivery.

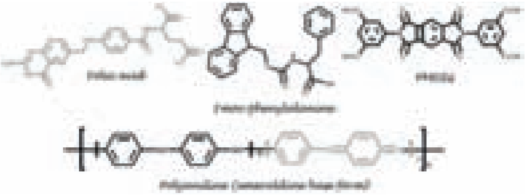
References:

[1] Nair, B. P.; Pavithran, C.; Sudha, J. D.; Prasad, V. S. Langmuir**2010**, 26,1431-1434.
[2] He, J.; Wei, Z.; Wang, L.; Tomova, Z.; Babu, T.; Wang, C.; Han, X.; John T. Fourkas, J. T.; Nie, Z. Angew. Chem. Int. Ed. **2013**, 52, 2463 –2468.

Integrated nanostructures of supramolecular gelators and polyaniline towards photovoltaic applications

Priyadarshi Chakraborty, Partha Bairi and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India

Conductive gels are a special candidate in the family of hybrid gels which have emerged as new generation smart functional materials due to the mingling of soft nature, stimuli responsiveness and thermo-reversibility of the supramolecular gels with the mechanical and electronic property of the conductive component. Here three low molecular weight gelators namely Folic acid (F), Fmoc-protected phenylalanine (FP) and 5,5'- (1,3,5,7-tetraoxopyrrolo [3,4-f] isoindole - 2, 6-diyl) diisophthalic acid (PMDIG) are used to produce co-assembled, conducting gels with polyaniline(PANI). The formation of PANI inside the gel matrices are confirmed by FTIR and UV-vis spectroscopy. UV-vis spectra also exhibit the polaron band transitions of the doped PANI. Both F-PANI and PMDIG-PANI gels exhibit fibrillar network morphogy but the branching is more in the F-PANI gel. The FP-PANI gel exhibits nanotubular morphology. The dc conductivity values of F-PANI, FP-PANI and PMDIG-PANI xerogels are 0.14×10^{-4}, 0.12×10^{-1} and 0.3×10^{-4} S/cm, respectively. The current-voltage (I-V) curves of the F-PANI gel shows a negative differential resistance (NDR) property both at forward and backward bias. The I-V property of the FP-PANI xerogel resembles to the behavior of a semiconductor-metal junction and that of PMDIG-PANI xerogel exhibits a signature of rectification property. A dye-sensitized solar cell is also fabricated using the PMDIG-PANI gel with a power conversion efficiency of 0.1 %.



References:

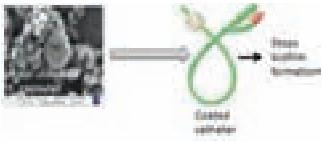
[1] Anilkumar,P.; Jayakannan, M. J. Phys. Chem. B **2010**, 114, 728-736.
[2] Li, C.; Hatano,T.; Takeuchi, M.; Shinkai, S. Chem.Comm. **2004**, 2350-2351.
[3] Chakraborty, P.; Bairi, P.; Roy, B.; Nandi, A. K. ACS Appl. Mater. Interfaces **2014**, 6, 3615–3622.
[4] Bairi, P.; Chakraborty, P.; Shit, A.; Mondal , S.; Roy, B.; Nandi, A. K. Langmuir **2014**, 30, 7547–7555 .

Self-assembled capsules from telechelic poly N-glycidyl histidine ether-tannic acid complex for inhibition of bio-film formation in urinary catheter

Denial Mahata[1], Santi M. Mandal[2], Amit Basak[3], Golok B. Nando[1]*
[1]Department of Rubber Technology Centre,
[2]Central Research Facility, Indian Institute of Technology Kharagpur,
Kharagpur, 721302, India

Indwelling catheter is the major cause of catheter-associated urinary tract nosocomial infections. Infections are very common due to rapid microbial adhesion and subsequent biofilms formation on device. Therefore, strategies to prevent urinary tract infections are in great demand in recent years. In this presentation, a hydrophilic biocompatible telechelic polymer, N-glycidyl histidine ether (GHEP) was synthesized by the ring opening polymerization and prepared composite with tannic acid to form GHEP-TA complex. The self-assembled product of GHEP-TA complex form a unique toroidal like capsules which coated on natural rubber latex urinary catheter. The self-assembled capsules were characterized by UV-Visble, fourier transformed infrared (FTIR), 1HNMR and dynamic light scattering (DLS) analyses. The surface morphology of coated catheter was characterized by field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) and contact angle measurements. Biofilm forming ability of common UTI pathogen, E. coli was tested in vitro. Results revealed the significant reduction of the association of urinary pathogens on the capsules coated catheter. Thus, coated catheter is an effective to long-term use and hindered catheter-associated infection.

Figure:



References:

[1] Bhunia, H. P.; Nando, G. B.; Basak, A.; Lenka S.; Nayak. P. L. Eur. Polym. J., **1999**, 35, 1713-1722.

[2] Mahata, D.; Mandal, S.M.; Nando G. B.; RSC Advances **2014**, 4, 48559-48562.

[3] Samanta, T.; Roymahapatra, G.; Porto, W.F., Franco, O.L.; Dinda, J.; Mandal, S.M. PLoS One, **2013**, 8, e58346.

Nanostructure formation of Donor-Acceptor, P4VP Complex *via* Template Hydrogen Bonding

B. Saibal[a], S. K. Asha*[a]
[(a)]Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Pune 411008, India
sk.asha@ncl.res.in

Nanostructuredself-assemblyof donor-acceptor materialsare highly desirable in the field of organic photovoltaics.Small molecule organic semiconducting materials have many advantages over their polymeric analogues, like crystallinity, high purity etc. However, it is a challenge to solution process and to fabricate them into films due to their strong tendency to crystallize. From this point of view, polymers are easily solution processable. Tailor made semiconducting polymeric materials with appropriate design can form a well ordered long range nano organization with high processability as well as high crystallinity which is the ideal requirement for organic photovoltaic device. It is a nontrivial task to transform a polymeric donor-acceptor system into a nanostructured assembly.In this present work we have assembled donor and acceptor materials randomly with P4VP back bone to obtain self-organized nano structure in the range of < 10 nm with increased donor acceptor interface. This challenging task was achieved by design of tailor made donor and acceptor molecules capable of H-bonding interaction with nitrogen atom of the P4VP backbone. Oligo(*p*-phenylenevinylene) based donor was synthesized with one cyanide (-CN) group on one side and hydroxyl (-OH) group at the other termini (Short name **OPVCN-OH**). Acceptor based on unsymmetrical perylene bisimide was developed with 2-ethylhexyl alkyl chain on one side and pentadesyl unit with free –OH group at the other termini (Short name **UPBI-OH**).[2]Supramolecular nano structure of P4VP and donor-acceptor molecules were made with the help of noncovalent H-bonding and π-π interaction. Complex formation was confirmed by FT-IR and ^{1}H NMR spectroscopy. Solid state supramolecular structural characterization was done by small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WXRD) experiment. Transmission electron microscopy (TEM) was used to determine thin film morphology of all different supramolecular complexes of P4VP polymer. TEM morphology showed nice lamellar arrangement in the range< 10 nm. Absorption and fluorescence spectroscopy studies showed the effect of self-assembly on energy transfer between donor and acceptor molecule complexed with P4VP. Effect of self-organization of donor acceptor assembly on bulk mobility was measured via SCLC method.

References:

[1] B. Saibal.; A. Z. Ashar.; N. R. Devi.; K. S. Narayan.; S. K. Asha.ACS Appl. Mater. Interfaces**DOI: 10.1021/am5055542**.

[2] RekhaNarayan , Prashant Kumar , K. S. Narayan , and S. K. Asha. Adv. Funct. Mater**2013**, 23, 2033–2043.

[3] Asha Syamakumari, Rekha Narayan, ShekharShinde, Saibal Bhaumik. Patent Publication number **WO2013128475 A1**.

Thermally Induced Structural Changes in the Co-crystal formed by Poly(L-lactic acid) and Cyclopentanone

P. Shaiju[1], N. Sanjeeva Murthy[2] and E. Bhoje Gowd[1]*
[1]Materials Science and Technology Division, CSIR - National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India
[2]New Jersey Center for Biomaterials, Rutgers University,
The StateUniversity of New Jersey, Piscataway, NJ, USA.
*bhojegowd@niist.res.in

Poly(L-lactic acid) (PLLA) shows different crystalline forms such as α, α′ (δ), α″, β, and γ forms, depending on the experimental conditions used for the preparation. Recently,Marubayashi et al. reported the formation of co- crystals of PLLA, which they referred to as "ε"form, in presence of certain solvents at subambient temperatures. In the present work,structural changes occur upon the heating PLLA/cyclopentanone (CPO) co-crystals were analysed using variable temperature wide-angle and small-angleX-ray scattering (WAXS/SAXS), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) techniques. It has been found that the ε form transformed to the α form in a broad temperature range at around 50°C. During the phase transition, CPO moleculesresiding in the crystal lattice of the ε form leave the lattice and occupy the amorphous region transiently. On further heating, CPO evaporates from the amorphous region at its boiling temperature.In the small angle X-ray scattering (SAXS) measurements,the diffuse pattern (pickaxe shaped)was observed at lower temperatures and this could bedue tothe presence of solvent molecules in the crystal lattice. On heating, the diffuse pattern disappeared and a well-defined two point pattern appeared indicating the ε –to-α transition. On further heating, CPO molecules, which arenow in the amorphous phase facilitate the enhancement in the order of the αform.

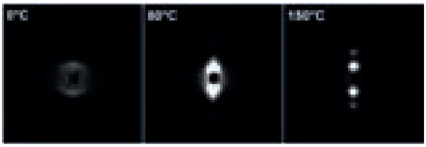


Figure: 2D SAXS patterns showing the structural changes of ε-form at different temperatures.

References:
[1] Marubayashi, H.; Asai, S.; Sumita, M. Macromolecules **2012**, 45, 1384–1397.
[2] Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. A.Prog.Polym. Sci.**2012**,37, 1657– 1677.

Non-covalent Side Chain Self-assembly Approach to Achieve Ideal Donor-Acceptor Morphology in the Active Layer of OPVs

Shekhar Shinde[1] and S. K. Asha[1*]
[1]Polymer Science and Engineering Division, CSIR-NCL, Pune- 411 008, India
[1]sk.asha@ncl.res.in*

Among all various fundamental processes of photoinduced charge generation in an organic photovoltaic cell (OPV), the step of exciton diffusion towards the donor-acceptor interface is very crucial to the device performance. The electron-hole pair is coulombically bound with the exciton binding energy. To overcome the exciton binding energy, donor and acceptor should be assembled in a way to provide interface in 10-20 nm scale range, so that charges can separate. Currently, many OPV devices are based on the blending of donor and acceptor materials. However, the unrestrained and microscale phase separation of the simple blends cannot provide optimized performance of the devices. Different types of non-covalent interactions which form the basis of supramolecular interactions are also extensively utilized to achieve donor-acceptor assembly in the nanoscale range. Among all of these secondary interactions, π-π stacking and hydrogen bonding are two secondary interactions that play an important role in the self assembly of pi-conjugated materials.

The current work describes non-covalent side chain polymer architecture to attain donor-acceptor self-assembly. A donor polymer backbone made up of segmented Poly(OPV-HEG), possessing carboxylic acid as pendent functionality was developed. Acceptor based on perylene di-imide small molecule possessing pyridine moiety on either one or both sides of perylene core was developed. The complex between donor polymer and acceptor small molecule was prepared by varying molar ratio according to number of repeating units of OPV segment bearing carboxylic acid functionality. The hydrogen bond formation was confirmed by using NMR and IR studies. TEM analysis was used to observe the nanoscale self assembly of the complex. The photophysical behavior of the resultant donor-acceptor complex was studied by using absorption and fluorescence spectroscopic technique. The packing parameter were obtained by using W-XRD technique. Thus, non-covalent side chain polymer approach was adopted to bring donor-acceptor close to each other in the nanometer length scale with better self assembled morphology.

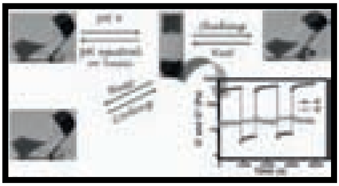
References

[1] Beijer, F. H.; Sijbesma, R. P.; Kooijman, H. A.; Speck, L.; Meijer, E. W.; J. Am. Chem. Soc. **1998,** 120, 6761-6769.

Thixotropic Supramolecular Hydrogel of Adenine and Riboflavin-5′-Phosphate Sodium Salt Showing Enhanced Fluorescence Property

Sujoy Das, Priyadarshi Chakraborty, Partha Bairi and Arun K. Nandi
Polymer Science Unit, Indian Association for the cultivation of Science,
Jadavpur, Kolkata-700 032, India

An equimolar mixture of riboflavin-5′-phosphate sodium salt (**RP**) and adenine (**AD**) dissolved in a phosphate buffer (pH 4.0; 1.0 % w/v) produces a red coloured transparent thixotropic hydrogel at 30 ^{0}C. FTIR spectra and WAXS patterns indicate self assembly via H-bonding between >C=O group of RP and amino / imino group of **AD** followed by supramolecular organization through a π-stacking process producing the fibrillar network structure. FESEM images clearly indicate that the nanofibres are produced from the intertwining of helical fibrils. The Uv-vis spectra indicate a red shift of π -π^* transition band of **RP** in the **RPAD** xerogel. On excitation of the **RPAD** hydrogel at 373 nm it shows twelve times enhancement of emission intensity with a 7 nm red shift of emission peak. This has been attributed to the enhancement of lifetime from 2.2 ns in **RP** to 3.4 ns in **RPAD** hydrogel. With increase of temperature, the fluorescence intensity of the **RPAD** hydogel at first increases till 40 ^{0}C, then decreases up to 55 ^{0}C and it again increases after 60 ^{0}C. The dynamic frequency sweep experiment of the supramolecular gel at a constant strain of 1% exhibits a wide linear viscoelastic region and a considerable higher G' value (460 Pa) than that of G'' (21 Pa) confirming the gel nature of **RPAD** system. The hydrogel shows high stiffness (G' / G'' = 3.3), a high yield stress (σ^*) (79.5 Pa) and a moderate critical strain γ(= 17.5 %). Time sweep experiment at both low (0.1 %) and high strain (100 %) indicate thixotropic property of the gel. **RPAD** hydrogel shows non-Newtonian viscosity at the shear rate region (0.1 -158 s^{-1}) and after that there is a sudden fall of viscosity.



References:

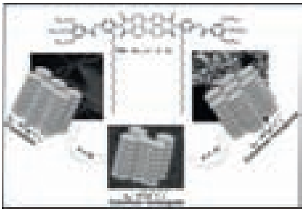
[1] Manna, S.; Saha, A.; Nandi, A.K. Chem. Commun., 2006, 4285–4287

[2] Bairi, P.; Chakraborty, P.; Mondal, S,; Roy, B.; Nandi, A.K. Soft Matter., 2014, 10, 5114–5120

3,4,5-Trialkoxy Gallate esters of Pentadecylphenol Functionalized Perylenebisimides: Liquid Crystalline Packing and SCLC Mobility

K. P. Prajitha, S. Chithiravel, K. Krishnamoorthy, S. K. Asha[1]*
[1]Polymer Science and Engineering Division, CSIR-NCL, Pune- 411 008, India
sk.asha@ncl.res.in

Perylene bisimides (PBI) are n-type semiconducting mesogens with high photo stability and high absorption coefficient in the visible region, making them a viable alternative for the fullerene derivatives in photovoltaics. The rigid structures of the PBI core with flexible alkyl chains at the imide position render the necessary structural requirements for inducing liquid crystallinity. For device application, the main requirement is the attainment of mesogenicity in a temperature range that is adaptable on a device substrate, with low clearing temperatures. Here we present a homologous series of pentadecyl phenol functionalized perylenebisimide terminated with trialkoxy gallate esters with the terminal alkyl chain length varied from n = 4 to 12 (PBI-En; n: 4-12).The higher members of the series with n > 8 exhibited thermotropic liquid crystalline phase that remained stable until room temperature. An odd-even oscillation was observed in the melting as well as isotropization enthalpies as a function of alkyl spacer length in the terminal gallate unit with the even spacers exhibiting higher values. The thermotropic LC phases were identified to be columnar rectangular and columnar hexagonal based on analysis of the WXRD pattern recorded in the LC phases. The columnar hexagonal phase exhibited a mobility value one order (10^{-3} cm^2 V^{-1} s^{-1}) higher than that of crystalline (10^{-4} cm^2 V^{-1} s^{-1}) and two orders higher than that of columnar rectangular phase (10^{-5} cm^2 V^{-1} s^{-1}). This study highlights the importance of molecular structural factors that are to be taken into consideration while designing materials for better charge transport.



References:
[1] Bhavsar, G. A.; Asha, S. K.; Chem. Eur. J. **2011**, 17, 12646-12658.
[2] Imrie, C. T.; Henderson, P. A.; Chem. Soc. Rev. **2007**, 36, 2096–2124.
[3] Prajitha, K.P.; Chithiravel, S.; Krishnamoorthy, K.; Asha, S. K. J. Mater. Chem. C, **2014**, DOI: 10.1039/C4TC01806K

Supramolecular Assembly of a Core-Substituted Naphthalene-Diimide (cNDI) Derivative and Impact on Excited State Dynamics

Haridas Kar, [a] Dominik W. Gehrig, [b] Frédéric Laquai*[b], Suhrit Ghosh*[a]
[a] Mr. Haridas Kar and Dr. Suhrit Ghosh ; Polymer Science Unit ; Indian Association for the Cultivation of Science; 2A & 2B Raja S. C. Mullick Road, Kolkata, India-700032
[b] Mr. Dominik W. Gehrig and Dr. Frédéric Laquai ; Max Planck Research Group for Organic Optoelectronics ; Max Planck Institute for Polymer Research
Ackermannweg 10, D-55128 Mainz, Germany
psusg2@iacs.res.in

Core-substituted NDI derivatives have gained significant attention in the recent past owing to their versatile photophysical and redox properties. However, unlike the parent NDIs, their core substituted derivatives have hardly been explored as a building block for supramolecular assembly which we envisaged would be of diverse interest in the arena of supramolecular materials for organic electronics. In the recent past we have studied self-assembly and photophysical properties of an amide functionalized amine-substituted NDI (cNDI-1). In aliphatic hydrocarbon solvents, it spontaneously assembles owing to H-bonding among the amide groups. Solvent dependent spectroscopic studies reveal a significant bathochromic shift of the absorption bands in hydrocarbons compared to $CHCl_3$ or THF indicating J-aggregation. This is further verified by appearance of sharp emission bands with small Stoke's shift holding mirror-image symmetry with the absorption bands in aggregated state. At higher concentration J-aggregation leads to macroscopic gelation, efficacy of which is found to be strongly dependent surprisingly on "structure" of the solvents and not the polarity which is counter-intuitive considering the self-assembly is driven by H-bonding. Based on several spectroscopic, microscopic and rheological studies, it is postulated that J-aggregation in all tested hydrocarbons initially lead to vesicle like spherical structures which in cyclic solvents remain unchanged for ever. However in linear hydrocarbons intercalation of the solvent molecules with the peripheral alkyl chains lead to cross-linking and morphology transition from vesicle to fibre producing macroscopic gel, rate of formation and strength of which are proportional to the length of the solvent chain as that determines the intercalation efficiency. Transient absorption spectroscopy reveals fast electron transfer in sub-ps time scale and remarkable prolongation of the life time (by more than one order of magnitude) of the charge-separated state as a result of J-aggregation which is highly desirable in light harvesting and photocatalysis. These findings will be elaborated in this presentation.

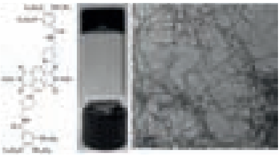
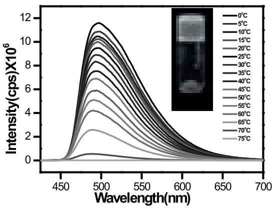


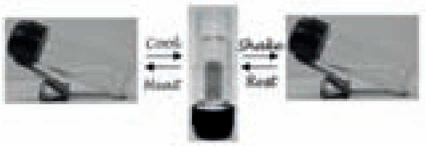
Fig 1: Structure of **cNDI-1** (left), gel image (c= 4.0mM) in decane (middle) and TEM image of the diluted gel (right)

Thixotropic, Fluorescent Organogel based on poly(alkyl aryl ether): Tuning of fluorescence property by Temperature and UV - irradiation

Sanjoy Mondal, Priyadarshi Chakraborty, Partha Bairi, and Arun K. Nandi
Polymer Science Unit
Indian Association for the cultivation of Science, Kolkata, India
psuakn@iacs.res.in

A low molecular weight gelator based on poly(alkyl aryl ether) has been synthesized and characterized by NMR, MALDI-TOF and FT-IR spectroscopic techniques. The gelation of the compound has been examined in a variety of polar and non- polar organic solvents. The morphology of xerogel of this compound has been investigated by scanning electron microscopy (SEM). The present system forms entangled fiber like morphology in methyl cyclohexane. The gel is highly fluorescent and the fluorescence intensity is enhanced in the gel state from that of the solution. The fluorescence intensity of the gel is also temperature dependent and it decreases with increasing temperature. Fluorescence property of the gel can be tuned by UV irradiation and the fluorescence intensity gradually decreases with increasing irradiation time. The organogel exhibits good mechanical properties and it also exhibits the exceptional property of thixotropy i.e. the gel reforms after breaking under mechanical forces. The thixotropic property is more prominent in non polar aliphatic solvents like methyl cyclohexane, cyclohexane and hexane.





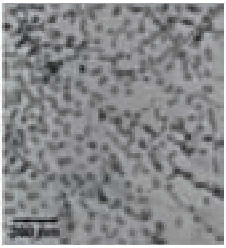
References:

[1] Rajamalli, P.; Prasad, E. Org. Lett. 2011, *1*3, 3714–3717.
[2] Rajamalli, P.; Prasad, E. Langmuir. 2013, 29, 1609–1617.

Deposition of TiO_2 nanoparticles on SWNTs via a self assembled PS-b-P4VP diblock copolymer template

Himadri Acharya
Centre for Soft Matters, Department of Chemistry, Assam University, Silchar-788011
**himadriau@yahoo.co.in*

TiO_2 nanoparticles decorated carbon nanotubes were synthesized by uniform dispersion of single wall carbon nanotube (SWNTs) in the self assembled diblock copolymer micelles followed by sol-gel synthesis. Well ordered TiO_2 nanoparticles were fabricated on the solid substrate through self assembly of poly(styrene)-block-poly(4-vinylpyridine) (PS-b-P4VP) and Ti-precursors (Titanium isopropoxide in isopropanol and toluene) by simple spin coating method. Thermal annealing at 6000C in air removes both blocks of the polymers from the substrate and results in well ordered arrays of TiO_2 nanoparticles and TiO_2 nanoparticles deposited SWNT. TEM and AFM shows the uniform dispersion of Ti-precursor embedded block copolymer micelle with the volume fraction ranging from 5-50%. The incorporation of single walled carbon nanotube (SWNT) during the formation of TiO_2 nanoparticles on substrate further leads to SWNT-TiO_2 nanocomposite arrays, which is promising for high performance thin film transistor and photovoltaic devices.



References:

[1] Bockstaller, M. R.; Mickiewicz, R. A.; Thomas, E. L. Adv. Mater. **2005**, 17, 1331 –1349.
[2] Hamley, I. W. Prog. Polym. Sci**. 2009**, 34, 1161–1210.
[3] Kim, H-C.; Park, S-M.; Hinsberg, W. D.; Chem. Rev. **2010**, 110, 146–177.
[4] Cano, L.; Gutierrez, J.; Tercjak, A. J. Phys. Chem. C **2013**, 117, 1151–1156.

Syntheses and characterization of novel ABA-type pendant benzoic acid containing tri-block copolymers and their applications

T. Rajasekhar, V. Santosh, A. Tejaswini, A. V. Sesha Sainath*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India
E mail: avss@iict.res.in

Block copolymers are playing a vital role in polymer science and technology due to their micro-phase separation / self-assembly nature in bulk and solution, which is the important possession as a base to develop various technologies such as nanolithography, templating, membranes, solar cell, holograph and medicinal applications. In recent years, many researchers have focused on well-defined polymers synthesis by employing various polymerization methods which include controlled and living polymerization methods. We hereby report novel ABA-type tri-block copolymers having acrylate containing pendant carboxylic acid segments (as 'A' blocks) from the initiation of telechelic polystyrene (as 'B' block) by reversible addition-fragmentation chain transfer process. The resulted tri-block copolymers were characterized to investigate the formation of vesicles /nano-particles in THF/water mixture, liquid crystalline properties after complexation with hydrogen bonding and their performance in fabrication of membrane in enhancing the antifouling properties are going to present.

Tri-block copolymer/poly(vinylidene fluoride) (PVDF) blend ultrafiltration membranes were fabricated on a non-woven fabric. The blend membranes exhibited higher flux, higher molecular weight cut off values and better fouling resistance than that of neat PVDF membrane. We achieved 2.5 times higher water flux while maintaining the ~99% oil rejection from the feed of engine oil-water emulsion containing 1000 ppm oil in water compared to the neat PVDF membrane.

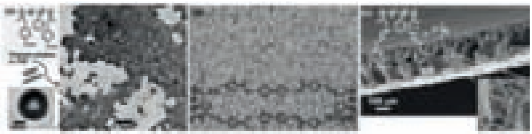


Figure 1. Tri-block copolymer functions (a) vesicles by self-assembly in THF and water mixture, (b) polarized optical micrograph of smectic texture of tri-block copolymer complex at 150 °C and (c) fabricated ultrafiltration blend membrane cross section.

Acknowledgment: Authors thank Dr. A. V. R. Reddy, CSIR-CSMCRI, Bhavnagar for membrane studies.

Stimuli Induced Host-Guest Complexation of a PEG Amphiphile in Aqueous Medium

VijayaGowri A[1], Nabanita Sadhukhan[1]*, S. N. Jaisankar[1], and A. B. Mandal[2]*
[1]Polymer Division, CSIR-Central Leather Research Laboratory,
Adyar, Chennai – 600 020, India
[2]Chemical Laboratory, CSIR-Central Leather Research Laboratory,
Adyar, Chennai – 600 020, India
*Email: nnsadhukhan@gmail.com

Stimuli-responsive host-guest inclusion complexes have attracted much interest due to their application in the wide range of fields of materials sciences, structural biology and pharmaceutical chemistry, namely as memory storage, smart supramolecular polymers, drug delivery systems, sensors, and functional nano devices. In biological system, cell membranes adopt to their surroundings continuously by undergoing reversible structural changes in response to external stimulus. Motivating by such biological phenomena, we have designed a water-soluble, stimulus-responsive short Poly(ethylene glycol) (PEG) amphiphile. The stimulus-responsive PEG amphiphile underwent conformational change in response to the external stimulus and could form inclusion complex with α-Cyclodextrin (α-CD) aqueous medium. The stimulus responsive inclusion and exclusion reactions of PEG amphiphiles with α-CDin aqueous medium were investigated. The synthetic methodology of PEG amphiphile and detailed investigation of stimuli induced host-guest complexationwith α-CD by ^{1}H NMR, and UV-visible spectroscopic methods are presented.

Thermoreversible gelation in Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer by arrested phase separation

Prashant A. Patil[1], Ashish K. Lele[1*] and Jyoti P. Jog[2].
[1] Complex Fluid and Polymer Engineering Group, Polymers and Advanced Materials Laboratory, CSIR-National Chemical Laboratory, Pune, India.
[2] Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune, India
*ak.lele@ncl.res.in

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biopolymer solutions in chlorobenzene show thermoreversible sol-gel transition. Solutions of various concentrations of this polymer were prepared in chlorobenzene. The isothermal and non-isothermal gelation kinetics at various supercoolings were probed using rheology. An incipient gelation stage (I) was studied using consecutive frequency sweep experiments and analyzed by Winter-Chambon criteria for gel point detection[1]. The second rapid gelation stage (II) of isothermal and nonisothermal gelation was analyzed using a rheology equivalent of Avrami and modified Avrami equations respectively. The Avrami exponent of 3-4 obtained experimentally suggests three dimensional growth of the network formed during gelation. Small amplitude oscillatory temperature sweep rheological experiment shows hysteresis similar to first order transition crystallization. In creep experiment during sol-gel transition, instrument inertia coupled with gel network elasticity shows viscoelastic ringing (creep ringing) like damped oscillations. Late stage creep ringing data fitted to single mode Jeffrey and Kelvin-Voigt model.

Reference:

1. Natalia V. Pogodina and H. H. Winter, Macromolecules, **1998**, 31, 8164-8172.

Composition Dependent Crystallization Behaviour of Double Crystalline Diblock Copolymer

Chitrita Kundu* and Ashok Kumar Das Mahapatra
Department of Chemical Engineering, IIT Guwahati, Assam
**c.kundu@iitg.ernet.in*

The molecular architecture of diblock copolymer is usually manipulated by adjusting the constituent blocks as it exhibitsself-assembled microdomain characteristic [1]. Diblock copolymer which consists of two chemically distinct repeat units manifests a rich variety of morphologies including lamellar, spherical or cylindrical microstructures over a wide range of block composition [2].Usually the block with higher melting point crystallizes first followed by the second block having lower melting point introducing sequential crystallization within diblock copolymer [3]. During crystallization, first crystallizing block creates confinement for the crystallization of second block. As a result, the crystallization of second block slows down with the formation of less crystalline materials[3-5]. Therefore an intense study associated with the crystallization behaviour of diblock copolymer is inevitable as the system having competitive crystallization along with microphase separation which dictates the final crystal morphology.

We investigate the crystallization behaviour of A-B diblock copolymer by varying the relativeblock length of B forweak and strong segregation strength between the blocks. In weak segregationlimit, the increment of the composition of B-block ensures theenhancement of crystallization temperature of B-block accompanying with higher crystallinity. On the other side, there is a small depression in crystallization temperature of A-block along with the formation of thicker and larger crystallites with the enhanced B-block composition. We attribute this non-intuitive crystallization trend to the dilution effect imposed by B-block. When the composition of the B-block is high enough, it acts like a “solvent” during the crystallization of A-block. A-block segments are more mobile and hence less facile to crystallize, resultingdepression in crystallization temperature. At strong segregationlimit, crystallization behaviour and morphological development are driven by the confinement effect, ratherthan block composition.

Acknowledgement: SERB-DST for research funding.

References:

[1] Darling, S. B. Prog.Polym. Sci. **2007**, 32, 1152 – 1204.
[2] Bates, F. S.; Fredrickson, G. H. Phys. Today**1999**, 52, 32-38.
[3] Sun, L.; Liu, Y.; Zhu, L; Hsiao, B. S.; Avila-Orta, C. A. Polymer**2004**, 45, 8181-8193.
[4] Nojima, S.; Akutsu, Y.; Washino, A.; Tanimoto, S. Polymer **2004**, 45, 7317 – 7324.
[5] Nojima, S.; Akutsu, Y.;Akabo, M; Tanimoto, S. Polymer **2005**, 46, 4060 – 4067.

Cellulose based Smart Hydrogel for cationic dye separation technology

Arpita Mandal and Debabrata Chakrabarty*
Department of Polymer Science and Technology, CU, Kolkata
**chakrabarty_deb@yahoo.com*

A pH sensitive smart hydrogel based on HEMA [1], MAA and cellulose [2] have been synthesized by using different comonomer ratio with MBA as a cross linker and KPS,NaHSO3 as initiator. The hydrogel are characterized in term of swelling-deswelling study, morphology and dye absorption investigation. Swelling is carried out in different solutions such as in different concentration of salt solution, different values of pH and various dye concentration. It is also studied in various metalion.

It is observed that swelling of the hydrogel is dependent on the pH and ionic strength of the medium. It also depends on the cationic size of the salt used in swelling medium.

The hydrogels are found to be efficient in the removal of cationic textile dyes from aqueous solution and it is effective in heavy metal ion separation from the aqueous solution as well.

References:

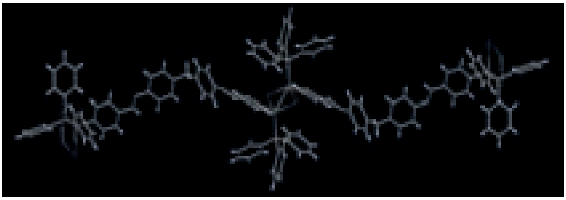
[1] Kulygin, Olga, and Michael S. Silverstein. "Porous poly (2-hydroxyethyl methacrylate) hydrogels synthesized within high internal phase emulsions."Soft Matter 3, no. 12 (2007): 1525-1529.

[2] Sannino, Alessandro, Christian Demitri, and Marta Madaghiele. "Biodegradable cellulose-based hydrogels: design and applications." Materials 2, no. 2 (2009): 353-373.2

Synthesis, structural characterization and catalytic activity of a copper(I)coordination polymer with novel pyridine-imine-phosphine ligand

Anupam Ghorai, Jahangir Mondal and Goutam K Patra*
Department of Chemistry Guru Ghasidas Vishwavidyalaya, Bilaspur (C.G.)
*patra29in@yahoo.co.in

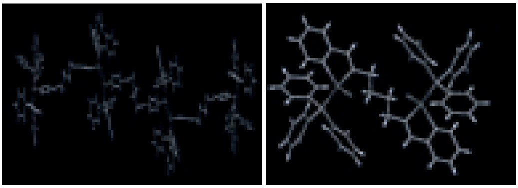
A copper(I) complex $[Cu^{I}_{2}(\mu\text{-}I)_{2}(L)(PPh3)_{2}]_{n}$(1) has been synthesized by reaction of a bidentateimino-pyridyl ligandL with copper(I) iodide and PPh_3 in 1:1:2 proportion. The ligand Lchelates two copper(I) atoms with its two peripheral pyridyl nitrogen atoms resulting a dinuclear complex of two copper centres bridged by two iodine atoms. Single crystal structure of the copper complex reveals that each copper center in the complex is surrounded by two bridged iodine atoms, one nitrogen donor site of the ligand and one phosphorous donor from triphenylphosphine moiety forming a distorted tetrahedral geometry. The potential applications of this complex as catalyst in synthesis of 1,3-benzoxazole and its derivatives have also been studied.



Solid state supramolecularcopper(I) halide complexes of imino-pyridyl ligands and triphenylposphineas co- ligand

Jahangir Mondal, Anupam Ghorai and Goutam K Patra*
Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Bilaspur (C.G.)
*patra29in@yahoo.co.in

Two copper(I) complexes $[Cu^{I}_{6}(\mu\text{-}I)_4I_2(L^1)_3(PPh_3)_8]$(1) and $[Cu^{I}_{2}Br_2(L^2)(PPh_3)_2]$(2), have been prepared by reactions of two bis(schiff base) imino-pyridylligands L^1 and $L^2$with PPh_3 and copper(I) halides respectively. $[Cu^{I}_{6}(\mu\text{-}I)_4I_2(L^1)_3(PPh_3)_8]$(1) is hexanuclear, whereas $[Cu^{I}_{2}Br_2(L^2)(PPh_3)_2]$(2) is only dinuclear.In 1, the ligand L^1chelates two copper(I) atoms with the two peripheral pyridyl nitrogen atomswhilein 2, the ligand L^2 chelates two copper(I) atoms using both imino nitrogen atoms and pyridyl nitrogen atoms. All theCu(I) ions both in 1 and 2, possess tetrahedral coordination environment. The metal–organic frameworks 1 and 2 show strong photoluminescence property at room temperature in chloroform solution. The emission spectra show blue shifts in comparison to the free ligands.

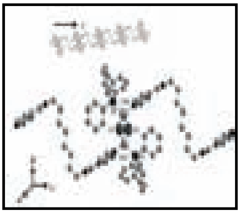


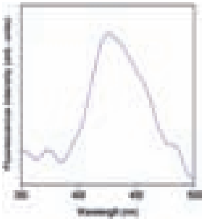
12

Photoluminescent Cu(I) coordination Polymers tailored by copper(I) halides, novel iminopyridylschiff bases and triphenylphosphine

Goutam K Patra* and Pankaj K Pal
Department of Chemistry Guru Ghasidas Vishwavidyalaya, Bilaspur (C.G.)
*patra29in@yahoo.co.in

Four photoluminescent copper(I) coordination polymers, $[Cu^{I}_{2}(\mu\text{-}Br)_{2}(L^{1})2(PPh_{3})_{2}]n$ (1), $[Cu^{I}_{2}(\mu\text{-}I)_{2}(L^{2})_{2}(PPh_{3})_{2}]n$ (2), $[Cu^{I}_{2}(\mu\text{-}Br)_{2}(L^{3})_{2}(PPh_{3})_{2}]n$ (3), and $[Cu(\mu\text{-}I)(L^{4})]_{n}$ (4), have been prepared by reactions of imino-pyridylbis(schiff base) ligands L^1, L^2, L^3 and L^4 with PPh_3 and copper(I) halides. We utilize the self-assembling behaviour of Cu^+ and I^- into a robust Cu_2I_2 - SBU unit in the designing of Cu(I) coordination polymers with the imino-pyridine based ligands. In all coordination polymers Cu(I) centres adopt tetrahedral coordination. Complexes 1–4 exhibit photoluminescence both in the solid state and in solution at room temperature. The emission has been attributed to be intra-ligand p–p* transition mixed with MLCT characters. The complexes are of very high thermal stability.





References:

[1] X.M. Zhang, R.Q. Fang, Inorg. Chem. **2005**, 44,3955.
[2] J.K. Kim, M.K. Hong, J.H. Ahn, M. Lee, Angew. Chem. Int. Ed. **2005**,44, 328.
[3] H.T. Zhang, Y. Song, Y.X. Li, J.L.Zuo, S. Gao, X.Z. You, Eur. J.Inorg.Chem.**2005**, 766.
[4] M. Elhabiri, J. Hamacek, J.C.G. Bu¨ nzli, A.M.A. Gary, Eur. J. Inorg.Chem.**2004**, 51.

Fabrication of Non Hexagonal Closed Pack array of Colloidal particles on a Flat Substrate by Template guided self assembly and transfer

Meneka Banik[1] and Rabibrata Mukherjee[1]
1Instability and soft patterning laboratory, Department of Chemical Engineering,
Indian Institute of Technology Kharagpur, Kharagpur – 721302, India

We present a controlled method for obtaining hexagonal close packed (HCP) ordered monolayer of polystyrene colloidal particles on flat substrates as well as isotropic and anisotropic topographically pattered substrates. Self organization of colloidal particles has many applications, particularly in fabrication of solar cells with advanced light management strategies. We have created two dimensional colloidal crystals with monodisperse polystyrene colloidal particles by simple spin coating technique. Appropriate amounts of surfactant molecules are added to the colloidal dispersion ahead of spin coating to ensure the formation of the HCP patterns. Parameters like coating speed, dilution of the colloids, amount of surfactant added and volume dispensed provide a control over the formation of HCP as well as the number of layers deposited.

Apart from obtaining HCP structures, we have also been working on obtaining ordered colloidal particle arrays with different geometric arrangements. For this purpose, we spin coat the particles onto a topographically patterned substrate, which are fabricated inhouse by soft lithography based techniques. The colloidal particles when spin coated on the patterned substrates, orient as per the confinement and we obtain particle array with non-HCP ordering. We have also attempted to transfer the particle array once they are formed on a flat template. Two techniques have been developed for facilitating this transfer mechanism. By the first technique, a flexible elastomeric substrate of Sylgard 184 is swelled by chloroform exposure and is then brought in conformal contact with the substrate to which the array is to be transferred. Whereas, in the second technique a PMMA layer containing the ordered arrangement of the colloidal particles is degraded by UV exposure. Under this condition, the particles detach themselves from the template and adhere to the target substrate. This allows the colloidal structures to be transported across substrates irrespective of their surface energy, wettability or morphology.

References

1. R. A. Weiss, X. Zhai, A.V. Dobrynin. Nanoparticle-Textured Surfaces from Spin Coating. *Langmuir* **2008**, 24:5218.
2. Nina V. Dziomkina, G. Julius Vancso. Colloidal crystal assembly on topologically patterned templates. *Soft Matter* **2005**, 1:265.
3. Peng Jiang, Tushar Prasad, Michael J. McFarland, Vicki L. Colvin. Two-dimensional nonclose-packed colloidal crystals formed by spincoating. *Applied Physics Letters* **2006**, 89:011908.

Supramolecular assembly of Poly(styrene)- b -poly(4 vinylpyridine) and Ferroceneacetic Acid: Fabrication of large scale periodic arrays of iron oxide nanometrials

Koomkoom Khawas, Pallavi Kumari and Biplab Kumar Kuila*
Center for Applied Chemistry, Central University of Jharkhand,
Brambe, Ranchi 835205, Jharkhand

Self-assembly of block copolymers (BCPs) or their supramoleculesin both bulk and thin film, has generated widespread research attention in the areas of nanoscienceand nanotechnology due to their formation of fascinating set of periodic structures in the nanoscopic length scale[1,2]. Block copolymer supramolecular assembly where a low molar mass additive is associated with one of the blocks by noncovalent interactions is a simple and powerful technique to introduce new functionalities into the block copolymer system as well as fine-tune its morphology [3]. Here, we have investigated a block copolymer supramolecular system consisting of polystyrene-b-poly (4-vinylpyridine) (PS-b-P4VP), and ferroceneacetic acid (FAA). The FAA molecules form supramolecules with PS-b-P4VP through H-bonding between the carboxylic acid group of FAA and pyridine ring of P4VP which is characterized by FTIR. The cylindrical microdomains created from PS-b-P4VP / FAA can be easily oriented normal or parallel to the substrate reversibly by annealing in different solvents. The differently oriented periodic microdomains created by PS-b-P4VP / FAA are easily converted to line or dot patterns of iron oxide nanomaterials by either plasma etching or pyrolysis. The crystal structure and magnetic properties of the iron oxide nanomaterials produced in this strategy was studied.

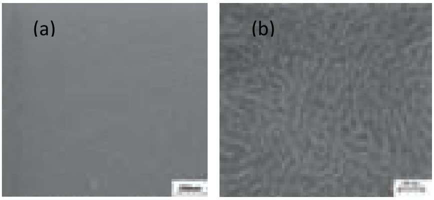


Fig.-1 SEM image of (a) dot (b) line pattern of iron oxide nanomaterials

References:.

[1] Ikkala, O. ten Brinke, G. Chem. Commun. **2004**, 2131.

[2] Kuila, B. K. Gowd, E. B. Stamm, M. Macromolecules **2010**,43, 7713.

[3] Sidorenko, A. Tokarev, I. Minko, S.; Stamm, M. J. Am.Chem. Soc. **2003**, 125, 12211.

Fabrication of one-dimensional conductive polymer nanowires using STM: A key step towards development of molecular devices

Swapan K. Mandal[1]*, Y. Okawa[2] and M. Aono[2]
1Department of Physics, Visva-Bharati, Santiniketan, India
2MANA, National Institute of Materials Science (NIMS), Tsukuba, Japan
*sk_mandal@hotmail.com

We demonstrate here a versatile technique to fabricate one-dimensional (1-D) conductive polymer nanowire at designated positions which is quite important towards fabrication of molecular devices. The process involves spontaneous chain polymerization initiated by a local single-molecule excitation using scanning tunneling microscope (STM) probe tip. The STM probe tip induced application of a certain voltage pulse to a self-assembled monolayer (SAM) of a diacetylene compound (DA; general formula R1–C≡C–C≡C–R2) where C≡C–C≡C is the diacetylene moiety, R1 and R2 are substituent groups) results the formation of polymer nanowire at designated positions. We have successfully carried out fabrication of conductive polydiacetylene (PDA; (=R1C–C≡C–CR2=)n) nanowires on both highly oriented pyrolytic graphite (HOPG) substrate and semiconducting MoS_2 substrates. We further demonstrate the connection of a single molecule and isolated metal nanocluster using such fabricated polymer nanowire. The data represents a key step for future advancement of molecular electronics as well as studying physics in 1-dimensional systems.

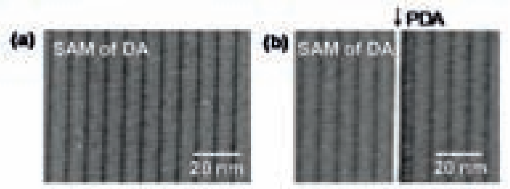


Figure 1. STM image of (a) a self-assembled monolayer (SAM) of a diacetylene (DA) compound, and (b) fabrication of a polymer nanowire using STM tip.

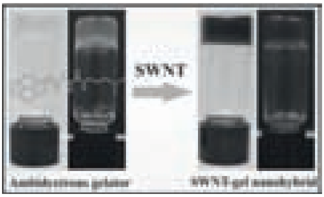
References:

[1] **Swapan K. Mandal**, Y. Okawa, T. Hasegawa and M. Aono, ACS Nano 2011, 5, 2779–2786.
[2] Y. Okawa, **Swapan K. Mandal** *et al*., J. Am. Chem. Soc. 2011, 133, 8227–8233.
[3] Y. Okawa, M. Akai-Kasaya, Y. Kuwahara, **S. K. Mandal** and M. Aono, Nanoscale 2012, 4, 3013–3028

Pyrene Containing Fluorescent Ambidextrous Gelator: Scaffold for Mechanically Robust SWNT-Gel Nanocomposite

Deep Mandal, Soumik Dinda and Prasanta K. Das*
Department of Biological Chemistry, Indian Association for the Cultivation of Science,
2A & B Raja S. C. Mullick Road, Jadavpur, Kolkata-700032
Email: subhabrata.maiti@gmail.com

Supramolecular gels are witnessing immense interest due to their potential applications in diversified area ranging from advance materials to biomedicine. With the rapid progression in the development of supramolecular soft materials, examples of low molecular weight gelators (LMWGs) with an ability to immobilize both water and organic solvents by the same structural scaffold is very limited and a challenging task. The present work reports the development of pyrene containing peptide based ambidextrous gelators (AG) having efficient capability of gelating both organic solvents and water. The organo and hydrogelation efficiencies of these gelators varied from 0.7-1.1 % w/v in various organic solvents and 0.5-5 % w/v in water at certain acidic pH (pH range = 2.0 to 4.0). For the first time these AGs have been utilized for preparing single walled carbon nanotube (SWNT) included soft nanocomposites both in hydro- and organogel matrix. A structure-property correlation study has been developed through a variation of the amino acids. The self-aggregation behavior of these thermoreversible gels was investigated through different spectroscopic and microscopic techniques such as circular dichroism (CD), FTIR, temperature dependent NMR, 2D NOESY experiments, luminescence spectroscopy, HRTEM, fluorescence microscopy and polarising optical microscopy (POM), which revealed that a balanced participation of hydrogen bonding, π-π stacking and van der Waals interactions as the driving force for gelation. Interestingly, these ambidextrous gels are intrinsically fluorescent which gets quenched upon inclusion of SWNT. Importantly, the rheological studies revealed that the inclusion of SWNTs within the ambidextrous gels improved the mechanical rigidity of the resulting soft-nanocomposites up to 3.8 fold compared to that of the native gels.



Reference: D. Mandal, T. Kar, and P. K. Das, *Chem. Eur. J.*, **2014**, *20*, 1349.

Reversible Bidirectional Shape Memory Effect in Polyurethane

Arpan Biswas and Pralay Maiti*
School of Material Science and Technology, IIT (BHU), Varanasi – 221005

Polyurethanes have been synthesised by using different diisocyanates and by varying the hard segment content (HSC). Stepwise self assembly has been observed from nano to microstructure through WAXS, SANS, AFM and POM of aliphatic polyurethane in comparison to aromatic polyurethane. Shape memory behaviour has been observed for different polyurethanes showing strong hard segment dependency. Aliphatic PU exhibit bidirectional reversible shape memory effect while aromatic PU does not show this behaviour. Temperature dependence structure property relationship has been worked out using POM and DSC showing direct connectivity between the shape memory effect with structural development in PU of varying constituents. A model has been proposed to explain the shape memory behaviour of novel polyurethanes. The morphological study at different temperature with polarising optical microscope (POM) and differential scanning calorimetric (DSC) study reveal that the rate of crystallisation in aromatic polyurethane is much slower than aliphatic polyurethane and the melting point of hard segment also increases with increase in hard segment content while it is not observed in aromatic polyurethane.

Micellar Disassembly of Dual-cleavable Stimuli-responsive Linear-Dendritic Block Copolymers

Nagendra Kalva and Ashootosh V. Ambade*
Polymer Science and Engineering Division, CSIR-National Chemical Laboratory,
Pune – 411008, India

Stimuli-responsive nanocarriers from amphiphilic polymers are promising for exerting control over release of payloads in drug delivery.[1,2] Light is an attractive stimulus due to its spatio-temporal control. Also, pH-degradable micelles have attracted interest because of the pH gradient present near cancer cells. It is important to develop polymeric nanocarriers equipped with a combination of different stimuli to achieve better control over drug release.[3]

Amphiphilic linear-dendritic block copolymers (LDBCs) offer several interesting features such as multivalent, perfectly branched dendron and chain entanglement of linear polymer. Stimuli-responsive LDBCs with pH or photo-cleavable units at the dendron periphery have been reported.[4,5] Introduction of cleavable linkages at the junction of hydrophobic and hydrophilic blocks is an interesting goal since application of stimulus leads to complete disintegration of the micellar assembly. We describe a dual stimuli-responsive LDBC with photo-cleavable *o*-nitrobenzyl group and pH-cleavable acetal linkage between the dendron and linear polymer. Self-assembly of the LDBCs in aqueous solution and subsequent stimuli-responsive disassembly was studied by UV-vis, fluorescence spectroscopy, dynamic light scattering (DLS) and TEM analysis.

References:

[1] Han, D.; Tong, X.; Zhao, Y. *Langmuir* **2012,** *28,* 2327-2331.
[2] Jin, Q.; Cai, T.; Han, H.; Haibo, W.; Wang, Y.; Ji, J. *Macromol. Rapid Commun.* **2014,** *35,* 1372–1378.
[3] Klaikherd, A.; Nagamani, C.; Thayumanavan, S. *J. Am. Chem. Soc.* **2009**, *131*, 4830–4838.
[4] Gillies, E. R.; Jonsson, T. B.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004,** *126*, 11936–11943.
[5] Sun, L.; Zhu, B.; Su, Y.; Dong, C.M. *Polym. Chem.* **2014,** *5,* 1605-1613.

Supramolecular Aggregate of Perylene and Melamine and its Sensitivity towards Cysteine and Homocysteine

Dines C. Santra, Arkapal Roy and Sudip Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science
2A and 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India
E-mail: psudcs@iacs.res.in

Fluorescent chemosensors based on "turn on" method have attracted much attention because of their high sensitivity and high potential in biological imaging. In contrast to covalent interaction, supramolecular aggregate formed through non-covalent interactions is considered to be powerful sensors. Perylene bisimide derivatives (PI) are important chromophores owing to their extensive use as pigments as a result of their high thermal stability and chemical inertness.[1] Because of their high quantum yield and excellent photostability, PI derivatives are also regarded as the best fluorophores for single molecular spectroscopy. However, most PIs which are insoluble in water due to the presence of large hydrophobic π conjugated ring, scarcely picked up for biological applications. Herein, supramolecular aggregates (PM) of PI with melamine (M) that have envisioned as a novel fluorescent probe for mercury ion, form selective complex (PMHg) with mercury ion at neutral medium (pH=7). This selective complex also exhibits high selectivity and sensitivity towards thiol-containing amino acids, and detects cysteine and homocysteine from healthy to abnormal levels under physiologically-relevant conditions.

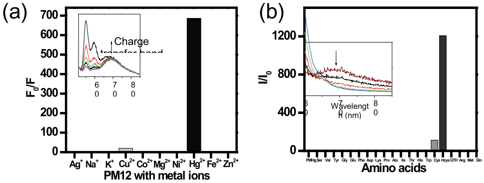


Fig.1. (a) Fluorescence spectra profiles of **PM12** (10 μM P) in HEPES buffer solution with various metal ions (20 μM). Inset spectra shows the gradual generation of charge transfer band. (b) Fluorescence responses of **PMHg** upon addition 100 equivalent of various amino acids and peptides. Inset spectra show the gradual decrease of charge transfer band.

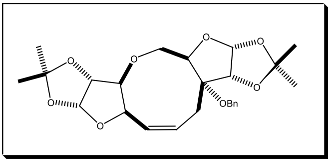
Reference

1. (a) F. Wurthner, *Chem. Commun.,* **2004**, 1564-1579; (b) H. Kaiser, J. Linder and H. Langhals, *Chem. Ber.,* **1991**, 124, 529; (c) K. Sugiyasu, N. Fujita and S. Shinkai, *Angew. Chem., Int. Ed.*, **2004**, 43, 1229–1233.

Ring Closing Metathesis, a tool for the synthesis of Chiral Macrocycles

Jhimli Sengupta
Department of Chemistry, West Bengal State University, Barasat, Kolkata-700126
E-mail address: jhimli_77@yahoo.co.in

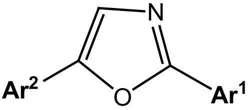
RCM is one of the most frequently used reactions for the synthesis of various sizes of cyclic compounds. Of the several catalysts developed for RCM, Grubbs first generation catalyst has remained the most user-friendly for the purpose. The corresponding second generation catalyst is more effective but more expensive. We have made dienes from pseudooligosaccharides and studied their RCM. One particular reason for such an interest is the possible synthesis of chiral medium-ring oxacycles by this approach.



Oxazole-based Dyes, Synthesis and to Study their Photophysical Properties

Suman Biswas*, Jyotirmay Maiti
Department of Chemistry, West Bengal State University. Kolkata-700126. West Bengal
su_man_b@yahoo.com

Oxazole, the five membered heterocyclic ring system has been known to the synthetic chemists well over a century. The presence of suitably substituted oxazole rings as building blocks of various cyclic and acyclic bio-active natural products[1] has drawn considerable interests of chemists of both synthetic and biological world. Recent advancements[2] have also shown that the oxazole ring systems, suitably substituted at its 2- and 5- positions, in synthetic dyes are emerging as novel class of compounds which possess interesting fluorescence properties with high quantum yields, large Stokes shift as well as favourable solvent profiles. Hence, the oxazole based dyes with different kinds of substituents at their 2- and 5- positions is the area of interest of our recent work. A number of compounds were synthesized involving van Leusen protocol[3] and recent modified transition metal catalysed arylation methodology[4] to oxazole ring by C-H activation. Subsequent characterization of these compounds by ^{1}H-NMR, ^{13}C-NMR, HRMS spectra has finally led us to study some photophysical properties. UV-absorption spectra of these synthetic dyes are being studied and attempts are being made to observe the supramolecular host-guest relationship by adding to cucurbit [7] uril at different concentrations.



2,5-disubstituted oxazole

References:

[1] For Review: Yeh, S.C.V. Tetrahedron **2004**, 60, 11995.

[2] (a) Palmer, D. C.; Venkatraman, S. Oxazoles: Synthesis, Reactions and Spectroscopy,Part A; J. Wiley & Sons: Hobken, NJ, **2004**.
(b) Tomoki, Y.; Tetsuya. S.; Koji, H.; Daisuke, M.; Akihiro, O.; Junzo, O.; Masahiro, M. Tetrahedron Letters, **2009**, 50, 3273–3276.

[3] Van Leusen, A.M.; Hoogenboom, B.E.; Siderius, H.; Tetrahedron Letters, **1972**, 23, 2369.

[4] (a) Lewis, J. C.; Wu, J. Y.;Bergman, R. G.; Ellman, J. A. Angew. Chem. Int. Ed. **2006**, 45, 1589. (b) Flegeau, E. F.; Popkin,M. E.; Greaney, M. F. Org. Lett., **2008**, 10, 2717.

Graphene Oxide Containing Hydrogel Based Nanohybrid Systems and Their Applications

Abhijit Biswas and Arindam Banerjee*
Department of Biological Chemistry
Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India
**bcab@iacs.res.in*

Graphene oxide based new hydrogel in presence of vitamin B_2/B_{12} or pyrene appended aromatic amino acid (tryptophan) have been made in aqueous medium. These gel-based soft materials have been used to synthesize various metal nanoparticles, including Au, Ag, and Pd nanoparticles, as well as nanoparticle-containing reduced graphene oxide (RGO)-based nanohybrid systems. One of these hydrogel materials can be exploited to make a trihybrid system by the stepwise inclusion of graphene oxide and metal nanoparticles. Thus, it can be said that GO-based gels act as a versatile reactors for the synthesis of different nanomaterials and hybrid systems on the nanoscale. These nanohybrid systems have been characterized by using TEM, XRD, XPS and Raman spectroscopic techniques. One of these nanohybrids has been used as a catalyst for C-C cross coupling reaction. The specialty of this hydrogel catalyst is the fascinating example of facile and straightforward procedure for the separation of the catalyst from the reaction mixture and thus the hydrogel catalyst showed excellent reusability (up to 15 times) without losing its activity significantly.

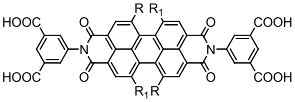
References:

[1] Biswas, A.; Banerjee, A. Chem. Asian J. **2014**, DOI: 10.1002/asia.201402695.
[2] Nanda, J.; Biswas, A.; Banerjee, A. Angew. Chem. Int. Ed. **2013**, 52, 5041–5045.

Water Soluble Perylene Derivatives and Formation of J- and H- Aggregates

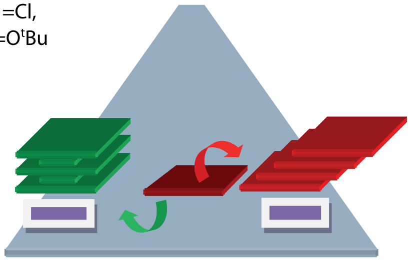
Kausik Bag, Sudip Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata-700032, India
Email:psukb@iacs.res.in

According to *Exciton* theory, the π-conjugated dyes which may be considered as a point dipole, interact with themselves with respect to transition dipole give rises to H-type (parallel) or J-type (head to tail) aggregation. In case of perylene based molecule, the interaction originates mainly from the core of the moiety resulting different kind of functional materials. H-type interaction of perylene based molecule generally shows n-type carrier mobility important for the field of electronic devices and J-type is prominent of showing extended exciton mobility exploited in solar cells. Previously, we have synthesized isophthalic acid appended perylene bisimides (PI) which is water soluble because of the four carboxylic groups attached with the molecule. PI molecules interact with melamine in 1:2 molar ratio forming a two-component highly fluorescent aggregates showing fibril network. The cross linking of the melamine functionality with that of PI molecule occurs in parallel fashion and thus there is the formation of H-type interaction. Interestingly, acidification of the PI causes J-type aggregations which are observed by spectroscopic studies. For core-substituted PI derivative, there is also formation of H-type aggregates after lowering the pH of the solution.



1

PI: R=R$_1$=H, **PBI:** R=H, R$_1$=Br, **PCl:** R=R$_1$=Cl,
PPy: R=H, R$_1$=pyrrolidine, **P^{t}Bu:**R=R$_1$=O^{t}Bu



Schematic diagram of the predicted aggregation mode

References:

[1] Sukul,P. K. ; Asthana,D.; Mukhopadhyay, P.; Summa, D.; Muccioli, L.; Zannoni,C.; Beljonne,D.; Rowan, A. E.; Malik, S. *Chem. Commun.,* 2011, **47**, 11858 – 11860

[2] Sukul, P. K.; Datta, A.; Malik, S. *Chem. Eur. J.*, 2014, **20**, 3019 – 3022

[3] Yagai, S.; Seki, T.; Karatsu, T.; Kitamura, A.; Wurthner, F. *Angew. Chem. Int. Ed.* 2008, **47**, 3367 – 3371

Stimuli-Induced Formation and Disintegration/Transition of Amphiphilic Diblock Copolymer Vesicles: Investigation by Energy Transfer between Donor-Accepter Molecules Encapsulated Into the Vesicle

Chiranjit Maiti, Rakesh Banerjee, Pousali Samanta, Dibakar Dhara*
Department of Chemistry, Indian institute of Technology Kharagpur,
West Bengal 721302, India
Email: dibakar@chem.iitkgp.ernet.in

Formation and disintegration/transition of self-assembled amphiphilic block copolymer nanostructures in response to external stimuli are important phenomena that have been widely explored for a variety of biomedical applications. In this presentation, we demonstratestimuli(thermo or pH) triggered assembly of block copolymer molecules in aqueous solution to form vesicles and their disassembly or transition to other nanostructureson changing the temperature or pH of the solution respectively. New block copolymers,PNIPA-*b*-PMAPTAC and poly(L-Trp-HEA)-*b*-poly(PEGMA) which were synthesized by using reversible addition-fragmentation chain transfer (RAFT) polymerization technique,are found to spontaneously form thermo and pH-responsive vesiclesin aqueous solutionrespectively. We showed that these vesicles are able to encapsulate both hydrophobic and hydrophilic guest molecules and hence can be used as a delivery vehicle. PNIPA-*b*-PMAPTAC copolymers at room temperature exist as unimers in aqueous solution and self-assemble into vesicles at temperature≥36 °C and thus able torelease the encapsulated cargo by simply decreasing the temperature of the medium due to disassembly.poly(L-Trp-HEA)-*b*-poly(PEGMA) copolymer undergoesreversible morphological transitions in aqueous solution on changing the pH of the solution, with vesicle formation happening at physiological pH and micelle formation at acidic pH. The pH-dependent vesicle-to-micelle transition resulted inselective triggered release of encapsulated hydrophilic guest molecules over hydrophobic ones.Further, these pH-responsive vesicles were successfully utilized to reduce $HAuCl_4$ and *in situ* synthesis of the gold nanoparticles, and this procedure was undertaken to selectively stain the vesicles wall. Nanostructures of amphiphilic block copolymer were very useful for energy transfer because they provided opportunities for precise positioning of the donor and acceptor. When vesicles were disintegrated or transitioned to micelles, in situ by a stimulus like temperature or pH respectively, the energy transfer molecules were released and diffused apart, reducing the energy transfer. By monitoring the energy transfer efficiency, the process of transition from vesicles to micelles and also release of the core-loaded probes to biological media can potentially be demonstrated.

Reference:

[1] Maiti, C.; Dey, D.; Mandal, S.; Dhara, D. *J. Phys. Chem. B.***2014,***118*, 2274-2283.
[2] Maiti, C.; Banerjee, R.; Maiti, S.; Dhara, D. *Communicated.*

Amyloid β on Nobel Metals: surface-enhanced Raman spectroscopy investigates the structure, while AFM investigates the function

Debanjan Bhowmik[1], Christina MacLaughlin[2], Shell Ip[2], Suman Nag[1], Bidyut Sarkar[1], C. Muralidharan[1], Gilbert Walker[2] and Sudipta Maiti[1]*
[1]Department of Chemistry, TIFR, Mumbai
[2]Department of Chemistry, Lash Miller Laboratories, UT, Toronto
*maiti@tifr.res.in

Medicinal activity of a molecule is highly dependent on the presence of a biologically important unit. We have designed two keto-tetrahydrocarbazole derivatives 2-((9-methyl-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-6-yl)oxy)acetic acid and 2-((7-methoxy-9-methyl-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-6-yl)oxy)acetic acid, both of which are efficient fluorophores. We have used rigorous spectroscopic investigations to elucidate the photophysical properties of the compounds in different solvents. Absorption maxima of the compounds have changed to a small extent in solvents with largely different empirical polarity parameters [ET(30)]. The fluorescence emission maxima of the compounds, on the contrary, have undergone red shift with increasing [ET(30)] of the solvents. Protic solvents were especially influencial in perturbing the excited states of the fluorophores. Calculations of dipole moment, free energy of solvation, reorganization energy, solvatochromic comparison method have been used to describe the excited state properties of the compounds. Binary solvent mixtures were used to demonstrate the dielectric enrichment of protic solvents in comparison with aprotic solvents.

Since their discovery, flavins have been recognized to play pivotal role in versatile biochemical redox reactions as they functions as both electrofiles and nucleophiles inside the complex biological enviroment. In this presentation we decipher the reaction pathways of Riboflavin (Vitamin B2) in presence of organic bases (N, N- Dimethylaniline and Triethylamine) in both homogeneous and heterogeneous media.

References:

[1] Ellis, R. J. Trends Biochem. Sci. **2001**, 26, 597 – 604.
[2] Minton, A. P. J. Biol. Chem. **2001**, 276, 10577-10580.
[3] Hall, Damien.; Minton, Allen P. Biochimica et Biophysica Acta.**2003**, 1649, 127-139.
[4] Schlesinger, A.P.; Wang, Y.; Tadeo, X.; Millet, O.; Pielak, G.J. J. Am. Chem. Soc. **2011**, 133, 8082 – 8085.

Reversible Thermo-Shear Gelation of Patchy Polymers

Indravadan Parmar, Ashish K. Lele, Manohar V. Badiger,
Prakash P. Wadgaonkar, AartiShedge
Polymer Science and Engineering Division, National Chemical Laboratory
*ia.parmar@ncl.res.in

Thermothickening polymers are amphiphilic stimuli responsive co-polymers and show a gelation upon increasing temperature and liquefy upon cooling in the aqueous media[1]. In the literature, polymers which show gelation an opposite behavior of gelation and liquefaction are less commonly encountered and most of them are naturally occurringpolymers [2].

We have observed for the first time an abrupt gelation of aqueous solution of hydropbhobically modified poly (N,N′ dimethyl acrylamide-co-acrylic acid) upon cooling by imposing low shear rate (0.5 Pa). A high molecular weight (5 x 10^6gm/mol) co-polymer was prepared by free radical polymerization of N,N′ dimethyl acrylamide (70 mol%) and of acrylic acid (30 mol%) and was subsequently modified by n - dodecyl amine (10 mol%) as a hydrophobe. Structure elucidation of base copolymer and hydrophobically modified polymer was performed by ^{1}H NMR and ^{13}C NMR spectroscopy.

Cooling a solution of the base copolymer at controlled temperature rate and at low shear rate resulted in small amount of thickening whereas cooling a solution of hydrophobically modified copolymer at identical conditions resulted in an abrupt and large increase in viscosity at critical temperature. Heating a solution of hydrophobically modified polymer at same rate of cooling showed an abrupt liquefaction at critical temperatures.In this work, we are trying to understand plausible mechanism of gelation upon cooling by Rheology, DLS and Fluorescence spectroscopy.

References:

[1] **K. Sui and X. Zhao**, Langmuir, 2012, 28, 153-160

[2] **H. Yoshioka, Y. Mori**, Polymers for Advanced Technologies, 1997, 9, 155-158

Nano Clays for Environmental Degradation of Polyolefins

R. P. Singh[1], Omkar S. Kushwaha[2, 3] and Namrata S. Tomer[1]
[1]Bharati Vidyapeeth Deemed University, Research and Development Centre in
Pharmaceutical Sciences and Applied Chemistry,
Poona College of Pharmacy, Erandwane Pune – 411 038, India
[2]Polymer Science and Engineering Division, Council of Scientific and Industrial
Research- National Chemical Laboratory, Dr. Homi Bhabha Road, Pune - 411008, India
[3]Academy of Scientific and Innovative Research,
2, Rafi Marg, Anusandhan Bhavan, New Delhi – 110001, India.
E-mail: rp.singh.ncl@gmail.com

Today, the rapid economic growth and urbanization of India facing issues of solid waste management: the most crucial health and environmental problems. In recent years, plastics have become a significant component of solid waste accounting for 20-27%. Plastic being non-bio-degradable, its decomposition does not take place at disposal site. Besides, plastic causes choking of drains and environmental pollution when burnt under uncontrolled condition.These observations indicate that our current use of plastics is not sustainable.Hence, biodegradation & / or recycling of plastics is receiving more attention, which will reduce the proportion of this waste component at disposal sites.Recycling is one of the most important actions currently available to reduce these impacts and represents one of the most dynamic areas in the plastics industry today. Recycling provides opportunities to reduce oil usage, carbon dioxide emissions and the quantities of waste requiring disposal.

Over the past 50 years in plastic industry, the success of thermoplastics of polyolefins based on petroleum resources can be attributed not only to the reliable raw materials basis but also to their versatile applications (packaging and biomedical devices) and to their melt-processability. The inertness and durability of polyolefins have made them a material of choice for many applications but seemingly also a disadvantage when it comes to their disposal or waste management. This present investigation aimed at using nanoclay (layered silicates) for enhancing the photo-oxidative degradation of polyolefins (PE, PP and their copolymers). The strategy involved here is preparing nanocomposites of polyolefins with clay as reinforcing nanoscale filler and pseudo-pro-oxidant and microcrystalline cellulose as biodegradable additive for enhancing the biodegradation. Investigation on mechanical properties and FTIR spectroscopy upon photo-irradiation suggested that the clay-containing samples are more susceptible towards photo-oxidation than the neat polymer and the composites with cellulose particles. Biodegradation studies by composting method indicated that incorporation of clay has no direct and significant effect on earlier stage of weight loss, show higher level of bio-disintegration when they are already photo-oxidated. Since the clay incorporated samples showed their vulnerability to photo-oxidation which is pre-requirement for biodegradation of polyolefins, it is suggested that the acceptable level of biodegradation can be achieved by incorporation clay followed by photo-oxidation.

Molecular motifs for sticky additives that influence crystallization of PEO

Sudhakar Shrivastava, Vanka Kumar and Guruswamy Kumaraswamy*
Polymer Science and Engineering, CSIR-NCL, Pune
*g.kumaraswamy@ncl.res.in

Design of additives remains an art more than science. Some years ago, our simulations had suggested[1] that "sticky" molecular additives could alter the route to polymer crystallization. However, this had not been experimentally realized so far. Here, we present results that suggest a design strategy for molecules that act as "sticky" additives, that influence polymer crystallization. We investigate the crystallization of polyethylene oxide (PEO) that is an FDA-approved biocompatible polymer. PEO is used as a matrix for controlled release of drugs. Therefore, controlling the crystalline morphology of PEO has implications for controlled release applications. We use derivatives of phenol, since these are molecularly miscible with PEO and investigate their effect on PEO crystallization. We use DSC, optical microscopy and SAXS to characterize isothermal crystallization of additivated PEO. We find that bifunctional additives, such as, for example, resorcinol or para-aminophenol, that have groups that interact strongly with the PEO are "sticky". Such additives depress the melting point of the polymer – however, remarkably, they do not decrease the equilibrium melting point at loadings of 5%. The crystallization rate is also suppressed relative to neat PEO. SAXS investigations reveal that while the melting point and crystallization rate are decreased, the lamellar thickness and long spacing increase. We argue that our results point to accumulation of these additives at the lamellar basal planes that gives rise to an increase in the lamellar surface energy.

References:

1. Dasmahapatra, A. K.; Nanavati, H*.; Kumaraswamy, G*. Polymer crystallization in the presence of sticky additives. *J. Chem. Phys.* 2009, *131*, 074905.

Thin film Polyamide Composite Membranes- potential Application towards the removal of Pesticides from water

A. Bhattacharya *, Paramita Manna, Romil Mehta
Reverse Osmosis Discipline, Central Salt and Marine Chemicals Research Institute,
G. B. Marg, Bhavnagar, Gujarat - 364002, India
*amit@csmcri.org

Apart from the desalination activities, thin film Polyamide composite membranes spread their wings in different separation arena (viz. removal of organic pollutants, pesticides). The preparation of the tailor-made membranes is an art. The nature of the thin film composite membrane is not only instrumental, it depends upon the chemistry of Polysulfone /Polyether sulfone membrane as well as polyamide coating layer. The base asymmetric polysulfone membrane controls the permeation whereas polyamide coating layer controls the separation.

In recent years, attention has been focused regarding the priority to supply safe drinking water. There are several techniques (viz. active carbon filtration, ozone treatment, membrane separation) to remove the pesticides from water. Membrane separation technique has its potentiality and advantageous amongst all. There are several factors (e.g. nature of membranes, nature of pesticides, presence of organic and inorganic matters, techniques) that influences the separation are to be discussed.

Miscibility in solutions and gels of poly (vinyl alcohol) and hyaluronic acid: evolution tracked through rheological characteristics

Jagadeeshwar Kodavaty and Abhijit P. Deshpande*
Department of Chemical Engineering,
Indian Institute of Technology Madras, Chennai - 600036
abhijit@iitm.ac.in

Gels made of poly vinyl alcohol (PVA) and hyaluronic acid (HA) have several promising applications in various biomedical implants and drug delivery systems [1,2]. These swellable hydrogels can be prepared by crosslinking either of or both the polymers. Due to significant internmolecular interactions, both the polymers have range of meso- and micro-phase structures in solution. These structures affect the gelation and crosslinking behaviour, and in turn, gelation affects the microstructure. Therefore, sol-gel transition as well as final gel properties are closely interlinked with the evolving molecular assembly processes in these blends.

In the present work, the crosslinking reactions of PVA with glutaraldehyde and HA with divinyl sulfone were used to prepare gels. PVA and HA solutions were blended to make the hybrid hydrogels. Given the extensive ionic and hydrogen bonding interaction centers in the polymers, semi-dilute solutions exhibit signficant non Newtonian behaviour as a function of concentration and pH. The rheological characterization during gelation, and of the hydrogels was carried out using small amplitude and large amplitude oscillatory shear. Different types of molecular organizations, at different HA contents, lead to different signatures in rheological response [3]. These differing rheological responses can be identified during gelation, and persist in the final gels. Optical and electron microscopy was used to examine and confirm the morphological features during and after gelation.

References:

[1] Baino, F. Acta Biomater. **2011**, 7, 921-935.
[2] Almeida, H.; Amaral, M. H.; Lobao, P.; Lobo J. M. S. Drug Discov. Today **2014**, 19, 400-412.
[3] Kodavaty, J.; Deshpande, A. P. J. Appl. Polym. Sci. **2014**, DOI: 10.1002/app.41081.

Dissection onto Interior Lamellar Assembly in Polymers Crystallized with Periodical Birefringence Patterns

Eamor M. Woo
Department of Chemical Engineering,
National Cheng Kung University, Tainan, 701-01, Taiwan
emwoo@mail.ncku.edu.tw

It has been long known that many polymers, from the earlier olefin polymers, polyethylene (PE), to aliphatic and aryl polyesters, when crystallized in thin films, could display periodical optical ring patterns. In this study, new light is shed to establish correlations between the outer surfaces and inner interiors of petro-based or biodegradable semicrystalline polymers crystallized with periodical lamellar assembly, which were examined in details by using various microscopy techniques: scanning electron microscopy (SEM), polarized-optical microscopy (POM), and atomic-force microscopy (AFM), wide- and small-angle X-ray analyses. Correlations between the surfaces and interiors of crystal lamellae packed into periodical patterns such as ring bands or regular dendrites were examined in several polyesters and biodegradable polymers [1-5]. Thin-film vs. bulk polymers exhibit different lamellar assemblies. For examples, the 3-D spherulites in the bulk PNT are not always well-rounded full spheres; they can be hemispheres owing to nucleation on the surface side or multi-shell cones (spheres sliced off both poles) when thickness or growth is confined. Furthermore, 3-D views on PLLA spherulites reveal a periodical up-and-down pattern of up to 100 micron pitch, with the convex (ridge) portion filled with tiny twisted crystals but the concave (valley) portion filled with amorphous chains. Such confinement in thin films leads to appearance of concentric rings of various shapes, which originate their development from inner or substrate nuclei. Comparison of fractured surface of multi-shell conformation model with that of lamellae twisting model in spherulite indicates that inner lamellae are arranged differently from those surfacing to the top. Based on these revolutionary novel 3D approaches of direct viewing interiors in comparison with thin-film top surfaces, this study has offered novel insights to put one step forward on these historically long-debated crystal issues.

References:

[1] E. M. Woo, L. Y. Wang, and S. Nurkhamidah, **Macromolecules**, 45, 1375-1383 (2012).
[2] E M. Woo, and S. Nurkhamidah, Y. F. Chen, **Phys. Chem. Chem. Phys., 13 (39), 17841–**17851 (2011)**.**
[3] G. Lugito, L. Y. Wang, E. M. Woo, "Chemical and Morphological Alterations Effected by Methylamine Reactions on Polyesters", **Macromol. Chem. Phys.**, 215, 1297-1305 (2014).
[4] G. Lugito and E. M. Woo, "Interior Lamellar Assembly in Correlation to Top-Surface Banding in Crystallized Poly(ethylene adipate). **ACS Crystal Growth & Design**, pub. On-line (2014).
[5] G. Lugito, C. Y. Yang, and E. M. Woo, "Phase Separation Induced Lamellar Re-Assembly and Correlation with Spherulite Optical Pattern Change", **Macromolecules**, pub on-line (2014).

High Throughput Screening For Thermoplastic Compounds - A New Development Tool

Ralf Bode, Jürgen Stebani, Gerhard Maier*
Polymaterials AG, Kaufbeuren, Germany
*g.maier@polymaterials.de

Adjusting property profiles and developing new grades of blends and compounds often require a large number of experiments to handle the complexity of the mixture. When new materials, such as biogenic polymers, new fillers or additives, or more complex systems, such as ternary and quaternary blends, are involved, there is often no or little prior experience. Using conventional methods of compounding, injection molding and testing, it can take many months and even years to develop appropriate compounds because a large number of experiments are necessary. Without a sufficiently large body of experience, it is not possible to reduce the number of experiments to a level that can be handled with conventional methods within a reasonable amount of time. Polymaterials' High Throughput Screening system can reduce the time required to study 50-300 thermoplastic compounds including mechanical testing to only one or two weeks. Thus, combinatorial screenings as well as the generation of predictive models based on suitable experimental designs are possible to identify the most useful combination of components, establish the presence or absence of interactions between these components, and evaluate the range of properties that can be achieved. Examples for successful application of the system are the study of the interaction of flame retardants and synergists with glass fibers, the adjustment of the Tg of a semicrystalline polymer without affecting the melt temperature, development of tough PLA compounds, and the optimization of the mechanical properties of blends by screening for the most suitable grades of the starting polymers.

Patent information as an enabler for Research Opportunities

Arup Ghosh, Partha sarathi Pal, Nallapusa Vennela,
Sriram Balaji Renga Nathan & Asim Pattanayak
Legal Affairs – Intellectual Property Analysis Team
SABIC Technology Center, Bangalore, India

In today's business environment, Intellectual Property (IP) plays a key role towards developing impactful research opportunitiesand building IP assets both in academia & industriesfor monetization. Over the time,patent information becoming more and more critical for research success by providing competitive edge to the scientists & technologists. It has been observed that the technology information from patent is often ignored to be utilized as a vitalresourcesduring research planning and development. Patent information not only reveals the threats and opportunities for research and innovation through the state-of-the-art analyses; it also helps in assessing potential risk or road block in future during commercialization of the product in the market by conducting techno-legal analyses. In this paper, we will introduce the importance of patent and how it brings value to the organization in creating/protecting IP and building IP strategy to gain higher business impact through case studies.

References:

[1] Assad Abbas; Limin Zhang; Samee U. Khan. World Patent Information xxx. **2014**, 1-11.
[2] www.wipo.int/edocs/mdocs/mdocs/en/wipo.../wipo_ip_mnl_13_1.pdf
[3] https://www.thevantagepoint.com/resources/articles/Frey-White-Spaces-or-Black-Holes.pdf

Multiwalled carbon nanotubes and graphene based hybrid polymer nanocomposites

Arup R. Bhattacharyya
Department of Metallurgical Engineering & Materials Science
Indian Institute of Technology Bombay, Powai, Mumbai - 400076, India
Email: arupranjan@iitb.ac.in

Carbon nanotubes (CNTs) and graphene based polymer nanocomposites have gained enormous research interest in the academic as well as industrial community due to the outstanding properties associated with CNTs and graphene. However, the ‘agglomerated’ dispersion of CNTs (or graphene) in the respective polymer matrix along with inadequate interfacial interaction between the CNTs (or graphene) and the polymer matrix make it a challenge to achieve outstanding properties associated with CNTs/graphene.

In this context, multiwall carbon nanotubes (MWNTs) have been ‘de-agglomerated’ with the aid of an organic modifier; Li-salt of 6-amino hexanoic acid (Li-AHA). Li-AHA modified MWNTs have been used to intercalate inside the partially exfoliated expanded graphite (EG) gallery. Transmission electron microscopic (TEM) observation along with selected area electron diffraction (SAED) pattern have indicated hexagonal ‘dot’ pattern in case of Li-AHA modified MWNTs/EG hybrid mixture, whereas unmodified hybrid mixture showed ring pattern associated with poly-crystalline nature of EG. Hybrid nanocomposites of PA6 with EG/MWNTs were prepared via melt-mixing technique in a conical twin-screw Microcompounder. AC Electrical conductivity, morphology and thermal properties will be discussed in context to the effectiveness of the non-covalent organic modifier (Li-AHA) to achieve the intercalation of m-MWNTs inside the EG gallery in the composites.

Novel Blend Membranes from Poly (Dimethylaminoethyl Methacrylate) Grafted Natural Rubber and Poly (Vinyl Alcohol)

G. Unnikrishnan
Polymer Science and Technology Laboratory, Dept. of Chemistry,
NIT Calicut, NITC Campus P.O., Calicut-673 601, Kerala, India
E-mail: unnig@nitc.ac.in

Chemical modification of *cis*- polyisoprene in natural rubber is an emerging area of research. Grafting is one of the methods widely using for this purpose. In the present work, water soluble polymer poly (dimethylaminoethyl methacrylate) (PDMAEMA) was chemically grafted to the surface of hydrophobic natural rubber particles by a second stage polymerisation of dimethylaminoethyl methacrylate (DMAEMA) monomer. The process was initiated by a redox couple cumene hydroperoxide (CHP)/ tetraethylenepentamine (TEPA). The modified latex showed a significant increase in the colloidal stability at low pH. After removing the homopolymers, monomers and initiators by dialysis, the treated latex was blended with PVA, a hydrophilic polymer and casted into membranes. The blended and non blended membranes were characterized in terms of morphology (using SEM), compatibility (using FTIR), and thermal stability (using TGA). The particle size was examined using dynamic light scattering (DLS). Swelling and dye release studies were also done with the membranes.

Polymers for advanced composites applications

M. Sarojadevi, P. Thirukumaran, Shakila Asraf and S. Balaji
Department of chemistry, Anna University, Chennai – 600025, India
E. Mail: msrde2000@yahoo.com

Many applications require a structural composite to have an elastic modulus high enough to withstand numerous mechanical stresses and strains over a long period of time. One application is the underbody of jet aircraft exposed to the back blast of jet engines, especially the V/STOL (vertical/short take-off and landing) aircraft. Structural components of helicopter and automobile frames are also exposed to severe mechanical demands.

Advanced composites are lightweight, high strength and high modulus materials made with carbon/Kevlar fibers and thermally stable polymers used in the aerospace industry. A variety of resins are available for such applications. Epoxy resins meet the thermal and mechanical property requirements for the aerospace industry. But their applications restricted to about 120^0C because of their T_g. Condensation type polyimides have very high T_g (350^0C) but the processability into composites is extremely difficult. This problem with processability is overcome in the case of bismaleimides. But they are highly brittle. PMR type polyimides developed to overcome the brittleness of bismaleimides suffer with the carcinogenic nature of one of the constituents, the diamine monomer MDA. Phthalonitriles are known to be the polymers with highest thermal stability. Carbon fiber/phenolic resin composites find application as components for aircraft interior. Phenolics evolve volatiles during curing. Benzoxazines undergo addition curing without evolving any volatiles and are superior in this respect. The nano composites of these resins with POSS and functionalized MWCNT are also explored. The properties advantages and disadvantages of these resins will be discussed.

References

1. L.S.Jayakumari, V.Thulasiraman and M.Sarojadevi, Polymer Composites, 2008, 29**, 709 -716**
2. R. Hariharan, S.Bhuvana, N. Amutha and M. Sarojadevi, High Perf. Polym, 2006, 18, 893 -
3. G. Anuradha, S. Rakesh, M. Sarojadevi, Polymer Engineering & Science, 2009, 49, 889-895.
4. P. Selvakumar, K. Padmini, M.Sarojadevi and M. F. Leelavathi, journal of macromolecular science part A: pure and applied chemistry, 2010, 47, 76-88.
5. B. Govindaraj, M. Sarojadevi, Polymer composites, 2013, 34, 825-83.
6. S. Rakesh, C.P. Sakthidharan, V. Sudha, M. Selladurai, P. Sundararajan and M. Sarojadevi, High Performance Polymers, 2013, 25, 87-96.
7. M. Selladurai, P. Sundararajan and M. Sarojadevi, Chemical Engineering Journal, 2012, 203,333-347.
8. P. Thirukumaran, A. Shakila Parveen and M. Sarojadevi, Journal of RSC Advances, 2014, 4, 7959 – 7966.

Flocculation and adsorption properties of biodegradable gum-ghatti-grafted poly(acrylamide-co-methacrylic acid) hydrogels synthesized via microwave-assisted cross-linking

Hemant Mittal[1,2*], Arjun Maity[1] and Suprakas Sinha Ray[1,2*]
[1] Department of Applied Chemistry,
University of Johannesburg, Doornfontein 2028, South Africa
[2] DST/CSIR National Centre for Nanostructured Materials,
Council for Scientific and Industrial Research, Pretoria 0001, South Africa
* *mittal.hemant5@gmail.com*(HM)

The hydrogel polymer of the gum ghatti (Gg) with the co-polymer mixture of the acrylamide (AAm) and the methacrylic acid (MAA) was synthesized under the influence of microwave radiations. The synthesized hydrogel polymer was characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Moreover, the changes in the thermal properties of the Gg after the graft co-polymerization were examined using the TGA/DTA/DTG. It was observed that the Gg-cl-P(AAm-co-MAA) hydrogel polymer showed maximum swelling of 1959 % at 60 °C after 20 h of swelling time in neutral medium. Furthermore, the hydrogel polymer was successfully utilized for the removal of saline from different petroleum fraction-saline emulsions. The flocculation capacity of the hydrogel polymer was also examined and it exhibited the maximum flocculation capacity in an acidic clay suspension with a 15 mg polymer does at 40 °C. Furthermore, the hydrogel polymer was employed for the adsorption of Pb^{+2} and Cu^{+2} from the aqueous solution and it were found to absorb 94 % and 75 % of Pb^{+2} and Cu^{+2}, respectively, from aqueous solutions. Finally, the Gg-cl-P(AAm-co-MAA) hydrogel was subjected to the biodegradation using the soil composting method and the different stages of biodegradation were characterized using the FTIR and SEM analysis. In summary, the Gg-cl-P(AAm-co-MAA) hydrogel was demonstrated to have potential for use as flocculants and heavy metal absorbents for industrial waste water treatment.

Influence of Processing Parameters on the Performance of Short Glass Fiber Reinforced Tasnee Polypropylene Composite

Kais As-Sultany, P.V.N. Sastry*, Mansoor A. Gafoor
Tasnee Plastics Research Centre (NIPRAS) National Industralization Company,
TASNEE Al-Jubail, Kingdom of Saudi Arabia
*E-mail :*p.sastry@tasnee.com*

Polypropylene (PP) is a versatile polymer, being effective for extensive commodity applications. The performance of PP is enhanced by reinforcing with various fibres viz. glass fibre, carbon fibre etc. as well with particulate fillers such as talc, calcium carbonate, mica etc. The present study describes the reinforcement of Tasnee PP with short glass fibre (SGF) in the concentration range 0-40 wt% in a twin screw extruder. The composites' performance has been observed with respect to the twin-screw extrusion conditions. The composite, PP/SGF40, properties have been significantly improved with the screw profile, screw speed and temperature profile. The residual fibre length has been found to be increased significantly (more than 200%) after the extruder's screw profile is modified. The enhanced fibre length is found to reinforce the composite effectively with improved interfacial interactions in presence of PP-g-MAH as compatibilizer. Tasnee'sPP/SGF high performance composite is found to exhibit tensile modulus (+75%), tensile strength (+80%), flexural strength (+15%), and more than 12 times of impact strength, compared to the competitor composite.The composite properties have been found to be comparable to that of fibre reinforced thermoset polyester.With its high performance, Tasnee PP/SGF40 composite has been found to swap the fibre reinforced thermoset polyester for water-meter box application.

References:

[1] Etcheverry, M. and Barbosa, S. Materials 2012, 5, 1084-1113.
[2] Mallick, P.K. Fiber Reinforced Composites, Materials, Manufacturing and Design, Marcel Dekker Inc., New York, NY, USA, 1997.
[3] Hull, D. and Clyne, T.W.An Introduction to Composite Materials, 2nd ed., CampbridgeUniveristy Press, Cambridge, UK, 1996.
[4] Thomason, J.L. and Vlug, M.A. Composites Part A: Applied Science and Manufacturing, 1996,27, 477-484.

Correlation of Visco-elastic and Acoustic Properties of a Polyurethane based Underwater Acoustic Absorber through Modeling and Experiment

V. G. Jayakumari[1], Rahna K Shamsudeen[1], K. M. Naseef Ali[2],
S. Kusumakumari[1], R. Rajeswari[1] and T. Mukundan[1]*
1. Materials Science Division,
Naval Physical and Oceanographic laboratory, Thrikkakara, Kochi 682021
2. Department of Materials Science and Technology, NIT, Calicut, India
*ms_npol@yahoo.com

Acoustic absorber panels are essential for providing a stealth coating for ships and submarines. Also, they are useful for anechoic lining for water filled tank facilities used for calibration and evaluation of underwater acoustic devices. Polymeric materials have been used in a variety of applications for the absorption, transmission and detection of sound[1-2]. All of these situations have their reliance on the viscoelastic nature of polymer materials. Therefore, correlation of visco-elastic and acoustic properties is vital in the design of acoustic absorber tiles. Visco-elastic measurements were carried out using dynamic mechanical analyser (DMA) in the tensile mode in 0.1 to 50 Hz frequency range. Time temperature superposition technique was used to generate modulus and damping properties in the acoustic range. These data were used as inputs for design of acoustic absorber tiles using FEM modeling. Gradient and multilayer designs with and without geometric inclusions were generated and their acoustic properties were modeled. Some of the best designs evolved were validated using pulse tube technique as well as acoustic evaluation in an anechoic tank facility. Acoustic absorber panels with echo reduction values >15 dB in selected frequency ranges with different thickness were developed.

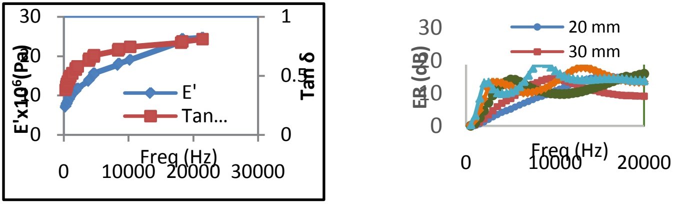


Fig. 1 (a)Superposed data of viscoelastic properties from DMA analysis; (b) FEM modeling result for acoustic performance of samples with varying thickness

References

[1] Corsaro, R. D. and Sperling L. H., *Sound and Vibration damping with Polymers*, ACS Symposium Series, Washington DC, **1990**.

[2] Jayakumari, V. G., Rahna K Shamsudeen, Ramesh, R., Mukundan, T., J. Acoust. Soc. Am., 2011, **130**(2), 724-730.

Effect of sol–gel modified nano calcium carbonate (CaCO3) on the cure, mechanical and thermal properties of acrylonitrile butadiene rubber (NBR) nanocomposites

Subhas Chandra Debnath*, Kumarjyoti Roy, Md. Najib Alam,
Swapan Kumar Mandal
Department of Chemistry, University of Kalyani, Kalyani, Nadia 741235, W.B, India

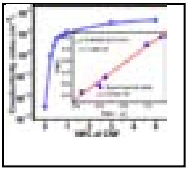
The main goal of this work is to modify surface of nano $CaCO_3$ with silica by an elegant approach of sol–gel method and also to compare the influence of sol–gel modified nano $CaCO_3$ with unmodified nano $CaCO_3$ in the cure, mechanical and thermal properties of acrylonitrile butadiene rubber (NBR) nanocomposites. The surface modification of nano $CaCO_3$ is characterized by Fourier transform infrared spectra and Field emission scanning electron microscopy. The modified nano CaCO3 causes significant improvement in the maximum rheometric torque and cure rate index value of NBR nanocomposites in comparison to unmodified nano $CaCO_3$. More importantly, incorporation of surface modified nano $CaCO_3$ provides substantial enhancement in the mechanical properties of NBR nanocomposites and at 4 phr (parts per hundred parts of rubber) filler loading level tensile strength of modified nano $CaCO_3$ filled NBR vulcanizates shows a large increment by 37.33 % compare to that of unmodified nano $CaCO_3$ filled NBR vulcanizate. Thermogravimetric analysis reveals that sol–gel modified nano CaCO3 delivers greater thermal stability in NBR nanocomposites than unmodified nano $CaCO_3$. The fantastic enrichment in the cure, mechanical and thermal properties of NBR nanocomposites containing surface modified nano $CaCO_3$ will be the part of great interest for rubber researcher regarding the broad application of sol–gel modified nano $CaCO_3$ as important filler in rubber industry.

Polyimide-Carbon Nanofiber Nanocomposites for Electrostatic Discharge and Electromagnetic Interference Shielding Applications

Lalatendu Nayak[1, 2*], Abhijit Adhikary[1], Eugene Byrd[1],
Tapan K. Chaki[2], Dipak Khastgir[2]
[1]Phillips Carbon Black Ltd, Kolkata, India
[2]Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India
*lalatendu.nayak@rp-sg.in

In recent times, aromatic polyimides have received considerable scientific and technological attention due to their outstanding characteristics such as exceptional tensile strength, excellent thermal, and radiation stability [1]. Because of their outstanding properties, they have been widely used in the manufacture of integrated circuits, thermally stable films, adhesives, coating, and components in spacecraft. When these are applied to space environment and some electronic instruments, electrostatic charges are accumulated on their surfaces, which cause unwanted heating and premature degradation of materials [2]. Therefore, there is a need to increase the electrical conductivity of polyimides.

The objective of present study is to prepare conductive polyimide (PI) - carbon nanofibers (CNFs) composite at very low percolation threshold. The combined advantage of in-situ polymerization of PI in the presence of highly graphitized CNFs and continuous probe type sonication throughout the polymerization provide electrically conductive PI composites with a significantly lower percolation threshold than previously reported. The electrical conductivity and electromagnetic interference shielding effectiveness (EMISE) of the composite with different weight percentage of CNFs (0.25-5 wt%) were investigated at room temperature. The measurement of EMISE was carried out using thin film of composites in a frequency range of 8.2–12.4 GHz (X-band). The DC conductivity of composites follows the percolation scaling law with a very low percolation threshold (0.5 wt% CNF). The electrical conductivity of the PI composite increases by more than ten decades of magnitude, from 5.8×10^{-16} to 2.03×10^{-6} mho.cm^{-1} by the addition of 0.5 wt% CNF [Fig.1]. The conduction mechanism in composites is explained in the light of power law dependent current (I)-voltage (V) characteristics. The composite of 0.07 mm thickness shows EMI SE above 12 decibel (dB) at 5 wt% CNFs loading. The experimental data suggests that the prepared composites can be used for the dissipation of electrostatic charge and EMI shielding purpose.



References:

[1] Nayak, L.; Chaki, T.K.; Khastgir, D. J. Mater. Sci. 2013, 48, 1492-1502.

[2] Luonga, N. D.; Hippia, U.; Korhonenb, J. D.; Antti J. Polymer 2011, 52, 5237-5242.

Study on the Structure-Properties Relationship of Isocyanate-terminated Castor oil-based Urethane Prepolymers

T. Gurunathan[1,2], Smita Mohanty[1,2], Sanjay K. Nayak[1,2,*]
[1]ARSTPS, Central Institute of Plastics Engineering & Technology,
Guindy, Chennai 600032, India
[2]Laboratory for Advanced Research in Polymeric Materials (LARPM),
Central Institute of Plastics Engineering and Technology, Bhubaneswar 751024, India
** E-mail: drsknayak@gmail.com*

Polylactide (PLA) is an important biodegradable polymer, used for numerous applications ranging from industrial packaging to tissue engineering. However, its inherent brittleness and limited thermal stability has restricted its penetration to niche markets. In this communication, the authors demonstrate that blending of PLA with castor oil-based polyurethane prepolymer (COPUP), with the addition of COPUP dispersed in the PLA matrix can overcome the inherent brittleness of the matrix polymer. NCO-terminated castor oil-based polyurethane prepolymer was successfully synthesized which occurred subsequently mixed with different concentration of PLA matrix using melt blending technique. The interfacial compatibilization between COPUP and PLA phase happened by the reaction of NCO groups with terminal hydroxyl groups of PLA was confirmed by FT-IR peak deconvolution technique. As indicated by the results of DMA and DSC, the glass transition temperature (T_g) of PLA and COPUP shifted closer together, indicating that the blend compatibility increased. The tensile properties and notched Izod impact strength of the PLA and toughened PLA are also being investigated. With 30 wt% COPUP concentration, the elongation at break of the blend reached 377.46 %, and a notched Izod impact 269.62 J m^{-1}. With improved toughness, the PLA/COPUP blends could be used as replacements for some traditional petroleum-based polymers.

Keywords: Castor oil-based polyurethane prepolymer; polylactide; toughening; mechanical properties.

In-situ citric acid mediated tuning of Au/Polyaniline composite structures from nanosphere to nanofibre: An efficient catalyst for nitro aromatic compound reduction

Sanjoy Mondal and Sudip Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science,
2A and 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India
E-mail: psusm@iacs.res.in.

Synthesis of 1D nanostructure of polyaniline (PANI) using template or without template is relatively new in the direction of PANI research. However, the technique without using any structure directing materials (templates) is the quite challenging task as it avoids post-polymerization cleaning step to receive PANI nanostructure.

In-situ synthesis of Au/PANI composite is reported here by reduction of $HAuCl_4$ in presence and absence of citric acid (CA) by simple solution mixing method at room temperature (25 °C). In absence of CA, $HAuCl_4$ itself plays dual role as dopent as well as oxidizing agent for oxidation of aniline to form PANI. Spherical like gold nanoparticals coated with PANI layer are seen (figure 1a). In presence of CA as a secondary dopant and $HAuCl_4$ as an oxidant, fibrous worm like morphology is formed and tiny gold particals are assembled to form gold nanorods that are finely coated by PANI film. Depending upon aniline to citric acid molar concentration morphology vary from spherical to irregular assemble structure to regular worm like structure. Importantly synthesized composite show superior catalytic activity towards toxic aromatic nitro compounds reduction.

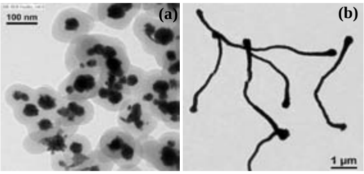


Fig.1. Au/PANI composites (a) Spherical morphology in absence of CA and (b) Worm like fibrous morphology in presence of CA.

Reference

[1] Jiaxing Huang and Richard B. Kaner *Chem. Commun*., **2006,** 367–376.

[2] Dan Li, and Richard B. Kaner *J. Mater. Chem*., **2007**, 17, 2279–2282.

New Benzoxazines from Renewable Resources for Green Composite Applications

R. Sathiyamoorthi , P. Thirukumaran and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai – 600025, India
msdre2000@yahoo.com

Fully bio-based composites composed of polybenzoxazine resins obtained from renewable natural resources (such as cardanol, furfurylamine and stearylamine) and bio-fiber such as jute fiber were prepared. The purity of the isolated cardanol was determined by Gas Chromatography (GC). The structure of cardanol and its benzoxazine monomers were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR & Mass spectroscopic analysis and its polymerization process was monitored by DSC analysis. The composites' tensile and flexural strength were measured by UTM and its impact strength was measured by IZOD impact tester respectively. The bio composite (PCF-Bzo/Jute fiber) shows superior thermal and mechanical (from TGA & DMA) properties when compared with stearylamine based composite (PCS-Bzo/Jute fiber). The surface morphologies of the fractured composites were analyzed by Scanning Electron Microscopy (SEM).

Key words: cardanol, stearylamine, furfurylamine, jute fiber.

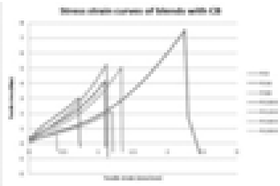
References

[1] Agag, T.; Takeichi, T. Macromolecules. **2001**, 24, 7257.
[2] Allen, D.J.; Ishida, H. J. Appl. Polym. Sci. **2006**, *101*, 2798.
[3] Yusuf Yagci, Baris Kiskan, N.Ghosh. J.Polym.sci. Part A **2009,** 47, 5565-5576.
[4] CaiFei Wang, ChunHua Zhao, J. polym.sci. Part A **2013**, 51, 2016-2023.

Characterization, curing, mechanical, Thermal behavior of NBR/PU blends

Mohammed sahal[1*], Dr. G.Unnikrishnan[2]
[1]Department of Mechanical engineering, National institute of technology,Calicut
[2]Department of Chemistry, National institute of technology ,Calicut
*mohammedsahal160@gmail.com

NBR has good oil resistant properties but inferior mechanical properties. Polyurethane has good stiffness and strength. Polyurethane was blended with NBR (up to 100 phr) and the blends were cured with Dicumyl peroxide. The curing and mechanical characteristics of NBR was investigated as a function of PU loading in the presence and absence of carbon black (CB).The addition of PU to NBR increased the cure rate of both unfilled and CB filled NBR.The mechanical properties of the blends enhanced substantially in the presence of CB .There was a fivefold increase in tensile and tear properties of the NBR/PU blends in the presence of CB along with a notable increase in SHORE A hardness.TGA analysis of blends were carried out. The hold temperature was upto 600°C.Results indicated an increase in thermal stability of NBR/PU blends in the presence of CB.



Investigation of SEM micro graphs of NBR containing PU indicated phase separation in the micro level. Addition of CB to NBR/PU blends homogenized the blend morphology to a certain extent, reduced the phase separation which could be the reason for the enhancement of mechanical properties and thermal stability of the NBR/PU blends.

References:

[1] C Radhesh kumar, Karger-Kocsis J. European Polymer Journal 38 (2002) 2231-2237
[2] T. Biswas, A. Das, S.C. Debnath, N. Naskar, A.R. Das, D.K. Basu. European Polymer Journal 40 (2004) 847-854
[3] Degrange J-M, Thomine M, Kapsa Ph, et al. Wear 2005; 259:6 84-92.
[4] Haiyan Moua, Fei Shen , Qingfeng Shi , Yizhou Liu , Chifei Wua, Weihong Guo. European Polymer Journal 48 (2012) 857-865

Oriented Crystallization of Polyethylene Templated by Vertically Aligned Carbon Nanotube Arrays

Sayan Ganguly[1], Santanu Chattopadhyay[1], Paul E Sokol[2] and N. C. Das[1]*
[1]Rubber Technology Centre, Indian Institute of Technology, Kharagpur
[2]Department of Physics, Indiana University, Bloomington, USA
*ncdas@rtc.iitkgp.ernet.in

Anisotropic mechanical, thermal and electrical properties of aligned carbon nanotubes (CNTs) are attractive for many potential applications such as ultrafast all-optical switches, EMI shielding, photovoltaic devices, gas sensors, and biocatalytic films [1]. Forming composites with polymer is one way to stabilize CNT arrays for applications. If the matrix is a crystalline polymer, CNTs can affect polymer crystallization [2]. CNTs-induced polymer crystallization has been studied in many polymeric systems such as polypropylene (PP), polyethylene (PE) and poly(vinyl alcohol) (PVA), etc. [2-5]. Epitaxialgrowth of PE on CNTs to form periodic crystal decoration has been observed in solutions [6]. The alignment order of vertically aligned CNTs on a flat surfaceusing small-angle x-ray scattering (SAXS) /small-angle neutron scattering (SANS) and SEM was reported [7]. In this work,we investigatealignment of VACNTs (Fig.1.) as well as templated crystal growth among VACNT arrays in bulk, where crystals orientation varies with the height from the substrate, following the alignment order of VACNTsusing SAXS/WAXS and SEM.

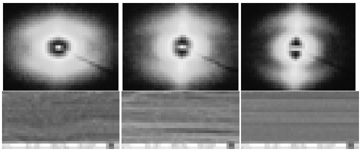


Fig.1: .2D SAXS scattering patterns (Top row), SEM images (bottom row) of CNTs morphology at 0.5, 3.5, and 6.0 mm from the substrate.

References:

[1] Rege, K.; Raravikar, N.R.; Kim, D.Y.; Schadler, L.S.; Ajayan, P.M.; Dordick, J.S. *Nano Lett.* **2003**, *3 (6),* 829-832.

[2] Haggenmueller, R.; Fischer, J.E.; Wine, K. I. *Macromolecules* **2006**, *39,* 2964-2971.

[3] Li, L.; Li, C.Y.; Ni, C. *J. Am. Chem. Soc.***2006**, *128*, 1692-1699.

[4] Li, L.; Li, C.Y.; Ni, C. *J. Am. Chem. Soc.***2006**, *128*, 1692-1699.

[5] Bhattacharyya, A.R.; Sreekumar , T.V.; Liu, T.; Kumar, S.; Ericson, L.M.; Hauge, R.H.; Smalley, R. E. *Polymer***2003**, *44*, 2373-2377.

[6] Wang,Benjamin N.; Bennett, Ryan D.; Verploegen, Eric.; Hart, Anastasios J.; Cohen, Robert E. *J. Phys. Chem. C*, **2007**,*111 (16),* 5859-5865.

[7] Das, N.C.; Yang, K.K.; Liu, Y.; Sokol, P. E.; Wang, Z.G.; Wang, H. J. Nano. Sci. Nanotechnology, **2011**, 11(6), 4995-5000.

Exploring the Potentiality of Agro-waste Based Plant: Green Composite from Saccharum spontaneum and Polypropylene to find its Application in Industrial Sectors

Ansuman Barman[a], Bhanu Bhushan Khatua[b*] and Bidhan Chandra Ray[c]
[a] Central Institute of Plastics Engineering & Technology, City Centre, Haldia (India)
[b] Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302 (India)
[c] Retd. Professor, Department of Chemistry, Jadavpur University,
(Res) Ananda Niketan, 27B East Road, Kolkata – 700 032 (India)
E-mail: khatuabb@matsc.iitkgp.ernet.in

Saccharum spontaneum, commonly known as Kaans grass (KG) can spontaneously grow in both fertile and poorer soil, normally considered as agricultural waste or weed. This plant has no specific application till date and left in the field as unattended, mostly used as cattle feed or fuelling in domestic purpose. It is tried to fabricate green composite using this plant, kaans grass as reinforcing filler (KG-filler) and polypropylene using maleic anhydride grafted compatibilizer (PP-g-MA). Effective interaction and thereby improved surface adhesion between the KG-filler and base polymer matrix, polypropylene were achieved by the coupling agent. The properties and performances of the composite were optimized with maximum KG-filler loading to minimize the cost. Study of tensile and impact strength showed significant improvement in both the properties due to reinforcement of KG-filler in the base polymer matrix. Dynamic mechanical analysis (DMA) showed reasonable increase in storage modulus and loss modulus, while the damping factor (tan δ) had no major deviation from the base polymer in the composites. Thermal analysis by TGA showed slight deviation in thermal stability only at higher KG-filler loading. FT-IR and morphological data by scanning electron microscopy (SEM) suggest interfacial interaction with the consequent strong adhesions between KG-filler and the polymer matrix. Melt flow properties confirmed the processability of PP-KG composite even with 60 phr filler content. Finally, this new composite has similar properties with other green composite family members derived from various natural resources and polymers. Thus, the fabricated green composite may find parallel applications in industrial sector like decking, railing, fencing, door and window frame, automobile parts etc.

Key words: Saccharum spontaneum, dynamic mechanical analysis, thermo-gravimetric analysis, maleic-anhydride grafting, reinforcement

References:

[1] Barman, A.; Shrivastava, N. K.; Khatua*, B. B.; Ray, B. C.; Green Composites Based on High-Density Polyethylene and Saccharum spontaneum: Effect of Filler Content on Morphology, Thermal, and Mechanical Properties. Polym. Composite. Published online in Wiley Online Library on 05-Jul-2014.

[2] Dányádi, L.; Janecska, T.; Szabó, Z.; Nagy, G.; Móczó, J.; Pukánszky, B.; Wood flour filled PP composites: Compatibilization and adhesion. Compos. Sci. Technol. 2007, 67, 2838–2846.

[3] Mirmehdi, S.M.; Zeinaly, F.; Dabbagh, F.; Date palm wood flour as filler of linear low-density polyethylene. Compos. Part B-Eng. 2014, 56, 137–141.

Extruded Polymers/Blends/Composites Cooled In Water: A Study of Heat Transfer

Rakesh Kumar*[1], Rajnish Kumar[1], Osei Ofosu[2]
[1]Birla Institute of Technology, Mesra, Patna Campus, Patna - 800014, India
[2]CSIR Materials Science and Manufacturing, P.O. Box 1124, Port Elizabeth 6000, South Africa
*E-mail: krrakesh72@gmail.com

The commodity articles from native polyethylene (PE) and polypropylene (PP) or blends PP and PE as well as composites of PP and PE are widely used. To reduce the carbon footprint, native biopolymers such as polylactic acid (PLA) or its composites are explored as commodity plastics. All these polymers / blends / composites have to be extruded before the fabrication of end products. In this work, a heat transfer study from extruded polymer (PP and PE) to water used for cooling is carried out. In experimental study, the temperature of still water used for cooling after 1, 5 and 10 min were determined and it was correlated with the mathematical data. The extruded polymer interacts with air before being cooled in water. It has been observed that once the extruded polymer is immersed in still water there is maximum increase of 5°C in the temperature of still water (Figure). All the polymers (PP, PE and PLA) used in this work irrespective of the properties follow the same trend of heat transfer to water. Heat transfer study indicates that the most of the cooling of extruded polymer occurs by radiation while very less cooling occurs by conduction.

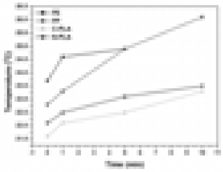


Figure - Temperature of still water at different time intervals after extruded PE, PP and PLA are immersed. Here C-PLA and N-PLA represent two grades of PLA.

Acknowledgement
I am grateful to the University Grant commission (UGC), New Delhi, India for granting me the Start-Up-Grant-Research-Fund because of which I am able to deliver the oral presentation in this conference.

Environmentally Degradable Polyethylene (HDPE)

Devendra M. Sonawane, ICT Mumbai

High Density Polyethylene (HDPE) is widely used in packaging application such as shopping bag, carrier bag, etc. But, waste generated from polyethylene bags is not suitable either for composting or land filling, because they are essentially non- biodegradable. Research is going on to find out oxo- degradable HDPE film for making shopping bag, counter bag or industrial sacks. The project deals with synthesis of catalyst or pro- oxidant to make HDPE Film degradable. The pro-oxidant filled HDPE film will be characterized for Fourier transform infrared spectroscopy (FTIR), QUV Weatherometer, Scanning Electron Microscope (SEM).

Keywords: HDPE, degradation, pro- oxidant.

Probing Surfactant Level Influence during Polyurethane Foaming using Surface Shear Rheology

Nilanjon Naskar[1], Chandan Sharma[1], Abhinav J. Jain[1], GHarikrishnan[1*]
[1]Department of Chemical Engineering, IIT Kharagpur
*nilanjonnaskar92@gmail.com

Surfactant plays a pivotal role in the stability of reactive polyurethane foaming.Current focus towards synthesizing polyurethane foam from bio-renewable resources has made vegetable oils a suitable candidate for replacing petroleum derived polyol. Castor oil is considered to be a prominent substitute as it has inherent hydroxyl groups. However, such renewable resources need alternative surfactant systems for ensuring the stability of foam. We have studied the influence of selected surfactants. Surface shear rheology was employed to study the in-situ development of surface viscoelasticity of non-foaming system and normal stress analysis were done for foaming system and both these results were combined together to predict various foaming transitional parameters. Scanning Electron Microscopy was used to study the residual parameters of cured foam and the upper limit of predictions were compared. It was observed that the foam height reduced in case of polyol based PUF, while it increased in case of castor oil based PUF.

References:

[1] Owen, M. J.; Kendrick, T.C.; Kingston, B.M.; Lloyd, N.C. J. Colloid Interface Sci. **1967**, 24, 141-150.
[2] Kaushiva, B.D.; McCartney, S.R.; Rossmy, G.R.; Wilkes, G.L. Polymer **2000**, 41, 285-310.
[3] Zhang, X.D.; Macosko, C.W.; Davis, H.T.; Nikolov, A.D.; Wasan, D.T. J. Colloid Interface Sci.**1999**, 215, 270-279.

Synthesis and characterization of camphor sulphonic acid dopedPolyaniline-MoO$_3$ nanocomposite

S Dhanavel[1], E A K Nivethaa[1], V Narayanan[2] and A Stephen[1,*]
[1]Material Science Centre, Department of Nuclear Physics, University of Madras,
Guindy Campus, Chennai-25, India.
[2]Department of Inorganic Chemistry, University of Madras,
Guindy Campus, Chennai 600 025, India
*E-mail- *stephen_arum@hotmail.com*

Nowadays, Intrinsically conducting polymers(ICP), have elicited much interest due to its good conductivity, solubility and easy preparation. These ICP's include polythiophene, polyacetylene, polyaniline and polypyrrole, etc.,[1] Among these, polyaniline has considerable interest because of its environmental stability, electrochemical, optical, electrical and redox properties and various possible applications like rechargeable batteries, biosensors, electrochromic devices and photocatalytic material[2,3].A nanocomposite of Camphor sulphonic acid doped polyaniline-MoO$_3$ nanocomposite was prepared by chemical oxidative polymerization method. The prepared sample was characterized and evaluated by X-ray diffraction analysis(XRD), FTIR, HR-TEM analysis. The XRD pattern showed the semicrystalline nature of polyaniline and also the diffraction peaks to be in good agreement with the structure of MoO$_3$. The FTIR pattern shows the various stretching and bending modes of Polyaniline. And also UV-Vis and FESEM revealed the successful formation of Polyaniline-MoO$_3$ composite.

Keywords: polyaniline, MoO3, FTIR, Uv-Vis analysis

References:

[1] Taylor and Francis Group. In: SkotheimT.A.;Reynolds J.R. (Eds.), Hand-book of conducting polymers, vols. I and II, Third edition, CRC press, New York, **2007**.
[2] SambhuBhadra, D'pakKhastgir, Nikhil K. Singha, JoongHee Lee, Prog. Polym. Sci. **2009**, 34, 783-810.
[3] Nafday R. A.; KelkarD.S.Thin solid films, **2005**, 477, 95-99.

Chitosan/silver/gold nanocomposite for the colorimetric sensing of Hg

E A K Nivethaa[1], S. Dhanavel[1], V Narayanan [2], and A Stephen[1,*]
[1]Material Science Centre, Department of Nuclear Physics, University of Madras,
Guindy Campus, Chennai-25, India.
[2]Department of Inorganic Chemistry, University of Madras,
Guindy Campus, Chennai 600 025, India
E-mail: stephen_arum@hotmail.com

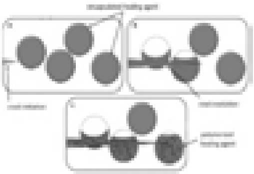
The need for ecofriendly materials that can be used in potential applications like the sensing of harmful pollutants and can be used as a material that can be used directly or indirectly for the treatment of the diseases caused due to the exposure to harmful pollutants has motivated the search of such materials. Chitosan/silver/gold nanocomposite is one such material which can be used as a colorimetric sensor as well as for the photothermal therapy and as a drug delivery carrier. Chitosan/silver/gold nanocomposite was synthesized successfully using a simple and cost effective chemical reduction method. The XRD pattern of the nanocomposite shows the semicrystalline nature of chitosan and the face centered cubic structure of silver and gold. The HRTEM images show the formation of a polymer matrix nanocomposite structure with chitosan as the matrix and gold and silver as the filler phase. The average particle size as calculated from the HRTEM images is ~ 8 nm. The shifts and change in the intensity of the peaks corresponding to $NH_3^+$and N-H show the binding of silver and gold nanoparticles to the NH_2 groups of chitosan. The EDAX spectra of the composite confirms the presence of both silver and gold in it. The UV-Vis spectra shows a single peak whose intensity increases with the increase in the weight percentage of gold and silver in the composite. Application of the nanocomposite as a colorimetric sensor was studied and its use for the successful detection of mercury was observed by a visible change of colour from violet to wine red.

References:

[1] DaizyPhilipTrendsSpectrochimicaActa Part A**2009**, 73, 374–381.
[2] YongmingGuo, Zhuo Wang, WeisiQub, Huawu Shao, Xingyu Jiang Biosensors and Bioelectronics **2011**,26, 4064–4069.Hall, Damien.; Minton, Allen P. Biochimica et Biophysica Acta.**2003**, 1649, 127-139.

Preparation and Characterization of Self-healing composites

Failure in materials starts in the form of an internal micro/nano crack. Most of the times, locating such a crack is difficult and it is rather impossible to fix it. As a possible solution, we have successfully developed composite material that can autonomously heal itself in case of damage events. The concept of self-healing in materials is realized by incorporating a plurality of microcapsules in the composite. These microcapsules comprise of a liquid healing agent and an outer shell wall. Whenever a crack propagates, it ruptures the capsules. The healing agent then comes out into the crack due to capillary action and polymerizes thereby bridging the crack as shown in the adjacent diagram.



The microcapsules were prepared using a solvent evaporation induced phase separation technique. The shell wall material is PMMA (polymethylmethacrylate) and the healing agent can be any polymer resin or amine based hardener. We chose DGEBA (Digylcidal Ether of Bisphenol A) as the polymer resin and TETA (Triethylenetetramine) as the hardener and prepared microcapsules of both types. For morphological, chemical and mechanical characterization, we have used capsules of average size 217µm and 117 µm. we have incorporated 5 wt% and 7 wt% of microcapsules to prepare the self-healing composite samples (for tensile and bending tests).

- **FESEM** images show good size and surface morphology of the microcapsules (Fig.2).
- **TGA/DTA** studies indicated high thermal stability of the capsules.
- **FTIR spectroscopy** confirmed proper encapsulation of the healing agent.
- **Tensile tests** (ASTM D638) reveal that the tensile strength of the self-healing composites decreases with respected to neat resin samples (without capsules). The tensile strength also decreases if we increase the percentage wt. of microcapsules in the system.
- **3-point bending tests** (ASTM 5045) indicate that smaller the size of the microcapsules, higher is the fracture toughness of the self-healing composite.
- We have achieved an average **healing efficiency of 82 %** for the composites by allowing a micro-crack to propagate though a SENB sample and then allowing it to heal itself.The decrease in tensile strength can be negotiated by lowering the size of the capsules to nano level. Healing efficiency can be further increased by using different combination of healing agent and base matrix. **This technology once properly validated can be used in coatings, paints, adhesives, aerospace, biomedical, sports and other engineering applications.**

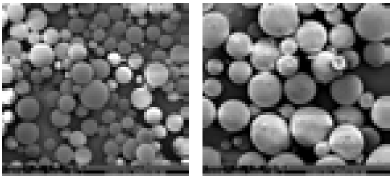


Fig 2: showing FESEM images of (a) DGEBA microcapsules (b) TETA microcapsules

Exploring the role of copper terephthalate metal organic framework towards improving the energy absorption characteristics of epoxy thermosets

Saurabh Chaudhary[1], Manju[1,2], Surekha Parthasarathy[1],
Arunachala Ramanan[2], Prasun. Kumar. Roy[1]*
[1]Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India
[2]Department of Chemistry, Indian Institute of Technology Delhi, New Delhi-16, India
*pk_roy@yahoo.com

We have explored the energy absorption characteristics of CuTPA.DMF (metal organic framework) filled epoxy composites, for potential application as a blast mitigating retrofitting polymer coating. CuTPA.DMF was synthesized by the solvothermal procedure in the presence of N,N- Dimethyl formamide (DMF). The porous CuTPA.DMF was homogeneously dispersed in the epoxy resin by ultrasonication (0.1-0.7%) w/w which were cured using triethylene tetraamine hardener to prepare MOF reinforced composites. Structural and thermal characteristics of the composites were evaluated and the mechanical properties were determined under different strain rate regime. High strain rate studies (~10^3 s^{-1}) of selected compositions were performed on a Split Hopkinson pressure bar and the effect of addition of CuTPA.DMF on the energy absorption characteristics were established. Our studies revealed that introduction of CuTPA.DMF at low loadings (0.5%) lead to an increase in the toughness of the base resin but with increase in the extent of loading, the mechanical properties deteriorated. Neat epoxy samples fractured in a brittle fashion, but in the presence of CuTPA.DMF, the sample exhibited ductile failure, which was explained on the basis of a crack pinning mechanism.

References:

[1] Yot, P. G.; Ma, Q.; Haines, J.; Yang, Q.; Ghoufi, A.; Devic, T.; Serre, C.; Dmitriev, V.; Ferey, G.; Zhong, C.; Maurin, G. *Chemical Science* **2012**, *3*, 1100.

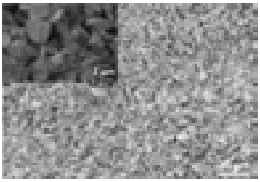
[2] Elangovan, D.; Nidoni, U.; Yuzay, I. E.; Selke, S. E. M.; Auras, R. *Industrial and Engineering Chemistry Research* **2011**, *50*, 11136.

[3] Manju; Roy, P. K.; Ramanan, A.. *RSC* Advances **2014**, *4*, 17429.

Tough epoxy nanocomposites with two- dimensional molybdenum disulphide

Saurabh Chaudhary, Surekha Parthsarthy, Rajesh Chopra,
Prasun Kumar Roy
Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India
pk_roy2000@yahoo.com

Two-dimensional (2D) transition metal dichalcogenide offer unique opportunities to tailor the mechanical, thermal, electronic, and optical properties of polymer nanocomposites. In the present work, bulk molybdenum disulfide (MoS_2) was exfoliated into nanoplatelets, and subsequently dispersed in a cycloaliphatic epoxy resin at low loading fractions (< 1% w/w). The tensile and fracture properties of the nano composites were determined which revealed that MoS_2 nanoplatelets are highly effective at enhancing the mechanical properties of the epoxy at very low nanofiller loading fractions (below 0.3 % w/w). The was found to increase from 34 MPa to The tensile strength and G_{IC} increased by 41 % and 50 % respectively on introduction of 0.3 % nano filler. This was also accompanied with an increase in the tensile modulus (~ 40%) with no decrease in glass transition temperature. Our results clearly highlight the potential of 2D nanoplatelets as reinforcing filler in polymeric composites. Post-mortem morphological studies of the fracture surfaces were performed to arrive at the principal toughening mechanisms behind the experimental findings.



SEM micrographs of molybdenum disulfide. Inset shows the filler at high magnification

References:

1. EKsik,O.; Gao,J.; Shojaee,A.; Thomas,A.; Chow,P.;Bartolucci,F.;Lucca,D.A.;Koratkar,N.; *acs nano*; **2014**,doi: 10.1021/nn5014098
2. Matusinovic, Z.; Shukla,R.; Manias,E.;Hogshead,C.G.; Wilkie,C.A.; *Polym. Deg. & stab*; **2012**.97,2481
3. Chaudhary,S.; surekha,P.; Kumar,D.; Roy,P.K.; *Polym. Compos.* , **2014**, doi: 10.1002/p.c.22927

Synthesis of Interpenetrating Polymer Network (IPN) from Epoxydized Soybean Oil (ESO) based Polyurethane (PU)

Subhajit Das[1], Dr. Smita Mohanty[2], Dr. S. K. Nayak[3]
[1, 2] Laboratory for Advanced Research in Polymeric Materials (LARPM),
Patia, Bhubaneswar 751 024, India.
[3] Central Institute of Plastics Engineering & Technology, Guindy, Chennai 600 032, India
Email: subhajit.now2013@gmail.com

Due to rapid exhaustion of fossil fuel, it's the time to think about some alternate sources, majorly green sources i.e. bio-based or vegetable oils. Among different bio-based resources, vegetable oils are rather cheap, easily available & above all eco-friendly. Various vegetable oils are available in the market such as soybean, castor, linseed, jatropha etc. –OH group, which is as such absent, should be introduced first in soybean oil to make it polyol. PU can be synthesized from this mentioned polyol & finally the desired IPN is produced from the PU. Soyban oil in an epoxidized form i.e. ESO is commercially available.

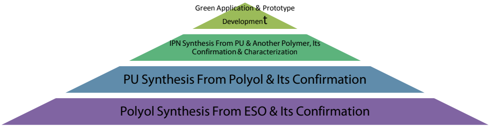
Polyol, synthesized from commercially available ESO [1], is confirmed by FTIR spectra [2] [3]. Then polyurethane is synthesized using this polyol, isophorone diisocyanate and DBTDL catalyst [4] & confirmed by FTIR as well [5]. The synthesized PU is thermoplastic in nature & easily soluble in acetone or MEK, which is further used for making the PU desolve to carry out the synthesis of IPN.

Now it's the turn to produce IPN from the synthesized PU & examined its mechanical properties like tensile strength, flexural, impact, shear, pencil hardness, scratch resistance; optical properties like refractive index, haze, clarity, gloss; thermal properties like DSC, TGA, DMA, flammability; electrical properties like dielectric, dissipation factor, surface resistivity; morphology like SEM.

IPN have been synthesized using that PU along with another polymer with an initiator & crosslinker [4]. The prepared product is transparent and flexible after curing. The synthesized IPN is confirmed by FTIR and SEM study.

Prototype application of the formed IPN may be in the field of coating like paint or adhesive.

TOTAL PROCESS IN BRIEF



Keywords: Vegetable oil, IPN, curing, coating

References:

[1] Thomas F. Garrison, Michael R. Kessler, Richard C. Larock. Polymer. **2014**, 55,1004 – 1011.
[2] Miray Sakarya, Sennur Deniz. Akademik Platform. **2014**, 1394 – 1402.
[3] A. A.Beltrán, L.A.Boyacá. Latin American Applied Research. **2011**, 41, 69 – 74.
[4] P Mallu, Siddaramaiah, R Somashekar. Bull. Mater. Sci. **2000**, 23, 413 – 418.
[5] Stefan Oprea, Veronica Oprea. Materiale Plastice. **2010**, 47, 54 – 58.

Toughening of vinyl ester with core-shell poly(siloxane)-vinyl ester microspheres

Nahid Iqbal[1], Devendra Kumar[1], Prasun K Roy[2]
Department of Applied Chemistry and Polymer Technology,
Delhi Technological University, Delhi 110042, India
Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India
pk_roy2000@yahoo.com

We have explored the potential of core-shell poly(siloxane)-epoxy microspheres towards improving the dynamic properties of a conventional vinyl ester resin. Poly(siloxane) microspheres were prepared by suspension polymerisation of vinyl terminated siloxane, where the particle dimensions could be tailored by varying the operating parameters, particularly stirring speed and feed concentration. The core was subsequently coated to introduce an external sheath compatible with the vinyl ester resin, with an aim to aid its homogeneous dispersion in the thermosetting resin. Toughened VE composites containing varying amounts of both coated and uncoated microspheres were prepared by curing under ambient conditions, and their mechanical properties were evaluated under both quasi-static and dynamic loading conditions. The introduction of coated poly(siloxane) led to a proportional decrease in the tensile strength and modulus. Significant improvements in the impact strength of USP could be achieved, which corroborated with significant increase in mean critical stress intensity factor. Morphological investigations of the fractured surface revealed the presence of characteristic features which were used to establish the underlying routes responsible for the toughened nature of the VE composites.

References:

[1] Roy P, Iqbal N, Kumar D, Rajagopal C (2014) Polysiloxane-based core-shell microspheres for toughening of epoxy resins. J Polym Res 21 (1):1-9. doi:10.1007/s10965-013-0348-5

[2] Bagheri R, Pearson RA (2000) Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance. Polymer 41 (1):269-276

Compressive behaviour of epoxy syntactic foam containing hollow epoxy microcapsules

A.V. Ullas [1], Devendra Kumar[1], Prasun K. Roy[2]
[1]Department of Applied Chemistry and Polymer Technology,
Delhi Technological University, Delhi 110042, India.
[2]Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India
pk_roy2000@yahoo.com

In this paper, we demonstrate the successful application of interfacial engineering for the preparation of spherical microcapsules containing liquid epoxy resin in the core. The approach relies on the preferential reaction of polydimethylsilicone insoluble epoxy resin and amine based hardener to form a crosslinked spherical polymer at the interface, when used in non-stoichiometric amounts, leaving the excess epoxy largely unreacted within the core. Among the various features, tailorability is the biggest advantage of this route as both the core-content and particle dimensions can be altered by varying the operating parameters, particularly stirring speed and resin:hardener ratio. The encapsulated epoxy can be subsequently removed from the core by solvent extraction in toluene. Spherical microcapsules with a core content of 25 % could be obtained when the reaction was carried out at 600 rpm, while maintaining the medium at 70 °C at resin: hardener:: 100: 2. Epoxy syntactic foams containing hollow epoxy microcapsules were prepared by room temperature curing of cycloaliphatic epoxy with triethylene tetramine. The effect of microcapsule concentration on the compressive behaviour of the foams was investigated.

References:

[1] Yu X, Zhang C, Ni Y, Zheng S.. J Appl Polym Sci. 2013;128,2829-39.
[2] Rao CNR, Kulkarni GU, Agrawal VV, Gautam UK, Ghosh M, Tumkurkar U.J Colloid Interface Sci. 2005,289,305-18.

Implementation of a Tri-block Copolymer towards Designing an Aqueous Two-phase system

Arabinda Chakraborty and Kamalika Sen*
Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700 009, India
*kamalchem.roy@gmail.com

A completely new aqueous biphasic system was obtained by mixing an aqueous solution of a tri-block copolymer poly (propylene glycol)-block-poly (ethylene glycol)-poly (propylene glycol) [PPG-PEG-PPG] with an aqueous solution of an inorganic salt disodium tartrate. A wide range of biphasic region was found for various concentrations of the copolymer (30-90) w/w% and sodium tartrate 1-2 M. The phase diagram of the two-phase system was constructed by simple turbidometric titration method at 298 K[1]. Binodal curve was obtained for the biphasic compositions of PPG-PEG-PPG (40 % w/v) and Na-tartrate (1.4 M) system. The component predominantly in the bottom phase was plotted in the abscissa (Na-tartrate) and the component predominantly in the top phase was plotted as the ordinate (PPG-PEG-PPG). The experimental binodal curves were further fitted by the following equation proposed by Merchuk et al :

$$Y = A\exp[(BX^{0.5}) - (CX^{3})] \qquad (1)$$

The tie-lines(TL) associated with the phase diagrams were obtained by a simple gravimetric method. Each TL was determined by the lever-arm rule through the relationship between the top phase composition and the overall system composition and for which a system of four equations and four unknown factors were solved. The tie-lines were correlated using Othmer-Tobias and Bancroft equation. An acceptable agreement between the calculated and experimental tie-line data was obtained.

References :

[1] Hatti-Kaul R. Methods in Biotechnology: Aqueous Two Phase Sytems, Methods and Protocol, Humana Press, Totowa New Jersey, **2000**, 11.

[2] Chakraborty A.; Sen K. L-Proline Based Aqueous Biphasic System: Design and Application to Isolate the Alkaline Earths J. Chem. Eng. Data. **2014**, 59, 1288-1294.

Chemical modification of thermoplastic starch by reaction with MDI

Sukhila Krishnan[1*], Smita Mohanty[1] and Sanjay K.Nayak[1]
[1]Laboratory for Advanced Research in Polymeric Materials (LARPM),
Central Institute of Plastic Engineering and technology (CIPET), Bhubaneswar,Odisha, INDIA
*sukhilaajith@gmail.com

Starch is a biopolymer that is extensively accessible from agriculture/nature and thus is renewable and cheap. Also, starch-based materials are biodegradable, providing a great advantage over traditional non-biodegradable synthetic polymers. Though, the poor processibility and product performance of starch have greatly hindered the extensive application of starch in real applications. Currently, thermoplastic starch (TPS) has been used as an substitute for synthetic plastic in several commercial products. But, TPS shows some limitations mainly due to its brittle and hydrophilic nature, which has to be resolved to widen its application.The objective of the work we report here was to initiate a chemical modifications on TPS and to build up a process to control its chemical structure using a solution process which can reduce its water sensitive properties.(1,2) The method involves in cleavage of starch amylose and amylopectin chain backbone to plasticize with glycerol and water in batch mixer and then the prepared TPS was reacted in solution with diisocyanates i.e, 4,4'-Methylenediphenyl Diisocyanate (MDI).This diisocyanate was used before with great success for the chemical modification of TPS surface. The method utilized here will form an urethane linkages between reactive isocyanate groups (–NCO) and hydroxyl groups (-OH) of starch aswell as of glycerol. Finally, new polymer synthesised shows a reduced crystallinity, less hydrophilic and enhanced compatibility with other polymers. The TPS was prepared by Haake Rheomix 600 batch mixer with roller rotors operating at 50 rpm. The produced material is then refluxed for 5hrs with MDI in toluene with constant stirring. These materials produced are characterized by Fourier Transform Infrared Spectra (FTIR), DSC, X-Ray diffraction and mechanical tests.

References:

[1]. Avérous, L., Frigant, C., Moro, L., **2001**. Plasticized starch–cellulose interactions in polysaccharide composites. Polymer 42, 6565–6572

[2]. Dufresne, A., Vignon, M.R., **1998**. Improvement of Starch film performances using cellulose microfibrils. Macromolecules 31,2693–2696.

Microencapsulation of healing agents for self-healing applications

Manorama Tripathi[1,2], Raman Dviwedi [2], Devendra Kumar[2],
Prasun Kumar Roy[1]*,
[1]Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi-110054, India
[2]Department of Applied Chemistry and Polymer Technology,
Delhi Technological University, Delhi-110042 India
*pk_roy2000@yahoo.com

Different healing agents (cycloaliphatic epoxy and unsaturated polyester (UPR)) were encapsulated in poly(urea-formaldehyde) (PUF) shell by emulsion polymerisation route[1]. Morphological investigations reveal the rough texture of spherical microcapsules, which was attributed to the presence of protruding polymer nanoparticles on the surface. The core content of the microcapsules both for epoxy and UPR, as evaluated by solvent extraction technique[2] was found to be 55-65%, irrespective of the healing agents being encapsulated. The curing kinetics of self-healing epoxy compositions was also investigated by non-isothermal differential scanning calorimetric (DSC) studies. The studies highlighted the autocatalytic nature of epoxy curing, which remained unaltered due to introduction of the above-mentioned fillers. The kinetic parameters were determined using both Friedman and Kissinger–Akahira–Sunose (KAS) method, which were used to predict the curing behaviour of compositions at higher heating rates using KAS method. Epoxy composites containing microcapsules (5-20% w/w) and appropriate curing agent were prepared and their mechanical properties were studied under both quasi-static and dynamic loadings. The tensile and impact properties were adversely affected due to incorporation of the microcapsules, while substantial improvement in the fracture toughness of the base matrix was observed. The self-healing efficiencies were quantified in terms of the ratio of impact strengths of healed and virgin specimens. The healing efficiency increased with increasing amount of microcapsule in the formulation and reached maxima (103 ± 5 %) at 20 % (w/w) loading.

References

1. Blaiszik, B.J. Sottos, N. R. White, S.R. Compos. Sci. Tech. 2008,68, 978-986
2. Yuan, L. Liang, G. Xie,,J. Liand, L. Guo, J. *Polymer* 2006, 47, 5338-5349 .

Fabrication and Characterization of Monomer and Radiation Modified Bioresorbable Polymeric Composite

Kamol Dey[1]*, Sumon Ganguli[1], Ruhul A. Khan[2] and Mubarak A. Khan[2]
[1]Department of Applied & Environmental Chemistry, Faculty of Science,
University of Chittagong, Chittagong-4331, Bangladesh
[2]Institute of Radiation and Polymer Technology,
Bangladesh Atomic Energy Commission, Savar, Dhaka-1000, Bangladesh
*kamoldey@cu.ac.bd

Bioresorbable composite has gained tremendous interest in the field of biomaterial research. Ionizing radiation offers unique advantages for the modification of polymers for biomedical applications [1-2]. In the present study, bioactive and biocompatible natural polymers chitosan and gelatin (G) were used to prepare bioabsorable composite film through solution casting process followed by UV irradiation with different dose strength. 2-hydroxyethyl methacrylate (HEMA) was used as a cross-linking monomer onto chitosan polymer and phosphate glass (PG) as an inorganic reinforcement filler into gelatin polymer. Four different formulations (namely F1, F2, F3 and F4) were developed varying the concentration of HEMA and solvent methanol (MeOH) along with fixed quantity of photoinitiator to treat the chitosan film. On the other hand, gelatin based composite films were prepared varying mass ratio of G, PG and HEMA. Incorporation of PG and HEMA improved the mechanical properties of the gelatin based composite film. At the same time, the investigated chitosan film was prepared in 2% acetic acid solution and the film was soaked into four formulations for various time spans to investigate the effect of monomer concentration and soaking time on the performance of chitosan composite film. UV radiation was employed to induce cross-linking and photo-grafting. The evidence of cross-linking was provided by Fourier Transform Infrared Spectroscopy. The results regarding monomer concentration as well as UV dose strength on the yield of cross-linking were presented in terms of polymer loading, mechanical performance, water absorbance and thermal stability. The prepared composite films would have a potential use in biomedical application.

References:

[1] Saba, N.; Tahir, P.; Jawaid, M. Polym. **2014**, 6, 2247-2273.

[2] Hussain, A.; Takahashi, K.; Sonobe, J.; Tabata, Y.; Bessho, K. J. Maxillofac. Oral Surg. **2014**, 13(1), 29–35.

Polyacryloyl Hydrazide based pH sensors and ion exchange coatings

Rewati Raman Ujjwal, Anuj Kumar, Umaprasana Ojha*
Department of Chemistry, Rajiv Gandhi Institute of Petroleum Technology,
Raebareli Ratapur Chowk, UP-229316, India
*Email -uojha@rgipt.ac.in

Polyacryloyl hydrazide (PAH) was used for the synthesis of ion exchange epoxy resins and polymer-dye conjugates. PAH was cured with Bisphenol A diglycidyl at 65 °C to prepare defect free and transparent epoxy resins. Epoxy resins displayed superior mechanical properties (tensile strength = 1–42 MPa, ultimate elongation = 2–72%) compared to the commercially available epoxy resins. Intersetingly, the resins exhibited a glass transition temperature around 67° C suggesting the shape of the resins may be modified above this temperature. However, overall reshaping may not be possible due to the presence of inherent chemical cross-links in the samples. PAH was conjugated with a suitable azo dye at room temperature to synthesize pH sensors for aquous solutions. The sensing was visible to necked eye through distinct color change. Acidic pH up to 4.5 and basic pH up to 9.9 could be effectively sensed using the above material.

Key Words: Polyacryloyl hydrazide, Epoxy resins, Bisphenol A diglycidyl.

Reference:

1. Kumar, A.; Ujjwal, R. R.; Mittal, A.; Bansal, A.; Ojha, U. *ACS Appl. Mater. Interfaces* 2014, *6*, 1855-1865.

Preparation and characterization of novel nanostructured polyamide 6/fluoroelastomer thermoplastic vulcanizates

Shib Shankar Banerjee[1] and Anil K. Bhowmick[2]*
[1]Department of Materials Science and Engineering, School of Engineering and Technology, Indian Institute of Technology Patna, India
[2]Rubber Technology Centre, Indian Institute of Technology Kharagpur, India.
*anilkb@rtc.iitkgp.ernet.in

Present work reports the development of novel nanostructured polyamide 6 (PA6)/fluoroelastomer (FKM) thermoplastic vulcanizates (TPVs) using batch mixing followed by micro-injection molding. Evolution of structure and physical properties at different stages of mixing and dynamic vulcanization were captured. Size of the dispersed FKM phase in continuous PA6 matrix decreased from ~ 450 to ~ 130 nm with increasing degree of cure and mixing time. In addition, tensile strength and Young's modulus increased (60 % and 65 % respectively) with increasing mixing time (1 min and 4 min). The role of injection molding in transforming the morphology and hence properties of these vulcanizates drastically was investigated for the first time. Nanometer-sized FKM particles (60-80 nm) were developed in TPVs after injection molding, which were clearly reflected from scanning electron microscopy and atomic force microscopy and also theoretically supported from the visco-elastic drop break up mechanism. Significant improvement of tensile properties of PA6/FKM blends was observed after injection molding and during dynamic vulcanization. For example, tensile strength and Young's modulus of a TPV were ~ 26 MPa and ~ 95 MPa respectively before injection molding, which increased to ~ 34 MPa and ~ 200 MPa after injection molding.

References:

[1] Banerjee, S. S.; Bhowmick, A. K. Polymer **2013**, 54, 6561 – 6571.
[2] Jha, A.; Bhowmick, A. K. Rubb Chem Technol **1997**, 70, 798-814
[3] Bhowmick, A. K.; Chiba, T.; Inoue, T. J. Appl. Polym. Sci. **1993**, 50, 2055 - 2064.

Tuning of Physico-mechanical properties of Biopolymers by Novel Carbon Dots prepared from tea

Achyut Konwar[a], Gitanjali Majumdar[b] and Devasish Chowdhury[a]
[a]Material Nanochemsitry Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Guwahati, Assam, India
[b] Department of Chemistry, Assam Engineering College, Jalukbari, Guwahati, Assam, India
E-mail: achyutkonwar88@gmail.com

Development of biodegradable and biocompatible polymeric materials up to the level to compete synthetic polymers is still a challenge for the scientific community throughout the globe. As a small contribution to this we introduce a new green source "Tea" to synthesize carbon dots (CDs) and its successful application in shaping interesting properties of various biopolymers, particularly chitosan and alginate. We prepared chitosan-CDs nanocomposite hydrogel film with varying percentage of tea CDs. The electrostatic interaction of positive charge on chitosan and negative charge on tea CDs was used for the successful preparation of a stable and robust chitosan-CDs nanocomposite hydrogel film. Interestingly, it was observed that chitosan–CDs hydrogel films are soft but tough with superior UV–visible blocking, swelling, thermal and mechanical properties in comparison to chitosan hydrogel film. Moreover chitosan-CDs films are more water repellent (hydrophobic) as indicated by their high contact angle values. Similarly, we have also studied the incorporation of tea CDs with alginate hydrogel film cross linked by different cations. The tea CDs also helped in improving properties like UV blocking, surface properties etc. of the alginate hydrogel film.Thus, tea CDs can be used as an effective green source for fabrication of such green soft but tough biocompatible biopolymer nanocomposite hydrogel films. These hydrogel films also offer tremendous biomedical and industrial applications due to their interesting and important properties.

Polypropylene/Layered Double Hydroxide Nanocomposites: Influence of LDH Particle Size on the Crystallization Behavior of Polypropylene

Baku Nagendra and E. Bhoje Gowd
Materials Science & Technology Division, CSIR-NIIST, Thiruvananthapuram, Kerala
bhojegowd@gmail.com

Highly dispersed isotactic polypropylene (iPP) nanocomposites were prepared by incorporating two different sized Mg-Al LDH nanoparticles with different loadings from 1 to 10 wt% using a modified solvent mixing method. Larger sized LDH nanoparticles (2-3 μm) were prepared from the gel form of Mg-Al LDH and the smaller sized nanoparticles (200-300 nm) were prepared by sonication of as-synthesized LDH particles. Such obtained LDH nanoparticles were carefully characterized using Wide-angle X-ray diffraction (WAXD), transmission electron microscopy and scanning electron microscopy. WAXD and atomic force microscopy results indicate that the LDH nanoparticles were highly dispersed in iPP matrix. The influence of LDH particles size and concentration on the thermal stability, spherulitic morphology, melting behavior, isothermal crystallization kinetics and lamellar structure of iPP were investigated. Incorporation of low loadings of sonicated LDH particles (e.g. 1-2.5 wt%) show substantial effect on thermal stability, spherulite size, crystallinity and crystallization half-time and lamellar morphology of iPP compared to the pure iPP and that of nanocomposites with larger LDH particles with same concentration. The better nucleation ability of iPP in presence of sonicated LDH can be attributed to the high surface area LDH nanoparticles along with its better dispensability within the polymer matrix. Another important finding of this work is that the incorporation of LDH nanoparticles doesn't change the crystallization growth mechanism and crystal structure of iPP.

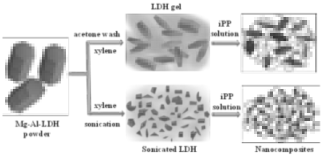


Figure 1. Schematic illustration of the polymer nanocomposites preparation based on isotactic polypropylene and LDH

References:

[1] Ray, S. S.; Okamoto. M. Prog. Polym. Sci. **2003**, 28, 1539-1641.
[2] Leroux, F.; Besse. J. P. Chem. Mater. **2001**, 13, 3507-3515.
[3] Wang, Q.; O'Hare, D. Chem. Rev. **2012**, 112, 4124-4155.

Syndiotactic Polystyrene – Polyhedral OligomericSilsesquioxanes Nanocomposites with Ultra Low dielectric Constant for Microelectronics Applications

[1]Angel Mary Joseph, [1]K. P Surendran and [1]E. Bhoje Gowd*
[1]Materials Science & Technology Division,
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Thiruvananthapuram, Kerala, India – 695019
*bhojegowd@gmail.com

The ever increasing demand for the miniaturization of electronic devices urge the researchers to concentrate on novel ultralow dielectric constant materials as interlayer dielectrics in the place of conventional silica. These ultra low dielectric constant materials can decrease the Resistance-Capacitance time delay, power consumption and signal cross talk[1].Polymer composites are good alternatives in place of silica since it is possible to tune the dielectric properties of the polymer composites by the judicious selection of fillers. In the present investigation we have synthesized syndiotactic polystyrene (sPS)-POSS composites via the solution blending in xylene followed by hot pressing. SPS is of great academic and industrial importance because of its crystallization behavior and the related changes in physical properties[2]. POSS, on the other hand, is an organic inorganic hybrid with inorganic core and organic functional groups attached on the periphery[3]. POSS maintains intrinsically low dielectric constant due to their microporosity of the cube cage structure.Here we used vinyl and aminopropyl functionalized POSS, in order to tap the advantage of their increased hydrophobicity. The dielectric characteristics of sPS-POSS composite with 6 vol % of filler, is very promising with a very low dielectric constant of 2.03 at 1 MHz. The composites were further characterized by WAXD , SEM, DSC, TGA etc.

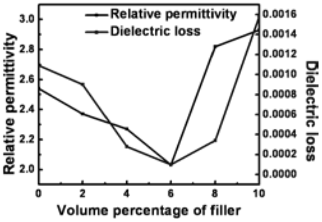


Figure: Variation of relative permittivity and dielectric loss with respect to filler volume fraction at 1 MHz

References:

[1] Baklanov, M. R.; Marneffe, J.F.;Shamiryan, D.; Urbanowicz, A. M.; Shi, H. J. Appl. Phys.**2013**,113, 041101.

[2] Gowd, E. B,; Tashiro, K.; Ramesh, C.;Prog. Polym. Sci. **2009** , 34, 280-315.

[3] Sharma, B.; Verma, R.; Baur, C.; Bykova, J.; Mabry, J. M.; Smith, D.W.; J. Mater. Chem. C. **2013**, 1,7222.

Novel synthesis of Poly (o-anisidine) (POA)-Hollow Glass microsphere composite for industrial application

M. N. Mali, K. V. Yeole, S. T. Mhaske*
Department of Polymer and Surface Engineering,
Institute of Chemical Technology, N. P. Marg, Matuga (E), Mumbai-400019
stmhaske@gmail.com

Poly (o-anisidine)-Hollow glass microsphere (POA-HGM) conducting composite was prepared by in situ polymerization of o-anisidine with ammonium persulphate as initiator by the addition of HGM. The synthesized materials were characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible absorption (UV-visible), X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrical conductivity measurements. FTIR spectroscopy determines the interaction between the POA and HGM. The crystalline nature of POA-HGM was determined by XRD. The band gaps of POA & POA-HGM measured by UV-visible spectroscopy. Morphological study shows the improvement in the HGM structure. POA-HGM nanocomposites thus synthesized were incorporated into epoxy based composite formulation and its electrical property was studied. The aim of this study was to develop a facile method for the synthesis of eco-friendly composite material having superior electrical properties.

Keywords: Poly (o-anisidine), Hollow glass microsphere, Composite, Conductivity.

Molecularly Imprinted Polymer Composite Membranes with High Adsorption Selectivity for Chiral Separation of Phenylalanine

Nasrullah Shah[1]*, Joong Kon Park[2*], Muhammad Balal Arain[1],
Touseef Rehan[3]
[1]Department of Chemistry, Abdul Wali Khan University Mardan, Mardan, Pakistan
[2]Department of Chemical Engineering, Kyungpook National University, Taegu, Korea
[3]Department of Biochemistry, Quaid-i-Azam University, Islamabad, Pakistan
* *nasrullah@awkum.edu.pk*

Two types of composite imprinted membranes, i.e., Composite membrane comprised of D-Phe imprinted beads and D-Phe imprinted membrane or CMDIBDIM and composite membrane comprised of L-Phe imprinted beads and L-Phe imprinted membranes or CMLIBLIM, were synthesized by phase inversion technique after a uniform dispersion of beads within the polymeric solutions using simple physico-mechanical process. The incorporated P (MAA-co-EGDMA) beads and the P (AN-co-AA) solutions were prepared by suspension polymerization and in situ polymerization method respectively. The assemblies of the prepared CMDIBDIM, CMLIBLIM and control membranes were employed in ultrafiltration for chiral separation of D, L-Phenylalanine racemate solution. CMDIBDIM and CMLIBLIM showed higher values of water holding capacity, percent swelling ratio, adsorption capacity, and adsorption selectivity. However, the percent rejection of template and counter enantiomer were lower than that of control membranes. Compared to control membrane, the CMDIBDIM and CMLIBLIM showed inverse permselectivity. These composite membranes having better adsorption and separation ability for the Phenylalanine racemate solution will be suitable in the future for various other applications such as drug delivery systems, sensors, scaffolds etc.

Keywords: Molecularly imprinted composite membranes; Phe imprinted beads; Phe imprinted membranes; ultrafiltration, adsorption selectivity

Shape-Recoverable Polyurethane-Urea Composite using Carbon-Silica Inorganic Nanohybrids

Rohit Ranganathan Gaddam,[a] Srinivasarao Pilla,[a] D Vasudevan,[b]
Ramanuj Narayan [a] and KVSN Raju [a*]
[a]Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India
[b]Electrodics and Eelctrocatalysis Division,
CSIR-Central Electrochemical Research Institute, Karaikudi-630006, India
*kvsnraju@iict.res.in

The present work demonstrates a robust method for the generation of Shape recoverable polyurethane-urea films using a graphitic carbon-silica nanoparticle. For the present work, carbon nanoparticles (GNP) were prepared from a natural source via thermal vapour deposition techniques. The silica nanoparticles were then covalently anchored onto the GNP surface. The formations of carbon-silica nanohybrid (CSH) structures were established through the electron microscopy images and other spectroscopic techniques. The CSH were dispersed in different weight percentages into a polyether polyols and then reacted with diisocyante to form polyurethane nanocomposite. The presence of unreacted amino groups in the CSH is helpful in urea linkage formation, which leads to uniform dispersion in the polymer matrix. The prepared polyurethane composite posses exceptional physico-chemical properties owing to the presence of nanoparticulates. Interestingly, the resulting composite showed excellent shape recovery behavior. The shape recovery behaviors of the obtained films were observed when a temperature of 60°C was applied. The recovery of shape is found to increase with increase in CSH content. It is found to correlate with the increase in the nanomaterial content. The study presents an in-depth understanding of polymer behavior in presence of nanomaterials.

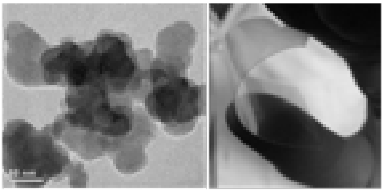


Figure: Scanning electron microscope image (left) of Carbon-silica inorganic hybrid and CSH based polyurethane-urea film (right)

References

[1] R. R. Gaddam, S. Kantheti, R. Narayan and KVSN Raju, RSC Advances, **2014**, 4, 23043-23049

[2] Z. Yao and K. C. Tam, Macromol. Rapid Commun., **2011**, 32, 1863–1885.

[3] S. Kantheti, R. R. Gaddam, R. Narayan and KVSN Raju, RSC Advances, **2014**, 4, 24420-24427

Fabrication and characterization of blend hybrid biocomposite based on poly (lactic acid)/ banana fiber/ natural rubber

Sajna. V. P[1], Smita Mohanty[1, 2], S. K. Nayak[1, 2]
[1]Advanced Research School for Technology & Product Simulation, Central Institute of Plastics Engineering and Technology, Chennai-600 032, India
[2]Laboratory for Advanced Research in Polymeric Materials, Central Institute of Plastics Engineering and Technology, Bhubaneswar, Orissa-751024, India
sajnavp88@gmail.com

This research work aims to study the effect of natural rubber (NR) on the mechanical, thermal and morphological properties of the biocomposite based on polylactic acid (PLA) and banana fiber (BF). NR toughened PLA/BF biocomposite with tuneable properties was successfully prepared by melt mixing followed by injection molding. The mechanical, dynamic mechanical and thermal properties have been studied to observe the effect of the natural rubber on PLA/banana fiber biocomposites. It was found that at 10 weight % NR loading in the blend improves the toughness and favours the crystallisation ability of PLA. A composite with 10 wt% of NR possessed the highest mechanical properties for both tensile and impact properties. The scanning electron micrograph (SEM) demonstrated the discrete rubbery phases between the PLA and the rubber particles. The glass transition temperature shifted to a lower temperature in the dynamic mechanical analysis (DMA) for the rubber-toughened PLA.

Key words: Poly(lactic acid), Natural rubber, banana fiber, blend, hybrid bio composites, crystallisation ability.

Low viscous Hyperbranched Epoxy/Poly (amido-amine) Modified Montmorillonite Thermosetting Nanocomposites

Bandita Kalita[1], M Ahmaruzzaman[2], Neelotpal Sen Sarma[1]
[1]Polymer Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Guwahati-781035, Assam, India
[2]Department of Chemistry, National Institute of Technology Silchar, Assam, India
Email: banditakalita.kalita@gmail.com

High performance tough epoxy thermosets with excellent adhesive strength is one of the most in demand materials for advanced engineering applications. In the present investigation, a hyperbranched epoxy resin was synthesized by a single step controlled polycondensation reaction using an A2 + B3 approach. This hyperbranched epoxy was low viscous and hence easily applicable for various purposes. And then, a tough and highly flexible hyperbranched epoxy and poly(amido-amine) modified Na-MMT based thermosetting nanocomposite was prepared. The FTIR, XRD and TGA confirmed the successful modification of the montmorillonite nanoclay. The morphology of epoxy/clay nanocomposites were determined by X-ray diffraction (XRD). The poly(amido-amine) cured hyperbranched epoxy nanocomposite thermosets exhibited high thermostability (up to 285.206 °C, 287.545 °C and 287.787 °C), tensile stress (110.24 MPa, 120.30 MPa and 142.98 MPa), tensile strain at break (17.30 %, 34.66 % and 25.13%), extension at break (4.32, 8.66 and 6.28 mm), exceptionally high max load capacity (330.74 N, 360.92 N and 428.97 N). Thus, the studied epoxy nanocomposite has great potential to be used as an advanced epoxy thermoset. It was also found that the nanocomposite thermosets have got best properties in alkali and alcohol resistance, and water resistance. The acid resistance was also studied.

References:

[1] Ajayan P.M., Schadler L.S., Braun P.V. (2003). *Nanocomposite science and technology*. Wiley. ISBN 3-527-30359-6
[2] Karak, N., 2009. Fundamentals of Polymers: Raw Materials to Applications, PHI Learning Pvt. Ltd., New Delhi
[3] Giannelis, E.P., 1996. Polymer layered silicate nanocomposites. Adv. Mater. 8, 29–35
[4] Gilman, J.W., 1999. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl. Clay Sci. 15, 31–49

PEEK Based Composites: Studies on the effect of fillers on the thermal and gamma radiation attenuation properties of the fabricated composites

Subhash Mandal and Sarfaraz Alam*
Polymer Division, Defence Materials and Stores Research and
Development Establishment, G T Road, Kanpur-3, India
*sarfarazkazmi@yahoo.com

High performance composites were fabricated using the PEEK as matrix and PbO, PbO_2, Pb_3O_4 and $PbZrO_3$ as fillers by extrusion technique in a twin screw extruder. Specimens for the mechanical testing were prepared by the injection molding method. The composites were evaluated for mechanical properties (tensile strength, tensile modulus, elongation at break, izod impact strength) and thermal properties by differential scanning calorimetry (DSC) & thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) has been employed to study the phase structure. Gamma radiation attenuation test of the composites was carried out using ^{99m}Tc as source energy. The HVL (half value layer) of the tested composites was found in the range 0.6 to 1.1 cm and TVL (tenth value layer) was found in the range 1.9 to 3.6 cm. The HVL and TVL of the neat PEEK were found 3.2 cm and 10.7 cm respectively.

References:

1. Nelson, G.; Reilly, D. Gamma-Ray Interactions with Matter. **2010**.
2. Chilton, A.B.; Shultis, J.K.; Faw, R.E. Principles of Radiation Shielding. **1984**.
3. Van Vlack, L.H. Physical Ceramics for Engineers. **1964**, 12, 223.

Graphene Oxide Polymer Hybrid and Functionalized Graphene: Versatile Application to Sensing and Drug Delivery

Aniruddha Kundu and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India

We have prepared fluorescent graphene oxide (GO) using nontoxic polymers like methyl cellulose (MC) and poly(vinyl)alcohol (PVA). The non-covalent functionalization is proved by several spectroscopic techniques. Both GO-MC and GO-PVA hybrid exhibit enhanced fluorescence property than GO at pH 4. GO-MC hybrid is utilized for the sensing of nitro-explosives whereas GO-PVA hybrid is employed to selectively sense toxic Au^{3+} ions. In another study we have fabricated functionalized graphene namely, sulfonated graphene (SG) which also shows improved fluorescence property than GO at pH 4. Due to the strong overlap between the emission spectrum of SG and absorption spectrum of riboflavin (RF, vitamin B_2) at pH 4, it has been tactfully used as donor for the FRET process to selectively detect vitamin B_2. Functionalized graphene based drug delivery vehicle have conquered a significant position since functionalization improves biocompatibility and stability in cell medium, leaving sufficient graphitic basal plane for drug loading through π -π stacking. In this study Poly(N-isopropylacrylamide) (PNIPAM) is covalently grafted from the surface of GO. PNIPAM grafted GO (GPNM) exhibits improved dispersibility in aqueous as well as cell medium, better bio-compatibility and cell viability (evaluated using MTT assay) compared to GO. Interestingly, GPNM displays exciting temperature dependent fluorescence property in aqueous medium. Moreover both hydrophilic (DOX) and hydrophobic (indomethacin) drugs are loaded on the surface of GPNM hybrid showing its efficacy as an efficient carrier of both types of drugs. Cellular uptake of free DOX and DOX loaded GPNM has been evidenced from fluorescence imaging. The release of DOX is achieved at pH 4, relevant to the environment of cancer cells. The pH triggered release of indomethacin is studied using UV-vis spectroscopy via alginate encapsulation.

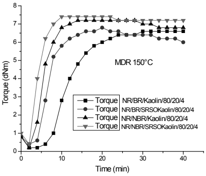
References:

[1] Sun, X.; Liu, Z.; Welsher, K.; Robinson, J. T.; Goodwin, A.; Zaric, S.; Dai, H. *Nano Res.* **2008**, *1*, 203–212.
[2] Kundu, A.; Layek, R. K.; Nandi, A. K. *J. Mater. Chem.* **2012**, *22*, 8139–8144.
[3] Kundu, A.; Layek, R. K.; Kuila, A.; Nandi, A. K. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5576–5582.
[4] Kundu, A.; Nandi, S.; Layek, R. K.; Nandi, A. K. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7392–7399.

Studies on blends of natural and synthetic rubbers containing organo-functionalized kaolin as Reinforcing Filler

Raji Vijay*, Surya Ramakrishnan, Rugmini Sukumar and A. R. R. Menon
NIIST-CSIR, Thiruvananthapuram, Kerala
*iamrajivv@gmail.com

Development of low cost *reinforcing fillers* based on china clay(kaolin) – a renewable natural resource as at least a partial substitution for carbon black/ precipitated silica being used in the rubber industry. *Rubber Seed Oil*, a low cost industrial by product and its derivatives being used as organo-modifier for kaolin to impart excellent compatibility with non-polar rubbers. The use of organically enhanced kaolin at very low dosage(< 10phr) as reinforcing filler for natural rubber(NR) system and blends of natural rubber(NR) with nitrile rubber(NBR) and poly butadiene rubber(BR) were investigated. It is reported that organo-modification leads to an increase in layer spacing of silicates due to the interalation of organomodifier betweeen the silicate layer, which could eventually leads to exceptional improvements in properties. Results obtained from a Moving Die Rheometer at 150°C showed considerable reduction in optimum cure time(t_{90}) along with a higher state of cure for NR/BR blends and NR/NBR blends containing 4 phr of the SRSO modified kaolin as against that containing the same dosage of unmodified kaolin, which is shown in the figure given below.The mechanical properties of rubber materials could improve by crosslinking. A study done on the series of NR-BR blend system showed a Cross link density hike at 1:1 composition. The ever-increasing demand for high performance polymers has shifted the focus of recent studies, from the development of new homopolymers to the development of new blends.



References:

[1] Preetha Nair, K.; Dr. Rani Joseph. Int. J. Sci & Eng. Res. **2012**, 3, 1-10.

[2] Jyothi, T. V.; Sunny, A.; Groeninckx, G.; Bhagawan, S.S.; Someswara Rao,S.; Sabu Thomas. J.Pol. Sci: Part B: Pol. Phy. **2000**, 38, 2189–2211.

Functionalization of Carbon Nanotube using Click Chemistry for high performance Polyurethane Nanocomposites

Sasidhar Kantheti, Rohit Ranganathan Gaddam,
Ramanuj Narayan and KVSN Raju*
Polymers and Functional Materials Division, CSIR-Indian Institute of
Chemical Technology, Hyderabad-500007, India
*kvsnraju@iict.res.in

Polymer-Carbon nanotube hybrids are amongst the most ideal architectures engineered, which brings to light many potential features useful for a wide range of applications like coatings with high corrosion resistance, thermo-mechanical stability, bacterial resistance, hydrophobicity and other applications like polymer based medical devices, cardio-vascular stents, actuators etc. The present work demonstrates development of novel polyurethane hybrid structures based on carbon nanotubes as a robust way of providing muti-functionality to the material. For the development of well dispersed nanocomposite, the solubility of carbon nanotube is a major concern. In order to overcome the problem of solubility, the carbon nanotube surface was modified with a hyperbranched polyether-polyol through a copper catalyzed azide- alkyne 1,3 dipolar cycloaddition reaction. This was followed by successful incorporation of these surface modified carbon nanotubes in various percentages (0, 0.5, 1 and 2 wt% with respect to polyol) into a polyurethane matrix. It is observed with 2 wt% loading of carbon nanotubes, the tensile strength of the polyurethane hybrid composite improved from 1.25 N mm^{-2} to 6.25 N mm^{-2}; the water contact angle improved from 54° to 108° and also the rate of corrosion reduced from 0.047 mm per year to 0.0019 mm per year. Thermal stability, mechanical strength, corrosion resistance and antimicrobial activity of the polyurethane hybrids improved considerably with the increase of carbon nanotube loading. The shape recovery behavior of the polyurethane hybrids drastically improved with CNT loading (**Figure**) which is attributed to the CNT's capacity of storing internal elastic strain energy during elongation of polyurethane film.

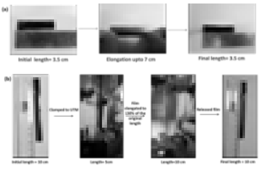


Figure: Testing of Shape recovery property for PUCNT film (a) manually and by using (b) Universal Testing Machine (UTM)

References

[1] S. Kantheti, R. R. Gaddam, R. Narayan and KVSN Raju, RSC Advances, **2014**, 4, 24420-24427

[2] Z. Yao and K. C. Tam, Macromol. Rapid Commun., **2011**, 32, 1863–1885.

[3] R. R. Gaddam, S. Kantheti, R. Narayan and KVSN Raju, RSC Advances, **2014**, 4, 23043-23049

pH Responsive and Low Fouling Ultrafiltration Polyvinylidene Fluoride/Amphiphilic CopolymerBlend Membranes

ChintaUday Kumar[1,3], Anupam Bera[1], Uma Chatterjee[2] and
Suresh K. Jewrajka[1]*
[1]RO Discipline, [2]EMP Discipline, CSIR-Central Salt and Marine
Chemicals Research Institute, Gujarat
[3]Department of Chemistry, BITS PILANI, Hyderabad Campus.

Polyvinylidene fluoride (PVDF) is widely used for the preparation of ultrafiltration membranes due to its film forming property, good chemical resistance, better thermal, mechanical properties and ease of sterilization [1, 2]. However, one short coming with the PVDF membrane is the severe fouling and low permeate flux owing to its hydrophobic nature [2-4]. Therefore, it is highly desirable to enhance both antifouling property and permeate flux of the membrane. In this regards, two types of copolymers such as agarose grafted by poly(methyl methacrylate) (Agr-*g*-PMMA) and a triblock copolymer of PMMA and poly2-(dimethyl amino)ethyl methacrylate (PDMA-*b*-PMMA-*b*-PDMA) were synthesized by atom transfer radical polymerization and used as additives for the preparation of PVDF blend ultrafiltration membranes. The PMMA content in the copolymers was ca. 70%. The PVDF to copolymers blend ratio was 74:26 (w/w).The PVDF/copolymers blend membranes were prepared by standard phase inversion process. The blend membranes (PVDF/Agr-*g*-PMMA and PVDF/PDMA-*b*-PMMA-*b*-PDMA) exhibited higher permeateflux and much enhanced antifouling property compared to neat PVDF membrane during ultrafiltration of bovine serum albumin (BSA).The enhanced permeate flux of the blend membranes is attributed to the higher porosity and pore density of the blend membranes compered to neat PVDF membranes as confirmed from porosity data and SEM analysis. In addition to enhancedpermeate flux and antifouling behaviour, PVDF/PDMA-*b*-PMMA-*b*-PDMA membrane also exhibited pH responsive permeate flux and rejection of both polyethylene glycol and BSA. The permeate flux enhances and rejections of both BSA and PEG decrease with increasing feed pH during ultrafiltration. This phenomenon is attributed to the swelling of PDMA-*b*-PMMA-*b*-PDMA due to enhanced protonation of DMA units at lower pH [5]. This effect lowers the pore size by pore swelling or partially blocking the pores by the copolymers at lower pH.

References:

[1] G-d. Kang, Y-m. Cao, J. Membr. Sci. 463 (2014) 145–165.
[2] J.F. Hester, P. Banerjee, A.M. Mayes, J. Membr. Sci. 73 (1992) 25-35.
[3] X. Chen, Y. He, C. Shi, W. Fu, S. Bi, Z. W.L. Chen, J. Membr. Sci. 469 (2014) 447–457.
[4] J.P. Hester, P. Banerjee, Y.Y. Won, A. Akthakul, M.H. Acar, A.M. Mayes, Macromolecules 35 (2002) 7652–7661.
[5] R. Muppalla, H.H. Rana, S. Devi, S.K. Jewrajka, Appl. Sur. Sci. 268 (2013) 355-367.

Biodegradability of potato starch filled polypropylene bio-composites

S B Roy[a], Dr. S C Shit[b], Dr. R A Sengupta[c] and Dr. P R Shukla[a]
[a]Dept of Chemical Engg., Dharmsinh Desai University, Nadiad, India
[b]Central Institute of Plastics Engineering & Technology, Chennai, India
[c]Dept. of Chemical Engg., Faculty of Technology & Engg.,
M.S. University of Baroda, Vadodara, India

In recent times, biodegradable materials have gained importance particularly for the protection of the environment from ever increasing plastic waste. A number of biological materials may be incorporated into biodegradable polymer. The main characteristic of biodegradable polymers is that they are biodegradable through the action of the microorganism in appropriate environmental conditions. When in contact with the biodegradable polymer, the microorganisms produce enzymes that break the material in progressively smaller segments reduces its average molecular mass, favoring its degradation in the environment. Incorporation of starch into a polyolefin matrix was proposed by Griffin as an effective means of accelerating the deterioration of plastics under biotic environmental exposure conditions. In this study, poly propylene (PP)/potato starch (PS) blend films were prepared using the two roll mill machine. The biodegradability of the films was investigated by soil burial method over a period of 4 months. The percentage weight loss of the bio-composites in the compost soil burial test was increasing with increasing PS content. The biodegradability of the bio-composites was enhanced with increasing starch content because the PS is easily attacked by microorganisms. Any changes in the various properties of the PP/PS before and after degradation were monitored using weight loss, FTIR spectroscopy, a scanning electron microscope (SEM) for surface morphology, a thermo gravimetric analyzer (TGA) for rapid determination of starch content and a differential scanning calorimeter (DSC) for crystallinity. We concluded from the results that use of these bio-composites will reduce the environmental problems associated with waste pollution and the study findings support the predicted application of bio-composites as green-composites or eco-materials.

References:

[1] Shogren, R. L, Doane, W. M, Garlotta, D, Lawton, J. W, Willett, J. L. PolymDegrad Stab. 2003, 79, 404-411.
[2] Yun, Y. H, Wee, Y. W, Byun, H. S & Yoon, S. D.. J. Polym. Environ. 2008, 16, 12-18.
[3] Franco, C. R, Cyras, V. P, Bulasmen, J. P, Ruseckaite, R. A, Vazquez, A. Polymer Degrad Stab. 2004, 86, 95-103.
[4] Avella, M, Erico, M. E, Laurienzo, P, Raimo, M, Rimedio, R. Polymer 2000,41, 3875-3881.
[5] Tang, S, Zou, P, Xiong, H & Tang, H. Carb. Polym. 2006, 72, 521-526.

Effect of ZnO nanostructure incorporation on mechanical properties and carbonization behavior of PAN

Ratyakshi Nain, Manjeet Jassal* and Ashwini K. Agrawal*
SMITA Research Labs, Department of Textile Technology,
Indian Institute of Technology, Delhi-110016
*manjeet@smita-iitd.com

Carbon nanofibers (CNFs) offer potential applications as heat-management materials, for reinforcement, high-temperature catalysis, membrane-based separation, and as components for nanoelectronics and photonics. Electrospinning is one of the most effective techniques used for producing carbon nanofibres from polyacrylonitrile (PAN). However, CNFs produced from electrospinning lack optimized molecular orientation in the fibers. Application of tension during thermal treatment particularly during stabilization is crucial for production of mechanically strong CNFs. Owning to their small dimensions, the application of tension by stretching of electrospun nanofibers is difficult, and hence alternate approaches need to be investigated to improve the molecular structure and orientation of CNFs.

The present study aims at incorporating anisotropic ZnO nanostructures in electrospun PAN nanofibers to improve the mechanical properties of the resultant CNFs. The effect of ZnO incorporation on carbonization behavior and hence graphitic domain size of obtained CNFs were evaluated using Scanning Electron Microscope and Raman spectroscopy, and were found to have profound effect on I_G/I_D value of CNFs.

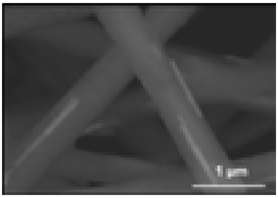


Figure: PAN nanofibers reinforced with ZnO nanorods

References:

1. Chae HG, Minus ML, Rasheed A, Kumar S. Polymer. **2007**, 48, 3781-3789.
2. Zhou Z, Lai C, Zhang L, Qian Y, Hou H, Reneker DH, et al.. Polymer. **2009**, 50, 2999-3006.

Quatenary Ammonium Salts from Rubber Seed Oil as an Organomodifier for Natural Rubber Clay Nanocomposites

Roshin Peter*, A. R. R. Menon
Functional Materials, MSTD, CSIR - NIIST
**peterroshin@gmail.com*

Nanocomposites based on polymer blends are one of the key areas of research now,due to their wide range applicability .They replaced conventional materials in many applications.Rubber also called Elastomer is one of the most important commercial polymers which exhibits unique physical and chemical properties.Clayswere organomodified by cation exchange reaction since interlayer space is available in layered silicates. It is modified using quaternary ammonium salts from Rubber seed oil considering its uniqueness with respect to long chain hydrocarbon.Many of the organomodifiers are expensive due to the depleting nature of their petrochemical source so far reports on the use of derivatives of fatty acid based on low cost,renewable natural resources as organomodifiers for silicate fillers have not been made.

NR/clay composites were prepared using quatenary ammonium salt as an organomodifier through melt compounding in a conventional two roll mill.A comparision of rubber blend vulcanizates with modified kaolin and Bentonite were studied.The morphological and mechanical properties were studied in ordrer to explain the effect of nanoclay.The morphology of the nanocomposites was studied by scanning electron microscopy(SEM),Transmission electron microscopy(TEM) and X-ray scattering.This revealed that the organic modification influenced silicate layers.Analysis of tensile properties,DMA and cross-link density showed its dependence on organically modified clay localization and blend composition.Composite with 5 wt% organomodified kaolin showed improvement in tensile strength and elongation at break.The low heat build -up characteristics of the organomodified clays may aid in the design and development of cooler running tyres.Thusorganomodification of layered silicates using Rubber Seed Oil will leads to commercially viable production of reinforcing nanofillers for rubber industry.

Ordering Meso Domains of Polymer Blend Thin Films by Topographic Confinement

Nandini Bhandaru and Rabibrata Mukherjee*
Department of Chemical Engineering, Indian Institute of Technology Kharagpur
**rabibrata@che.iitkgp.ernet.in*

When cast as a thin film, a blend of two immiscible polymers phase segregates spontaneously due to surface and interfacial properties. Spin cast films of these blends show a variety of random structures depending on the composition of the two polymers, the film thickness as well as the nature of the substrate. These surfaces can be potentially leveraged in a wide variety of applications as a template in the fields of tissue engineering, plasmonic solar cells etc.

In this work, poly(styrene) (PS)- poly(methylmethaacrylate) (PMMA) blend thin films of various concentrations and compositions are spin coated on flat as well as on different topographically patterned crosslinked poly(dimethylsiloxane) (PDMS) substrates and the phase segregated morphology in both the cases are compared. It was found that for any particular composition, below a certain critical blend concentration (Cn*), the phase segregation remains no more random and a specific perfect ordering of the two phases is observed due to the effect of physical confinement. Further, irrespective of the concentration, the presence of patterns results in a certain reduction in the domain size for each of polymer component. This alignment enhances the applicability of these surfaces as a template.

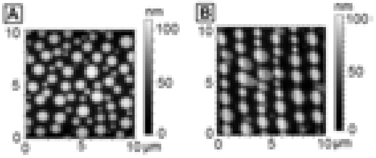


Figure 1: AFM scan of 2% 1:1, PS:PMMA film on (A) Flat PDMS and (B) Grating patterned PDMS substrates.

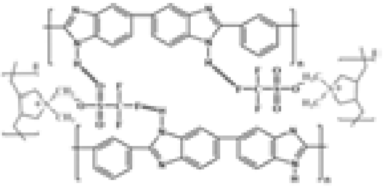
References:

[1] S. Y. Heriot and R. A. L. Jones, Nature Materials, 4, 782, 2005.
[2] M. Boltau, S. Walheim, J. Mlynek, G. Krausch and U. Steiner, Nature, 391, 877, 1998.
[3] B. D. Ermi, G. Nisato, J. F. Douglas, J. A. Rogers, and A. Karim, Phys. Rev. Lett., 81, 3900, 1998.
[4] 13. X-C Chen H-M Li , F. Fang , Y-W Wu , Mu Wang, G-B Ma ,Y-Q Ma, D-J Shu, and R-W Peng, Adv. Mater, 24, 2637, 2012.

New Approach of Employing Polymeric Ionic Liquid (PIL) for Enhancing Electrochemical Performance of Membranes for PEMFC

Anita S. Rewar, K. Sreekumar and Ulhas K. Kharul*
Polymer Science and Engineering Division,
National Chemical Laboratory, Pune-411008, India
*_uk.kharul@ncl.res.in_

Acid doped PBI membranes are being widely demonstrated for high temperature proton exchange membrane based fuel cell (HT-PEMFC) with advanced features such as high operating temperature, no water management, high CO tolerance, high thermal stability and good mechanical strength. Unfortunately, they possess lower conductivity [1,2]. To address this issue, ionic liquids have drawn significant interests because of their unique and attractive features, such as high ionic conductivity and wide electrochemical window, high thermo-chemical stability, lower flammability and negligible vapor pressure [3]. Although the use of ionic liquids (IL) in polymeric membranes is known to elevate the electrochemical performance of PEMFC, they suffer from drawbacks such as IL drain and lowering in mechanical properties that lead to deterioration in performance [4]. To mitigate these issues, we followed an altogether different path of blending polymeric ionic liquid (PIL), namely poly(diallyl dimethyl ammonium trifluoride methane sulphonate) (P[DADMA][TFMS]) with polybenzimidazole (PBI-I) and evaluated as membrane material for PEMFC. Physical property evaluation revealed that both, PBI-I and (P[DADMA][TFMS]) form miscible blends and are suitable for acid doping as a matrix. Owing to the presence of ionic liquid character in PIL, an increase in proton conduction was observed, conveying the success of proposed approach of blending PILs with PBI. Single cell evaluations further ascertained the benefits of this approach.



Possible mechanism of proton transfer in PIL/PBI blend membranes

References:
[1] S. C. Kumbharkar, et al., Euro. Polym. J.**2009**, 45, 3363.
[2] H. Vogel, et al., J. Polym. Sci.**1961**, 50, 511.
[3] J. W. Lee et al., J. Memb. Sci.**2010**, 357, 130.
[4] A. K. Mishra, N. H. Kim and J. H. Lee, J. Membr. Sci.**2014**, 449, 1

Interface Molecular Engineering of Ionic Liquid Integrated Graphene in PVDF Matrix with Improvement in Mechanical, Electrical and Dielectric Properties at a low Percolation Threshold

Nirmal Maity, Amit Mandal and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India

Graphene oxide (GO) functionalized with imidazolium ionic liquid (IL) by amidation reaction, is characterized by FTIR, Raman, X-ray photoelectron spectroscopy and transmission electron (TEM) and atomic force microscopy. The PVDF/GO-IL nanocomposite (PGL) films are flexible, hard, black colored where GO-IL is homogenously dispersed showing a fibrous network morphology. TEM image indicates dendritic morphology at 3% (w/w) GO-IL concentration. FTIR spectra indicate the formation of piezoelectric β-crystals of PVDF. WAXS study also substantiates 100% β-PVDF formation at this composition. The PGL composites exhibit a gradual increase of melting and crystallization temperature than PVDF due to higher melting β- PVDF formation and easier nucleation at GO-IL surface, respectively. The glass transition (T_g) and other crystalline relaxation temperatures increase with increase of GO-IL concentration due to nano-confinement. The maximum increase of storage modulus (73%), Young's modulus (333%) and tensile strength (628%) occur for 3% (w/w) filler concentration. An analysis of Young's modulus by Halpin-Tsai equation suggests that at low GO-IL concentration GO-sheets are randomly distributed but at higher concentration they are unidirectional oriented. A sharp increase of dc-conductivity of the PGL composite to ~10^{-2} S/cm with a percolation threshold of 0.1% (w/w) is observed in the composites. The dielectric permittivity increases from 7.5 for PVDF showing to a value of 13.5 for 3% concentration.

References:
[1] Mandal, A.; Nandi, A. K. ACS Appl. Mater. Interfaces, **2013**, 5, 747-760.
[2] Yang, L.; Wang, Z.; Ji, Y.; Wang, J.; Xue, G. Macromolecules, **2014**, 47, 1749–1756.
[3] Kim, H.; Abdala, A. A.; Macosko, C. W. Macromolecules, **2010**, 43, 6515–6530.

In Situ PEGylationof Thin Film Composite Membranes

Anupam Bera[1,2], Ravindra M. Gol[2] and Suresh K. Jewrajka[1,2*]
[1]AcSIR-Central Salt & Marine Chemicals Research Institute,
G. B Marg, Bhavnagar-364002, (Gujarat), India
[2]Reverse Osmosis Discipline, CSIR-Central Salt and Marine Chemicals Research Institute,
G. B. Marg, Bhavnagar, Gujarat, India

*In situ*PEGylation of conventional thin film composite membranes viz. conventional *m*-phenylenediamine (MPD)/trimesoyl chloride (TMC)-based reverse osmosis (RO) and piperazine (PIP)/TMC-basednanofiltration (NF)membraneswas performed to improvethe fouling resistance properties. Successful PEGylationof membranes was achievedby Michael addition reaction between excess MPD or PIP with acrylate terminated polyethylene glycol (AA-PEG-AA or MeO-PEG-AA)followed by interfacial polymerization with TMC on top of polysulfone support membrane. The formed adduct MPD-terminated PEG was best suited for PEGylation of RO membrane whereas the PIP-terminated PEG was best suited for the PEGylation of NF membrane [1,2]. The PEGylated membranes exhibited much enhanced antifouling property during desalination of protein contaminated water and similar salt rejection (R) compared to conventional non-PEGylated membranes. Figure 1 shows flux reduction (FR) vs. time plots for non-PEGylated conventional NF (NF-0), non-PEGylatedconventional RO (RO-0), PEGylated RO (RO-PEG) and PEGylated NF (NF-PEG) membranes. The PEGylated membranes exhibited low FR (10-12%) and much higher flux recovery ratio (FRR, 94-98%) compared to that of conventional membranes (FR=40-45% and FRR=70-71%). The salt rejection efficiency and the permeate flux of the membranes remained unaffected after PEGylation.

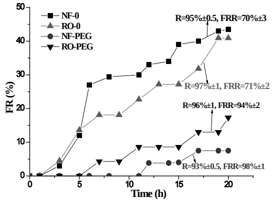


Figure 1. Antifouling property of PEGylated and non-PEGylated membranes

References:

[1] Gol, R.M.; Jewrajka, S.K.J.Membr. Sci.**2014**, 455, 271–282.

[2] Gol, R.M.; Bera, A.; Banjo, S.; Ganguly, B.;Jewrajka, S.K.J. Membr. Sci.**2014**, 472, 154–166.

Tethering of High Molecular Weight Polycaprolactone onto Functionalized Graphene

Titash Mondal[1,2], Rana Ashkar[3], Viktor G. Hadjiev[4], Paul D. Butler[3],
Anil K. Bhowmick[5*], Ramanan Krishnamoorti[2*]
[1]Department of Chemistry, IIT Patna, Bihar, India
[2]Department of Chemical and Biomolecular Engineering, University of Houston, TX, USA
[3]NIST Centre for Neutron Scattering, NIST, MD, USA
[4]Texas Superconductivity Centre, University of Houston, USA
[5]Rubber Technology Centre, IIT Kharagpur, West Bengal, India
*anilkb@rtc.iitkgp.ernet.in

Incorporation of nanoparticles of different dimensions into polymer matrix has attracted significant importance in the field of materials chemistry and technology.[1]Two of the most commonly used technique for synthesis of polymer nanocompositeare the "*grafting to*" and the "*grafting from*" methodologies.[2] Despite the simplicity involved in the "*grafting to*" technique, the popularity achieved is less due to the following problems (i) tethering of high molecular weight polymer is hard to be accomplished, (ii) low grafting density is realized.[3] In this present work, a facile synthesis route that partially addresses the drawbacks commonly associated with the "*grafting to*" technique is reported. Poly(ε-caprolactone) (PCL) and isocyanate modified graphitic platelets were used as the model system.Detailed structural data by techniques like small angle neutron and X-ray scattering indicated thatcorrelation length value for PCL was 10.2 Å, which was increased to 23.8 Å for the grafted samples.Neutroncontrast variation experiments revealed that the graphitic platelets were preferentially located between the lamella of crystalline PCL. Further,at the low q region, ultra-small angle neutronscattering measurementsdemonstrated q^{-2} dependence of the lamellar model and the q^{-3} dependence of the polymer model for the grafted samples. The resultant gaveapparently $q^{-2.67}$ dependence from the linear fit of the data. A thickness of ~20nm for the polymer tethered to the graphene sheets was observed. Further, tethering of graphitic platelets also induced structural confinement of the polymer chains. Based on the isothermal crystallization studies and Avrami fitting,it was revealed that the two dimensional graphitic platelets served as a template for the growth of PCL chains.

References:

[1] Bhowmick, A.K.; Bhattacharya, M.; Mitra, S.; Maji, P.K.; Choudhury, A.; George, J.J.; Basak, G.C.; Kumar, K.D. Kaunt. Gumm. Kunst.,**2010**, 63, 192-196.

[2] Krishnamoorti, R. *MRS Bull.*, **2011**, 32, 341-347.

[3] Balazs, A.C.; Emrick, T.; Russel, T.P. Science, **2012**, 314, 1107-1110.

Thermal Decomposition and Kinetic Reaction Model of Non-Woven/Fabric Hybrid Reinforced Unsaturated Polyester blends Composite

Edja F. Assanvo[1], Nilakshi Kakati[2], Dipul Kalita[2]and Shashi D. Baruah[1*]
[1]Petroleum and Natural Gas Division
[2]Cellulose Pulp and Paper Division,
CSIR-North East Institute of Science and Technology, Jorhat, 785006, Assam, India.
*baruah_shashi@yahoo.co.in

The thermal decomposition behavior of non-woven/fabric hybrid reinforced unsaturated polyester blends composite have been studied by differential scanning calorimetric (DSC), thermogravimetric (TG) and differential thermogravimetric (TGA) techniques using non-isothermal experiments and the decomposition kinetic reaction model was developed. The composite boards were produced by compressing moulding reinforcement of unsaturated polyester blend resins from soy flour (SF) and alkyd resin based on*Ricinodendron heudelotii*(*R.h*) oil with 0%, 5% and 10% (by volume) of *R.h* oil based alkyd resin. The thermal analysis was performed at four different heating rate, i.e., at 20,15, 10 and 3 °C min^{-1} in nitrogen atmosphere. The apparent activation energy (E_a) was determined using three isoconversional methods of Kissinger, Flynn-Wall-Ozawa and modified Coats-Redfern. Malek's kinetic algorithm procedure was used to determine the reaction model of the decomposition of the hybrid composite. With the increase of the alkyd resin content, the thermal stability of the hybrid composite improved and this corresponded with an increase in glass transition temperature (T_g).

References

[1] Thanamongkollit, N.; Miller, K.R.; Soucek, M.D. Prog. Org. Coat. **2012**, 73, 425-434
[2] Atiqah, A.; Maleque M.A.; Jawaid M.; Iqbal M. Composites : Part B **2014**, 56, 68-73
[3] Kissinger, H.E.Anal Chem.**1957**, 29, *1702-1706.*
[4] Ozawa, T.A. Bull. Chem. Soc Japan.**1965**, 38,1881-1886.
[5] Flynn, J.H.; Wall, L.A. J. Polym. Sci. Part B Polym.Lett.**1966**, 4 323-328
[6] Málek, J.ThermochimActa. **2000**, 355, 239-253

Processing and Performance Evaluation of Non-Woven/Fabric Hybrid Reinforced Unsaturated Polyester Blends Composites

*Nilakshi Kakati[1], Edja F. Assanvo[2], Dipul Kalita[1]
[1]Cellulose Pulp and Paper Division
[2]Petroleum and Natural Gas Division,
CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India.
*nkakati101@gmail.com

This paper focuses on the processing and performance characterization of non-woven/fabric hybrid reinforced unsaturated polyester blend resins composites. The composite boards were processed by compressing moulding reinforced unsaturated polyester blend resins from soy flour (SF) and alkyd resin from *Ricinodendron heudelotii* oil (*R.h*) at the increased ratio of *R.h* oil based alkyd resin of 0%, 5% and 10% (by volume). The blended unsaturated resin was characterized by FT-IR analysis, viscosity and zeta potential measurement. The chemical structure, water absorption, mechanical, thermal, morphological of the hybrid composite were investigated and it was found that the increase in the alkyd resin content has a significant effect on the quality improvementi.e. water absorption, mechanical and thermal properties. Morphological studies using scanning electron microscopy showed fiber cracking, debonding and fiber pulled-out as the main fracture mode of the composite and also revealed improved interfacial bonding between the matrix and reinforcement while using 10% of alkyd resin moiety in the blend. Hence this unsaturated polyester blend resins can be used in board production for general purpose applications.

References

[1] Sapuan, S.M.;Leenie, A.; Harimi, M.; Beng, Y.K. Mater. Des. **2007**, 27, 689-693
[2] Atiqah, A.; Maleque M.A.; Jawaid M.; Iqbal M. Composites : Part B **2014**, 56, 68-73
[3] Thakur, V.K. ; Thakur M.K. Carbohydrate polymers. 2**014**, 109, 102-117
[4] Thanamongkollit, N.; Miller, K.R.; Soucek, M.D.Prog. Org. Coat.**2012**, 73, 425-434

Silicon carbide nanoparticles incorporated soy protein bionanocomposites: Structural characterization and property investigation

Niladri Sarkar and Sarat K Swain*
Department of Chemistry, Veer Surendra Sai University of Technology, Sambalpur 768018, Odisha, India *Corresponding author
E-mail: swainsk2@yahoo.co.in

In the age of "green revolution" peoples hardly use the conventional non biodegradable synthetic polymer based packaging materials due to its polluting nature. So there is no disagreement in socially aware human beings regarding the replacement of synthetic polymers. Soya protein has its own importance in the field of food nutrition along with its unbelievable demand in different up-growing sectors, such as textile fibers, biodegradable membranes, biodegradable plastics, adhesives and packaging materials. Soya protein based bionanocomposites were designed by reinforcing SiC nanoparticles into the polymeric network of soya protein through low cost solution technique. The surface morphology of the prepared bionanocomposites was investigated by field emission scanning electron microscope (FESEM) whereas internal dispersion of nano SiC within soya protein was viewed from high resolution transmission electron microscope (HRTEM)images(shown in Fig-1).Crystalline nature of the bionanocomposites was examined from X-ray diffraction (XRD) and selected area electron diffraction (SAED) pattern. The chemical interactions within bionanocomposites were studied by Fourier transform infrared (FTIR) spectroscopy. Thermal stability and chemical resistivity of the prepared bionanocomposites were found to be superior as compared to the virgin soya protein with little scarification in biodegradability which may enable the synthesized bionanocomposite material for packaging applications.

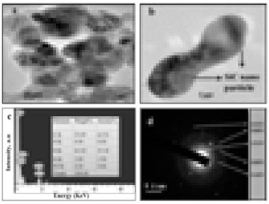


Figure-1. (a,b)HRTEM, EDS and (d)SAED pattern images of soy/sic bionanocomposite

References:

[1] Samir, A., Alloin, F., Sanchez, J. Y., Dufresne, A. Cellulose nanocrystals reinforced poly (oxyethylene). Polymer. **45,** 4149-4157 (2004).

[2] Dash, S., Kisku, S. K. and Swain, S. K. Effect of nanoclay on morphological, thermal and barrier properties of Albumin Bovine. Polymer Composites. **33,** 2201-2206 (2012).

Isocyanate free Curing of Glycidyl Azide Polymer

Sanjeevani Sonawane*, Javaid Athar, M. Anniyappan and A. K. Sikder
High Energy Materials Research Laboratory, Pune - 411 021, India
*sanjeevani_hs@yahoo.co.in

Glycidyl azide polymer (GAP) is an energetic binder and fuel used in composite solid rocket propellants. Hydroxyl functional azido polymers are commonly cured with polyisocyantes forming urethane linkage. However, existing curing systems have various problems such as isocynates are toxic compounds, react with moisture to release CO_2 and voids are formed in cured propellant. In recent years, to avoid problems associated with isocyanate cured systems, use of non-isocyanate curing systems are great interest. Presence of azido groups in GAP undergo the 1,3-dipolar cycloaddition reaction with acetylene compounds, forming 1,2,3-triazole ring system. Hence multifunctional dipolarophiles have been suggested an alternative curing agents for azido polymers. This paper reports method of synthesis of curators such 1,3-bis(prop-2-yn-1yloxy)benzene, 1,4-bis(prop-2-yn-1yloxy)benzene and 1,4-bis(prop-2-yn-1yloxy)-2-Nitrobenzene along with curing of GAP using these curators and also describes the properties of the cured binder systems with reference to high energy material application. Curing of GAP with aromatic bis-propargyl ethers was carried out at 50^0C for 3-5days. This curing reaction proceeds without catalyst via the formation of a 1,2,3-triazole ring system. The curing process was monitored by measuring curing profile with the help of Rheometer. Cured samples were characterized by spectral, thermal and mechanical properties. FTIR study confirmed that the absence of peak at 3289 cm^{-1}(alkyne CH stretching). DSC thermogram showed that exothermic peak at 257 ^{0}C. TGA showed two step decompositions in the temperature range of 120-290 and 290-575 ^{0}C with 62 % total weight loss. The cured GAP have found to retain their elastic behavior with better mechanical properties(T.S) as compared to isocyanate cured GAP.

GAP/aromatic bis-propargyl ethers curing procedure appear to offer an attractive alternative to conventional isocynate based systems because it does not require catalyst and can be cured at temperature range 30-50 ^{0}C for 3-5 days.

References

[1] K. Varma, Veena Choudhary, Bharti Gaur, Bimlesh Lochab, S Oberoi, R Chauhan. J. Applied Polymer Sci.**2005**, 101,779-786.
[2] Byoung Sun Min, Young Chul Park and Ji Chang Yoo , Propellants Explos. Pyrotech. **2012**, 37, 59-68.
[3] Eva Landsem, Tomas L. Jensen, Tor E. Kristensen, Finn K. Hansen,Tore Benneche, and Erik Unneberg, Propellants Explos. Pyrotech. **2013**, 38, 75-86.

Preparation, Characterization and property investigation of Starch/PVA/ $CaCO_3$ film

Gyanaranjan Sahoo, Gopal Chandra Pradhan and Sarat K Swain*
Department of Chemistry,
Veer Surendra Sai University of Technology, Sambalpur-768018, Odisha, India
** E-mail: swainsk2@yahoo.co.in*

The up-growing interest in study of biopolymer films has witnessed a steady increase of using biopolymer because they are eco-friendly alternatives to synthetic, non-biodegradable films. Starch/PVA/$CaCO_3$ nanobiocomposite films were prepared by solution casting method using glycerol as compatibilizer. The prepared nanobiocomposite films were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The fire retardant property of nanobiocomposite films was investigated from the measurement of limiting oxygen index (LOI) (Fig-1). The tensile strength thermal stability of nanobiocomposite films were enhanced with increasing percentage of $CaCO_3$. The oxygen permeability of starch/PVA/$CaCO_3$ was reduced with increase in $CaCO_3$ concentration. An increase in water absorbency and reduction in water solubility of nanobiocomposites were observed as compared to the neat copolymers. The biodegradability of nanocomposite films was marginally reduced with the incorporation of $CaCO_3$. The increase in fire retardant and oxygen barrier properties along with improvement in thermal and tensile properties of the prepared nanobiocomposite films may enable the material suitable for packaging application.

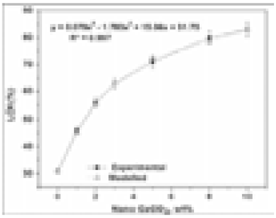


Fig-1. LOI study of starch/PVA/$CaCO_3$ bionanocomposite film.

References:

1. Yoon, S.D.; Park, M.H.; Byun, S.H. Mechanical and water barrier properties of starch/PVA composite films by adding nano-sized poly(methyl methacrylate-co-acrylamide) particles Carbohyd. Polym. **2012**; *87*: 676-686.
2. Yao, K.; Cai, J.; Liu, M.; Yu, Y.; Xiong, H.; Tang, S.; Ding, S. Structure and properties of starch/PVA/nano-SiO_2 hybrid films. Carbohyd. Polym. **2011**; *86*: 1784-1789.

Investigation of Temperature Independent Combustion behavior of an Energetic DNDA-57 Plasticizer by Molecular Dynamics Simulations

S Radhakrishnan*, R Vijayalakshmi and A K Sikder
High Energy Materials Research Laboratory, Sutarwadi, Pune - 411 021, India

The structure-function relationship study plays a central role in inducing mechanical responses at the molecular level and is highly topical with regard to emerging technologies. In advanced energetic compositions, a great challenge is to develop compositions that exhibit temperature independent combustion (Low Temperature Coefficient (LTC) effect). Langlotz and Mueller employed DNDA-57, a ternary mixture of 2,4-Dinitro-2,4-diazapentane (D5), 2,4-Dinitro-2,4-diazahexane (D6), 3,5-Dinitro-3,5-diazaheptane (D7) as an energetic plasticizer for the nitrocellulose (NC) based gun propellants and realized temperature independent combustion. Although the working mechanism of LTC effect of this plasticizer is not clearly understood yet, thermal properties of this mixture and combustion studies made clear that the efficiency of DNDA-57 mixture depends on its composition and its crystallization tendency. This structure-function study investigates the property that is responsible for the temperature independent combustion behavior in LTC class propellants in comparison with the conventional 2,4-dinitrotoluene (DNT) plasticized gun propellants.

Recent years, classical molecular mechanics have become a widely used method for the investigation of structural, thermodynamic and mechanical properties of amorphous polymers and plasticizers. In the present study, molecular dynamics calculations are performed using the COMPASS force field under periodic boundary conditions. Amorphous cell is built with 20 units of plasticizer molecules (DNDA57, D5, D6, D7 and DNT) and 2x2x2 supercells of these are considered as representative models for the study. In order to bring the model system to the most probable configuration consistent with target temperature and pressure, cell relaxations have been performed for the energy minimized cells using NVT-MD simulations. The final structure has been taken from the relaxation simulation and it is equilibrated by NPT-MD simulations for 1000 ps (production run) using Berendsen temperature and pressure control. Density of the cell is recorded in equilibrium process and a constant density is ensured at the end of production run which well correlates with experimental density. The final configurations of the MD runs are used as starting structure for a cooling cycle where the temperature is decreased in 10K steps from 373K to 193K. At each temperature an NPT-MD run is carried out for 200ps where 150ps allows equilibrium at the particular temperature and the last 50ps is used for the data sampling. The final configuration of each individual 200ps run is served as the starting structure for the subsequent one. For the last 50ps at every picosecond the thermal expansion coefficient (CTE) and specific density is sampled and the average value is taken as the result. Analysis of the computed results clearly reveals that CTE values of DNDA model are basically constant over the temperature range of 193 to 373K while it is increasing linearly with temperature in the case of pure DNT model. This phenomena of low thermal expansion exhibited by the DNDA can be attributed the temperature independent combustion behavior of DNDA 57 based propellants. The CTE behavior of individual of components viz., DNDA 5, DNDA6 and DNDA7 and glass transiton temperature predicted by the MD simulations will also be presented.

Synthesis, characterization and study of electrical and thermal properties of epoxy/EG nanocomposites

Subhra Ghantayat, Niladri Sarkar, Gyanaranjan Prusty,
Sarat K Swain *
Department of Chemistry, Veer Surendra Sai University of Technology,
Sambaipur-768018, Odisha,India,
** E-mail: swainsk2@yahoo.co.in*

Diglycidyl ether of bisphenol (epoxy resin) matrix reinforced with EG with concentrations of 3-9 wt% were fabricated. The structural, electrical and thermal properties of these composites were studied and compared. The structural information regarding epoxy/EG nanocomposite was obtained by X-ray diffraction study. The morphology and nanostructural behaviour of synthesized nanocomposites was investigated by FESEM and HRTEM respectively. The thermal stability was determined using thermo gravimetric analysis. The composites showed higher thermal stability in comparison with pure epoxy and thermal degradation of epoxy resin increased with incorporation of EG. The conductivity of epoxy resin increased with increasing concentration of graphite.

Assessing the critical concentration of NH_2 terminal groups on the surface of MWNTs towards chain scission of PC in PC/SAN blends: effect on dispersion, electrical conductivity and EMI shielding

Shital Patangrao Pawar, Suryasarathi Bose*
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, India

The localization and dispersion quality of as received NH_2 terminated multiwall carbon nanotubes (MWNT-I) and ethylene diamine (EDA) functionalized MWNTs in melt mixed blends of polycarbonate (PC) and poly (styrene-co-acrylonitrile) (SAN) was assessed in this study using rheo-electrical and EMI shielding measurements. In order to improve the dispersion quality and also to selectively localize MWNTs in the PC phase of the blends, EDA was grafted on to MWNTs by two different strategies like diazonium reaction of para-substituted benzene ring of MWNT with EDA (referred to MWNT-II) and acylation of carboxyl functionalized MWNTs with thionyl chloride (referred to MWNT-III). By this approach we could systematically vary the concentration of NH_2 functional groups on the surface of MWNTs at a fixed concentration (1 wt%) in PC/SAN blends. XPS was carried to evaluate the % concentration of N in different MWNTs and was observed to be highest for MWNT-III manifesting in large surface coverage of EDA on the surface of MWNTs. Viscoelastic properties and melt electrical conductivities were measured to assess the dispersion quality of MWNTs using a rheo-electrical set-up both in the quiescent as well as under steady shear conditions. Rheological properties revealed chain scission of PC in presence of MWNT-III which is due to specific interactions between EDA and PC leading to smaller PC grafts on the surface of MWNTs. The observed viscoelastic properties in the blends were further correlated with the phase morphologies under quiescent and annealed conditions. Electromagnetic interference (EMI) shield effectiveness in X and Ku-band frequencies were measured to explore these composites for EMI shielding application. Interestingly, MWNT-II showed the highest electrical conductivity and EMI shielding in the blends.

Effect of Filler Loading on Mechanical Response of Nitrile and Styrene-Butadiene Rubber Blend

Suhas Mukherjee[1], Shashi B. Singh[1], Dens Mohan A[2], Hashim Hameed[2],
Mohammed Thafseer V B[2], S Shyam Krishna[2], Bhatt Tushar Shriram[1]*
[1]Propellants and Special Chemicals Group, VSSC, Thiruvananthapuram
[2]Department of Chemical Engineering, NIT, Calicut
*bhatt_tushar@vssc.gov.in

Among all synthetic rubbers acrylonitrile butadiene rubber (NBR) is the most extensively used damping material in aerospace applications due to its wide ranges of physical mechanical and chemical properties [1].

Present work details the effect volume fraction of carbon black filler (N550 grade) on tensile failure behavior of the NBR-Styrene Butadiene Rubber (SBR) blend. Effect of filler volume fraction on Ultimate properties viz. tensile stress, elongation at break and tensile modulus was studied. Significant enhancement in ultimate tensile stress was observed with increase in filler volume fraction in the rubbery matrix. However, nearly 60% reduction was noted in failure elongation of the NBR when filler volume fraction was increased from 0 to 0.16. Empirical correlation between Shore A hardness and tensile modulus of the material was established with a reasonable degree of accuracy.

A semi-empirical relationship among strain energy, strain and filler percentage was developed based on Mullins and Tobin model [2]. Figure 1 depicts the variation of strain energy with strain and filler fraction computed based on the developed model.

The relation between strain energy at break point and filler concentration for NBR-SBR blend has been established using Gaussian distribution function with significant degree of accuracy. Optimum filler loading for maximized strain energy was predicted based on the Gaussian distribution function. The three dimensional relationship can be effectively used for prediction of ultimate tensile properties of the rubber blend for the known amount of filler content.

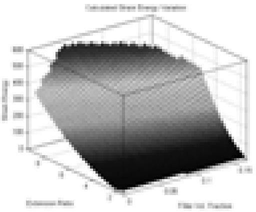


Figure 1: 3D plot correlating strain energy, strain and filler percentage

References:

[1] Park S W, International Journal of Solids & Structures.2001, 38:8065-8092.

[2] Jorgen S Bergstorm, Mary C Boyce, Rubber Chem Technol.Vol.72 PP633-656,1999

Thermoplastic-thermoset-co-cured network of PEEK-Alderene polymers and their composites: Neat resin and composite properties

Satheesh Chandran M*, Sunitha K, Dona Mathew, V.Lakshmana Rao, C P Reghunadhan Nair
[2]Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre
Thiruvananthapuram, Kerala, India-695022
*satheeshchandran.m@gmail.com

Allyl- terminated poly ether ether ketone with pendant methyl groups (PEEKMA) was incorporated in to Alder ene networks of O-Allylaralkyl phenolic resin (OAX) and bismaleimides (BMIs) in different proportions to form a thermoset-thermoplastic co-cured network without phase separation (Figure 1). PEEKMA was synthesized from Hydroxyl terminated PEEK (PEEKOH) [1] and it was blended with OAX and two types of BMIs viz 2, 2'-bis 4-[(4'-maleimido phenoxy) phenyl] propane (BMIP) and4, 4'Bismaleimidodiphenyl methane (BMPM).PEEKMA was found to co-react with the BMIs, without influencing the cure profile of the blends as evidenced from the three step cure pattern for the allyl- dominated and two stage pattern for maleimidedominated blends. The cross-link density of the cured polymers showed a decreasing trend with increasing PEEKMA loading above 5 wt % implying the co-reaction of PEEKMA with the base matrix. The mechanical properties of the carbon fibre- reinforced composites improved with PEEKMA content upto 5wt%. All maleimide rich combinations retained the interlaminar shear strength (ILSS)to more than 50% at 150°C and the percentage retention was better for the BMPM system compared to BMIP.The impact strength was also ameliorated by 38% for BMPM based composition upon PEEKMA addition while the blend of BMIP showed an increase of 67%. Maleimide rich systems conferred superior thermal stability to the cured blends. As the maleimide content increased, morphology of the cured blends changed from smooth to rough texture, and incorporation of PEEKMAabove 10% resulted in the formation of agglomerates of the PEEK moieties.

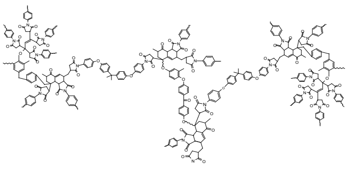


Figure1: The resultant cured network of BMI/OAX/PEEKMA

References:

[1] Bejoy Francis , Sabu Thomas, Jesmy Jose , R. Ramaswamy, V. Lakshmana Rao, , Polymer 2005,46, 12372–12385

Synthesis, characterization and rheological properties of hybrid PMMA/graphene oxide (GO) composites via surface initiated atom transfer radical polymerization (SI-ATRP)

N. Rajender and K. I. Suresh
Polymers & Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad-500007
E-mail: kisuresh@iict.res.in

Graphene is one of the most widely studied carbon nanomaterial for fundamental studies as well as for potential applications. It is a single atom thick, monolayer of sp^2-hybridized carbon atoms. Graphene sheets offer extraordinary electronic, thermal and mechanical properties and have potential applications in sensors, batteries, super capacitors, hydrogen storages and reinforcing agents. One possible route to harness these properties for applications would be the incorporation of graphene sheet into a composite material. Graphene oxide (GO), prepared from graphite is the common precursor materials for graphene. In the present work, the surface of GO was functionalized with the atom transfer polymerization initiator (ATRP) and subsequently polymethylmethacrylate (PMMA) chains were grown via living/controlled polymerization to yield the nanocomposites**.**

Among different polymerization methods, surface initiated atom transfer radical polymerization (SI-ATRP) has several strategic advantages over other methods of polymerization. This investigation reports the preparation and characterization of PMMA/GO nanocomposites from GO surface via SI-ATRP. To carry out SI-ATRP, the GO surface was first modified by incorporating an ATRP initiator (2-bromo propionyl bromide) onto the GO surface via grafting reaction. The prepared bromo-functionalized GO (GO-Br) was then used to carry out SI-ATRP of methyl methacrylate by varying the concentration of the initiator. Better conversion was obtained in the Cu/Bi-PY metal complex systems. The attachment of initiator on the GO surface was characterised by the solid state mas NMR, FTIR. Surface of the PMMA grafted GO (GPMMA) was characterized by FTIR, SEM, GPC and ^{1}HNMR. These SI-GPMMA composites were used to prepare the films and subsequently their thermal stability and activation energy were studied from TGA and DSC. Rheological properties of these GPMMA films were analysed by the DMTA.

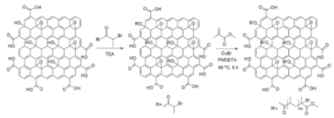


Figure1. Schematic representation of the Synthesis of polymethylmethacrylate (PMMA)/graphene oxide (GO) nanocomposites**.**

References:
1 M. J. Allen, V. C. Tung and R. B. Kaner, Chem. Rev., 2010, 110, 132.
2 C. N. R. Rao, K. Biswas, K. S. Subrahmanyam and A. Govindaraj, J.Mater. Chem., 2009, 19, 2457.
3 V. C. Tung, M. J. Allen, Y. Yang and R. B. Kaner, Nat. Nanotech.,2009, 4, 25.
4 B. Z. Jang and A. Zhamu, J. Mater. Sci., 2008, 43, 5092.

A unique strategy of compatibilizing immiscible binary blends by a mutually miscible homopolymer

Sourav Biswas[a], Goutam Prasanna Kar[a], Suryasarathi Bose[a*]
[a]Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, India
Email:sbose@materials.iisc.ernet.in

We developed a unique strategy to tailor the interface and render finer morphology in an immiscible polymer pair (PVDF/ABS) with a mutually miscible homopolymer (PMMA). The interfacial localization of the compatibilizer was manifested in a core-shell microstructure with ABS as the core and PMMA as the shell. This phenomenon was strongly contingent on the concentration of the PMMA in the blend. With the addition of 5 wt% PMMA in 90/10 PVDF/ABS blends, the droplet diameter of the dispersed minor phase (ABS) was remarkably reduced and a significant improvement in the mechanical properties was observed. This strategy was further extended to localize GO at the blends interface by chemically coupling it to PMMA.This study reveals that a mutually miscible homopolymer can render compatibility in an immiscible pair and can improve the stress transfer at the interface.

References:

[1] L. A. Utracki, Polymer blends handbook, Kluwer Academic Pub, 2002.
[2] K. Sharma, M. Sharma, A. Chandra and S. Bose, Macromolecular Chemistry and Physics, 2013, **214**, 2651-2669.
[3] M. Sharma, G. Madras and S. Bose, Macromolecules, 2014, **47**, 1392-1402.
[4] S. Bose, C. Ozdilek, J. Leys, J. W. Seo, M. Wubbenhorst, J. Vermant and P. Moldenaers, ACS Applied Materials and Interfaces, 2010, **2**, 800-807

Polymeric Self Healing Composites: Mimicking Nature to Enhance Performance

Shilpi Sharma and Veena Choudhary*
Centre for Polymer Science & Engineering,
Indian Institute of Technology Delhi, New Delhi (India)
**veenach@hotmail.com*

Self healing composites, which autonomically repair, are of particular interest now-a-days. The effect of diverse process parameters (reaction temperature, time, agitation rate, homogenization time, emulsifier concentration, stirrer types) and ingredients (melamine to formaldehyde ratio & core to shell ratio) on the yield percent, core content, morphology and on the shell wall thickness of the microcapsules were studied. In this article the role of reaction temperature on the yield percent, core content, morphology and on the size distribution of the microcapsules were investigated. Epoxy loaded poly (melamine-formaldehyde) (PMF) microcapsules was prepared by in-situ polymerization emulsion technique. Yield and core percentage increases as the microencapsulation temperature increases from 60 to 80°C. Structural (FTIR), morphological (optical microscopy and scanning electron microscopy) and thermal (TGA & DSC) characterization was done to investigate the effect of reaction temperature on the synthesized microcapsules. FT-IR spectra of PMF epoxy filled microcapsules showed the presence of epoxide ring. Optical & SEM micrographs showed that the prepared capsules are almost spherical with a perfect periphery, but showed the tendency to agglomerate. Thermal analysis showed that the capsules are thermally stable up to 300°C. Size distribution and mean diameter of microcapsules were determined with particle size analyzer. The mean size distribution of epoxy filled PMF microcapsules decreases (from 83-57 μm) as the microencapsulation temperature increases from 60 to 90°C. The results indicate that the PMF microcapsules containing epoxy have been synthesized successfully. Such microcapsules are expected to find applications in polymeric self healing composites.

References:

[1] E. N. Brown, M. R. Kessler, N. R. Sottos, and S. R. White, Journal of Microencapsulation, **2003**, 20, 719–730.

Development of Agar-Gelatin Hydrogel as Drug Delivery Matrices

Kaushal Kumar Mahato[1], Nira Misra[1], Pralay Maiti[2], Biswajit Ray[3]
[1]School of Biomedical Engineering, IIT-BHU, Varanasi.
[2] School of Material Science and Technology, IIT BHU, Varanasi.
[3] Department of Chemistry, BHU, Varanasi

The use of biocompatible hydrogels for various biomedical applications are currently gaining importance because of their low cost and easy fabrication. Such hydrogels are three dimensional polymeric networks, which can hold significant amount of water and undergo swelling upon exposure with water and other fluids. The aim of present work is to develop a cross-linked agar gelatin hydrogel using Glutaraldehyde as cross linker. The prepared hydrogel was characterized by FTIR. The gelation time of the prepared hydrogel was evaluated as a function of gelatin concentration. To know the hydrophilicity behavior, swelling behavior of the prepared hydrogel was evaluated using deionized water. Swelling behavior of hydrogels was also evaluated using different pH buffers. Biocompatibility of these hydrogels was explored. A model drug ciprofloxacin was loaded in these hydrogels and its in vitro release study was performed by UV visible spectrophotometer.

Keywords: hydrogel, glutaraldehyde, drug delivery

References:

[1] O. Wichterle,D. Lim, Hydrophilic gels in biologic use, Nature 185 (1960) 117.

[2] B.D. Ratner, A.S. Hoffman, Synthetic hydrogels for biomedical applications, in: Hydrogels for Medical and Related Applications, ACS Symposium Series, Vol. 31, American Chemical Society, Washington, DC, 1976, pp. 1–36.

[3] N.A. Peppas (Ed.), Hydrogels in Medicine and Pharmacy, Vols. I–III, CRC Press, Boca Raton, FL, 1987.

[4] A.S. Hoffman, Intelligent polymers, in: K. Park (Ed.), Controlled Drug Delivery, American Chemical Society, Washington, DC, 1997.

Polymer Blended (Vinylester/Epoxy) Nanocomposites with Improved Mechanical, Thermal, Electrical and Tribological Properties

A. Praharaj[1*], D. Behera[1], T. K. Bastia[1] and A. K. Rout[2]
[1]School of Applied Sciences (Chemistry),
[2]School of Mechanical Engineering, KIIT University, Bhubaneswar, Odisha,India
*ankita.praharaj017@gmail.com

The development of an inter-cross-linked polymer network of thermoset-thermoset blends have been extensively studied due to their enhanced mechanical properties. Among various polymer blends, modifications of Vinyl ester resin (VER) with epoxy matrix combinations are an attractive route to promote the performance of the thermoset matrix and to overcome the inferior properties of both the components. The primary goal of this research is to develop the VER/epoxy blended nanocomposites filled with amine – functionalized multiwalled carbon nanotubes (MWCNT-NH_2) and then to characterize thereof. For this purpose various blends of VER/epoxy (80/20 % w/w) polymers were prepared as a function of MWCNT-NH_2 in different weight ratios such as 1,1.5,2,2.5,3,4 & 5 wt % respectively. We have mainly focussed on the effect of MWCNT-NH_2 load on the mechanical, thermal, electrical and tribological properties of the nanocomposite systems. The appropriately cured samples gave excellent mechanical, thermal, electrical and tribological properties which increased with nanofiller content of up to 4 wt% but decreased thereafter due to the nucleating tendency of the nanofiller particles at higher concentrations. The above nanocomposites can be utilized for a wide range of structural, thermal and electrical applications.

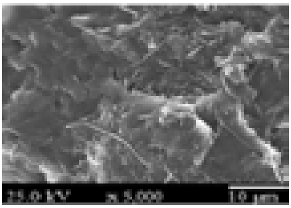


Figure 1: SEM of VER/epoxy nanocomposite filled with 4 wt% MWCNT-NH_2

References:

[1] Harishankar P.; Reddy Y.V.M.; Reddy K.M. International Letters of Chemistry, Physics and Astronomy, **2014**, 18, 75-90.

[2] Cheng X.; Xue Y.; Xie C. Material Letters. **2003**, 57, 2553-2557.

[3] Wetzel B.; Haupert F.; Zhang M.Q. Composite Science and Technology, **2003**, 63, 2055-2067.

[4] Peng G.; Gao L.; Zhan Z.; Haifengweng.; Hao W. Polymer Bull, **2009**,63, 911-919.

Polyamide-tethered polyhedral oligomeric silsesquioxane (POSS) nanocomposites and their gas transport properties

Parthasarathi Bandyopadhyay, Susanta Banerjee*
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
**susanta@matsc.iitkgp.ernet.in*

Polyamide-tethered polyhedral oligosilsesquioxane (POSS) nanocomposites (PAMIP) with well-defined architectures have been synthesized through Michael addition reaction between the maleimide-containing fluorinated new copolyamides (PAMI) with amino-functionalized POSS (POSS-NH_2) nanofiller. The chemical structures of the polyamide-POSS nanocomposites (PAMIP)s were characterized by ^{1}H-NMR and FTIR spectroscopy. The effects of POSS-NH_2 on the morphology and properties of the PAMIP membranes were examined by DSC, TGA, XRD and TEM analysis. POSS molecules tethered to polyamide form sphere shaped POSS aggregate cages (phase separated morphology) were confirmed by TEM analysis. In terms of gas transport properties, these hybrid membranes are very attractive because they support the mechanical stresses imposed in the permeation cells for their good combination of thermal and mechanical properties. All these PAMIP membranes showed very high permeability (P_{CO2} = 49.40 to 137.60 and P_{O2} = 10.40 to 32 barrer) for different gases (e.g., CH_4, N_2, O_2 and CO_2) compared to PAMI membranes (P_{CO2} = 19.60 to 115.00 and P_{O2} = 4.90 to 26 barrer) at 35 °C and 3.5 bar. This was attributed to the increase in the fractional free volume caused by the relatively low concentration of the bulky POSS unit in PAMIPs.

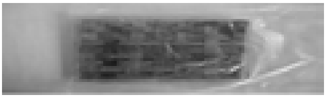
References:

[1] Bandyopadhyay, P.; Banerjee, S. Ind. Eng. Chem. Res. (accepted). **2014**.
[2] Robeson, L. M. J. Membr. Sci. **2008**, 320, 390-400.
[3] Liu, Y. L.; Lee, H. C. J. Polym. Sci. Part A: Polym. Chem. **2006**, 44, 4632-4643.

Mechanical properties of Unsaturated Polyester-Bamboo fiber composite laminate

Shivkumari Panda[1], Dibakar Behera[1], Tapan Kumar Bastia[1],
Prasanta Rath[1] and Arun Kumar Rout[2]
[1]School of Applied Sciences (Chemistry),
[2]School of Mechanical Engineering, KIIT University, Bhubaneswar, Odisha, India-751024
*dibakarkiit@gmail.com

Bamboo fiber is obtained from a source which is known for its renewability in terms of fast growth and better mechanical properties. The utilization of bamboo fiber for fabrication of biocomposites by using advance technology transforms future of coming generation. The well designed and engineered products from the bamboo fiber can help in making new revolution to sustain our natural resources. Thereby, based on this brief review the bamboo fibers can be utilized for advance and engineered product development for different applications. It will be an alternative way to develop the biocomposites which can be particularly used for daily needs of common people whether it is house hold furniture, house, fencing, decking, flooring, and light weight car components or sports equipments. Their low cost, easy availability and aesthetic designs will be the main driving force to transform the depended present to sustainable future.



Several treatment methods have been suggested to improve the fiber/matrix interface in natural fiber composites. This work examines the effect of treatment on mechanical and moisture absorption characteristics of 2-hydroxy ethyl acrylate(HEA) treated bamboo fabric reinforced thermosetting polyester composite laminate. All composite specimens with different weight percentages of fibers were manufactured using hand lay-up process and testing was done by using ASTM standards. Experimental results revealed that treated bamboo fiber composite shows enhanced tensile strength, flexural strength, and impact strength over untreated one. The content of natural reinforcement was found to be in the range of 25–33.3% for best results. Chemical treatment of fibers lowers the water absorption and results were comparable to glass fiber reinforced polyester composites.

References:

[1] Okubo, K. and Fujii, T., “Eco-Composites Using Bamboo and Other Natural Fibers and Their Mechanical Properties”, Proceedings of International Workshop on “Green” Compo-sites, **2002**, 17-21.

[2] Xiaosong Huang, Anil Netravali, Biodegradable green com-posites made using bamboo micro/nano-fibrils and chemi-cally modified soy protein resin, Composites Science and Technology**, 2009**, 69, 1009-1015.

Tailoring the physico-chemical properties of hyperbranched polyurethane using Oxidized Graphitic Nanoparticles

Srinivasarao Pilla, Rohit Ranganathan Gaddam,
Ramanuj Narayan and KVSN Raju*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India
*kvsnraju@iict.res.in

Hyperbranched polymers have been opted as an economic solution for coating technology owing to its globular structure, three dimensional architecture, densely packed surface functional groups and ease of preparation. The present work aims at enhancing the property of hyperbranched polymer through greener means by using castor oil derived precursors. It is well known that such oil based precursors have drawbacks of strength and shelf life. Therefore we incorporate a non-toxic, eco-friendly and bio-sourced graphitic nanoparticles into this polymer via covalent linkages. Here we prepared a versatile graphitic nanoparticle incorporated hyperbranched polyester-polyol, which was utilized in the development of polyurethane-urea nanocomposite with potential corrosion resistance, microbe resistance, enhanced thermo-mechanical and barrier properties. It is seen that there is a considerable increase in the physico-chemical property of the hyperbranched polymer with respect to the graphitic nanoparticle content. The study provides an in-depth analysis on the effect of nanomaterial on the hyperbranched polyester based polyurethane nanocomposite. The as-prepared coatings can find use in healthcare application, textile industry, marine coatings etc.

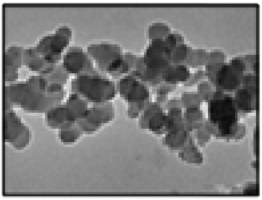


Figure: Transmission electron microscope image of oxidized graphitic nanoparticle dissolved in aqueous media

References

[1] R. R. Gaddam, S. Kantheti, R. Narayan and KVSN Raju, RSC Advances, **2014**, 4, 23043-23049

[2] C. Gao and D. Yan, Progress in Polymer Science, **2004**, 29, 183-275.

Effect of Mangiferin on thermal stability of PMMA

Shilpa Jaiswal, Monika, Amit kumar Ray, Nira Misra
School of Biomedical Engineering, Indian Institute of Technology,
(Banaras Hindu University), Varanasi-221005
shilpajais@gmail.com

Polymers constitute a versatile class of materials changing our day to day lives. Development in polymer science gave rise to novel drug delivery systems. Different polymers have been combined with different drugs. Poly methyl methacrylate is one such non biodegradable polymer which finds usage in orthopaedic surgery and as denture implants. On the other hand, Mangiferin, being a phytochemical has several therapeutic uses. In the present study, free radical polymerization of MMA was carried out in presence and absence of different doses of mangiferin. The compound produced was subjected to UV spectrophotometer and thermo gravimetric analysis. Degradation temperature was calculated. The results obtained, at 5% weight loss, indicated that degradation temperature dropped down initially with lower dose of mangiferin, but was found to increase with higher doses. This proved that addition of higher doses of mangiferin increased the thermal stability of the compound.

Tunable electrical conductivity and EMI shielding effectiveness obtained from different surface functionalized Multiwall Nanotubes in Polystyrene/ Poly(methylmethacrylate) blends

Rani Rohini, Suryasarathi Bose
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012

Polystyrene (PS)/Poly (methyl methacrylate) (PMMA) blends with different surface functionalized multiwall carbon nanotubes (MWNTs) were prepared by solution blending to develop materials with tunable EMI (electromagnetic interference) shielding materials. 1 wt% of different MWNTs like pristine (p-MWNTs), ~NH2 functionalized (a-MWNTs) and ~COOH functionalized (c-MWNTs) were incorporated in the blend. Localization of different MWNTs in the blend upon annealing was investigated using contact mode AFM (atomic force microscopy) on thin films. X-ray Photoelectron Spectroscopy (XPS) was used to study surface composition of the phase separated blends. The localization of MWNTs in the bulk was further observed by selective dissolution experiments. Interestingly, both p-MWNTs and a-MWNTs resulted in interconnected structures of PMMA in PS matrix upon annealing while, c-MWNTs led to dispersed PMMA droplets in PS matrix. Room temperature electrical conductivity and electromagnetic interference shielding effectiveness (SE) were measured in a broad frequency range. It was observed that both electrical conductivity and SE was strongly dependent on the type of surface functional groups on MWNTs. Interestingly, the SE for blends with p- and a-MWNTs was > 24 dB at room temperature, which is commercially important, and with very marginal variation in thermal conductivity.

References:

[1] Ugur, S.; Pekcan, O., Effects of annealing on morphology of polymer/polymer (PS/PMMA) blend; a fluorescence study. J. Appl. Polym. Sci. 2006, 100, 2104-2110.Minton, A. P. J. Biol. Chem. **2001**, 276, 10577-10580.

[2] Lee, M. S.; Ha, M. G.; Ko, H. J.; Yang, K. S.; Lee, W. J.; Park, M., Morphology and electrical conductivity of PS/PMMA/SMMA blends filled with carbon black. Fibers and Polymers 2000, 1, 32-36.

[3] Xiang, C.; Pan, Y.; Guo, J., Electromagnetic interference shielding effectiveness of multiwalled carbon nanotube reinforced fused silica composites. Ceram Int. 2007, 33, 1293-1297.

Morphology and Nonisothermal crystallization Kinetics of Polyethylene terephthalate (PET)/Reorganized PET – CNT nanocomposites

Amita Gaonkar[1], Vineeta Deshpande[2]
[1,2]Department of Physics, ICT, Mumbai

CNT possess extraordinary electrical, mechanical and thermal properties also have potential applications in manyareas such as biosensors, conducting agent, field-effecttransistor, and nanocomposites.Nanocomposites based on Polyethylene terephthalate (PET)/Reorganized PET and multiwalled carbon nanotubes were prepared by melt compounding. As received Polyethylene terephthalate structurally modified by precipitation technique with yield 98%. Nanoscale dispersion has been studied using Electron microscopy (SEM). FTIR spectra of PET nanocomposites investigated to study the possible interaction mechanism between PET and CNT. Melt mixed samples probed by differential scanning calorimetry. The various macrokinetic models namelythe modified Avrami, the Ozawa, the Liu model were applied to describe the crystallization kinetics under nonisothermal conditions. The Lauritzen – Hoffman parameters are estimated using effective activation energy equation proposed by Vyazoykin and Sbirrazzuoli. Lauritzen - Hoffman theory shows regime transition from regime II to regime I for temperature 210°C to 195°C. The activation energy calculated with Kissinger's method was lower for nucleated samples. The presence of multiwalledCNT, which acts as good nucleating agent, enhanced the crystallization of PET.

References:

[1] Avrami, M. J ChemPhys 1939, 7, 1103.Minton, A. P. J. Biol. Chem. **2001**, 276, 10577-10580.
[2] Ozawa, T. Polymer 1971, 12, 150.
[3] Kissinger, H. E. J Res Natl Bur Stand 1956, 57, 217.
[4] Liu, T.; Mo, Z.; Wang, S.; Zhang, H. PolymEngSci 1997, 37,568.
[5] Journal ofAppliedPolymerScience,Vol. 111, 1318–1327 (2009) VVC 2008 Wiley Periodicals, Inc.
[6] Journal of Polymer Science: Part B: Polymer Physics, Vol. 48, 1070–1100 (2010) VC 2010 Wiley Periodicals, Inc.
[7] Y. Geng, M. Y. Liu, J.Li. Shi, and J.K. Kim, Compos.A. 1876

Studies on Tensile and Flexural Properties of Flax fibre Reinforced Thermoplastic Composites

A. K. P. Dhanakodi, V. R. Giridev*

Department of Textile Technology, Anna University, Chennai.

Email: vrgiridev@annauniv.edu

Environmental concerns have led to manufacturing of high-performance engineering materials from renewable resources. Natural fiber reinforced composites are recyclable and light in weight. They exhibit similar properties to other synthetic fibre reinforced composites. In the present work, flax fibre and pp fibre web were produced by needle punched nonwoven technique and composites were made using compression moulding technique. Taguchi experimental design was adopted for the work. The variables taken for the study are fibre weight fraction, fabric weight and stitch density. The studies reveal that the tensile and flexural properties are greatly influenced by the above parameters and the present paper discusses the effects of these variables in detail.

Figure: Scanning electron micrographs of the fracture surface of Thermoplastic composites

Key words: Flax fibre, Polypropylene, Taguchi experimental design, Needle punching technique.

References:

1. Josephine Mattsson., Technical Analysis of Flax Reinforced Polypropylene, Master thesis, Department of Chemical Engineering, Karlstad University, Sweden, 2014.
2. Mieck, K. P., Lutzkendorf, R., and Reussanmann, T., Needle Punched Hybrid Nonwovens of Flax and PP Fibres – Textile Semiproducts for Manufacturing of Fibre Composites, Polymer composites, Vol. 17, No. 6, 1996, pp. 873-878.
3. Sandhyarani Biwas, Alok Satapathy., A comparative study on erosion characteristics of red mud filled bamboo-epoxy and glass-epoxy composites, Materials and Design, 31(2010), 1752-1767.
4. Maya Jacob John, Rajesh D. Anandjiwala., Chemical modification of flax reinforced polypropylene composites, Composites: Part A 40(2009) 442-448.

Coir as impact modifier in Polypropylene: A comparative study between PP/EPDM blends and PP/Coir Composites.

D. Purnima*, Sai SushmaIlluri
Department of Chemical Engineering,BITS-Pilani, Hyderabad,Telangana,India.
dpurnima@hyderabad.bits-pilani.ac.in

Coir is a residue which is obtained from coconut fruit. Recently coir is finding application as filler in polymer composites[1,2]. Polypropylene is a widely used polymer because of its properties such as low density and good chemical inertness which make it particularly suitable for wide range of applications. It has many potential applications in automobiles, appliances and other commercial products in which creep resistance, stiffness and some toughness are demanded in addition to weight and cost savings[3]. However, use of polypropylene is limited by the lack of good impact resistance.Various elastomers such as ethylene propylene rubber, ethylene propylene diene rubber, styrene ethylene butylenes styrene copolymer (SEBS) , ethylene vinyl acetate (EVA), polybutadiene and natural rubber have been used to improve the impact strength of PP .Among PP/rubber blends, the PP/EPDM blend has acquired some commercial success, and finds applications in various industrial fields such as automotive industry because the composition dependent properties of the blends can meet diverse requirements of industrial applications [4]. However nowadays since the petroleum reserves are depleting it would be beneficial if the improvementof impact property can be brought by addition of additive which would be from non-petroleum based source.When coir is incorporated in PP it was found to result in increase of impact strength of PP[1,2].The use of coir in PP has dual advantage of value addition to agricultural residue(coir) and also reduction in usage of petroleumbased material(EPDM). In this paper an attempt has been made compare the impact improvement and mechanical properties of PP/EPDM blends and PP/Coir composites.The composites and blends were prepared by varying the coir and EPDM respectively from 0 to 35%.

References:

1. Haque, M.; Islam, N.;Huque, M.Advanced Composite Materials.2010, 19, 91–106.
2. Haque, M. M.;Hasan, M.; Islam, M. S.; Ali, M. E. Bioresource Technology.2009, 100, 4903–6.
3. Pukánzky, B. Polypropylene Structure, Blends and Composites; Karger-Kocsis, J., Ed.; Chapman & Hall: 1995,Vol 3, Chap 1.
4. Mohamad, N.;Zainol, N. S.; Rahim, F. F.;Maulod, H. E. A.; Rahim, T. A.;Shamsuri, S. R.;Manaf, M. E. A..Procedia Engineering 2013,68,439 – 445.

Microstructure, Morphology and Optical properties of PVA films in presence of Manganese Chloride

M. Banerjee[1], Amit Jain[2] and G.S. Mukherjee[3]
[1]Nanoscience and Nanotechnology Lab., School of Physics,
Devi Ahilya University, Indore-452017
[2]Department of Physics, Medi-Caps Institute of Technology and
Management, Indore-453331
[3]Defence R&D Organization, Metcalfe House DRDO Complex, Delhi-110054
mandira_bm@rediffmail.com

Polymeric properties can be tailored by adding appropriate inorganics. Here films of pure polyvinylalcohol (PVA) of mol.wt. 72kDa and its $MnCl_2$ doped counterpart were prepared and characterized using XRD, FTIR, AFM and UV-VIS spectroscopy. Optical band gap of PVA film was found as 5.01 eV but it reduced by 2.4% on doping. Investigation of localized state of the material gave Urbach energy (E_u) value for PVA film as 0.70 eV but it increased to 0.82 eV on incorporation of 40% $MnCl_2$, thus implicating remarkable transformation from relatively long range order in pure PVA film to a distributive short range order in doped film as understood from XRD where sharp peak of PVA with interplanar distance, d_{pva}=4.48Å was shifted to a broadened peak corresponds in general to average interplanar distance (d_{dpva}) of 3.76Å; Such broadened peak neither belongs to pure PVA nor to pure $MnCl_2$ but to new textural phase resulting from strong interaction between PVA and $MnCl_2$ attributing substantial reduction in d-value. Broadened peak implicated interaction of Mn^{+2} with PVA are distributive in nature depending upon availability of active sites in chain primarily through remnant carbonyl (>C=O) rather than hydroxyl (OH) groups as revealed from FTIR features showing change of a triplet to doublet ~1650-1765 cm^{-1} range with very little change ~3350 cm^{-1} range. AFM supported distributive nanotexture of the doped film.

References:

[1] Migahed, M.D.; Zidan, H.M. Current Appl. Phy. **2006** 6, 91–96

[2] Paleari, A.; Meinardi, F.; Lauria, A.; Lorenzi, R.; Chiodini, N.; Brovelli S. Appl. Phy Letters **2007** 91, 141913

Synthesis and characterization of Ag-doped reduced graphene oxide based thermoplastic polyurethane nanocomposites

Taruna Bansala[1], Samrat Mukhopadhyay[1], Mangala Joshi[1*]
[1]Department of Textile Technology, Indian Institute of Technology Delhi, New Delhi, India
*mangala@textile.iitd.ac.in

Graphene filled polymer composites have many potential applications in electromagnetic shielding, antistatic, corrosion-resistant coating, and other applications that demand mechanical and functional attributes such as stiffness and barrier capabilities. But chemically reduced graphene has lower conductivity values, which can be resolved with the doping of Silver nanoparticles. These nanoparticles act as a useful nanospacer and conductor, which not only increase the interlayer distance between the sheets but also improve the electrical conductivity between layers. The nanocomposites based on Polyurethane (PU) matrix are an attractive material with many unique properties, including good elasticity, high impact strength and elongation, resistance to low temperature, and excellent bio-compatibility.

In this study, we present synthesis and characterization of Ag-doped reduced graphene oxide nanosheets along with processing, morphology, and properties of thermoplastic polyurethane (TPU) based reinforced with CNT, graphene and Ag- doped reduced graphene oxide. We compare these nanofillers via melt compounding and solution casting. A recirculating, conical twin-screw extruder is being used to blend TPU with nanofillers under dry N_2 environment. In solution casting, both TPU and nanofillers dispersed in DMF were mixed together to form homogeneous mixture and poured into petridish to form thin films. Melt-blended samples were further processed into thin films by hot pressing. Different concentrations of these nanofillers varied from 0.1 to 2 (wt%). The state of dispersion of nanofillers has been studied through Scanning Electron Microscopic analysis, Electrical Conductivity measurements, Atomic Force Microscopy, zeta potential and Raman spectroscopy.

References:

[1] Zhengxia Xu, Hanyang Gao, Hu Guoxin, carbon **2011**, 49, 4731–4738.

[2] Hsi-Wen Tien, Yuan-Li Huang, Shin-Yi Yang, Jen-Yu Wang, Chen-Chi M. Ma, carbon **2011**, 49, 1550–1560.

Effect of WS_2 nanotubes reinforcement on thermal and mechanical properties of cross-linked PVA

A. K. Sonker[a], R. Bajpai[b], X. M. Sui[b], V. Verma[a], R. Tenne[b], H. D. Wagner[b*]
[a] Department of Materials Science and Engineering,
Indian Institute of Technology, Kanpur, India
[b] Department of Materials and Interfaces, Weizmann Institute of science, Rehovot, Israel

Cross-linking of polymers is a vital tool for modification of polymers and its properties. Poly vinyl alcohol (PVA) is a water soluble polymer containing many hydroxyl groups on its chains joined together by inter and intra chain H- bonds. Modification of hydroxyl groups of PVA has been done by cross-linking of PVA with dicarboxylic acid, glutaric acid in this work. Cross-linking mechanism is a simple esterification reaction. Carboxylic groups of dicarboxylic acid react with hydroxyl groups of PVA to form ester bridge networks between PVA chains. In the present work, WS_2 nanotubes (WSNT) were used as reinforcement to improve the mechanical properties of PVA and cross-linked PVA samples. WSNT reinforced cross-linked PVA samples were subjected to different characterization methods. FTIR spectroscopy has confirmed the formation of ester linkage between dicarboxylic acids and PVA. In the swelling study it was found that cross-linking has reduced the water uptake of cross-linked PVA samples. Scanning electron microscopy (SEM) has shown the uniform dispersion of WSNT in the PVA matrices. Cross-linked PVA and WSNT reinforced cross-linked PVA samples have higher thermal stability than neat PVA samples as shown by Thermograviemetric analysis (TGA). Tensile testing has indicated that WSNT reinforced cross-linked PVA samples has higher tensile strength and toughness than cross-linked PVA and neat PVA samples. The WSNT reinforced glutaric acid cross-linked PVA is a bio-nanocomposite for different applications like implants, bio-mimic structures and filtration systems etc.

Key words: Cross-linking, WS_2 nanotubes, mechanical and thermal properties.

Ferrocene based functional organic-inorganic hybrid polymers

E. Ramu, Ramanuj Narayan, K. V. S. N. Raju*
Polymer and Functional Materials division - CSIR-Indian
Institute of Chemical Technology, Uppal road,Hyderabad-500007
**kvsnraju@iict.res.in*

Ferrocene is an aromatic prototypical metallocene. By the incorporation of ferrocene into the organic polymer results an easy way to develop organic-inorganic hybrid material. Ferrocene generally gives electrical, magnetic and optical properties. In this present work we have synthesized Ferrocene rich, fire retardant, anticorrosive hyperbranched polyurethane using alkyne-azide click chemistry. The prepared hyperbranched polyazido-polyol is attached with alkyne containing ferrocene moiety by means of click chemistry and converted the ferrocene rich polyol into polyurethane. This hyperbranched polyurethane structure has been characterised by FT-IR, ^{1}H-NMR, ^{13}C–NMR, UV-visible spectroscopy, ESI-MASS. The effect of ferrocene moiety on the properties of hyperbranched polyurethanes is studied for thermal, mechanical, morphology and antibacterial properties by TGA, DMTA, UTM, SEM and AFM respectively. Fire retardant, anticorrosive properties were studied by cone calorimetry, impedance spectroscopy respectively.

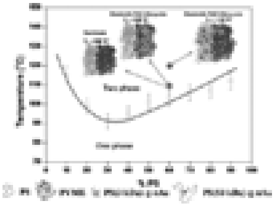
References:

[1] Zhu,C.; Yang,B; Zhao,Y.; Fu,C.; Tao,L.; Wei,Y**. Polym. Chem.**, **2013**, **4**, 5395-5400
[2] Ouyang,Mi.; Wang,P; Yu,W., Huang,S.; Sun,J.; Hu.B.; Lv,X.; Fu,Z.; Zhang,C. J. Electrochem. Soc. **2014**, 161, H337-H342

Polystyrene Grafted Gold Nanoparticles in PS/PVME Blend: Effect on Demixing Behavior

Goutam Prasanna Kar, Suryasarathi Bose [*]
Department of Materials Engineering, Indian Institute of Science, Bangalore
*sbose@materials.iisc.ernet.in

The phase separation in an LCST blend of PS/PVME (polystyrene/poly(vinyl methyl ether)) was studied using melt rheology in the presence of polystyrene grafted gold nanoparticles. Two different PS chains were grafted on to the gold nanoparticles; one with 3 kDa PS and with grafting density of ca $\Sigma = 1.7$ chains/nm^2, and the other with 53 kDa PS and with grafting density of ca$\Sigma = 1.2$ chains/nm^2. The localization of the gold nanoparticles in the phase separated blends were monitored *in situ* using a hot-stage AFM and confocal Raman imaging. Interestingly, gold nanoparticles grafted with 3 kDa PS (PS(3 kDa-g-nAu)) were localized in the PVME phase whereas, gold nanoparticles grafted with 53 kDa PS (PS(53 kDa-g-nAu)) were localized in the PS phase of the blend. Intriguingly, PS(53 kDa-g-nAu) delayed the demixing in the blends by 12 °C with respect to the neat blend. This study clearly demonstrates that by tuning the localization of the nanoparticles in the blends, the thermodynamic miscibility can also be tuned.



References:

[1] Chandran, S.; Begam, N.; Padmanabhan, V.; Basu, J. K. Nat. Commun. **2014**, in press

[2] Bharati, A.; Xavier, P.; Kar, G. P.; Madras, G.; Bose, S. J. Phys. Chem. B **2014**, 118 (8) 2214– 2225

[3] Green, P. F. Soft Matter **2011**, 7 (18) 7914– 7926

[4] Xavier, P.; Bose, S. J. Phys. Chem. B **2013**, 117 (28) 8633– 8646

Room Temperature Non-covalent Wrapping ofPolycarbazole on Multi-wall Carbon Nanotubes

Madhurima Das, Saptarshi Ghosh, Amarnath Sen, Somenath Roy*
Sensor & Actuator Division,
CSIR-Central Glass & Ceramic Research, Institute, Kolkata-700032, INDIA
sroy@cgcri.res.in

Conducting polymers find widespread applications in solar cells, flexible electronics and OLED devices, primarily for their low rigidity and good electrical conductivity, especially after doping[1]. Among the conducting polymers, polycarbazole (PCz) and its derivatives have been gathering considerable attention in organic photovoltaic cells, heterojunction devices and so on [2-3]. Despite its favorable attributes like thermal and environmental stability, the sensor applicability of pristine PCz is limited due to its relatively low electrical conductivity ($>10^{-9}$ S.cm^{-1} in the undoped state) [4]. To get around the conductivity issues, the polymer is often doped with iodine, sulfonic acid to reduce the percolation threshold. In this study, we have used multi-wall carbon nanotubes (MWCNT)as a filler to increase the conductivity of PCz. The polymer was synthesized from a carbazole monomer by *in-situ* chemical oxidative polymerization. Linear four probe measurements on the palletized PCz-MWCNT composite revealed a sheet resistance value of around 1 MΩ/□. In a PCz-MWCNT composite, the polymer wraps around the nanotubes through noncovalentπ-stacking interaction, while the nanotubes providerelatively conducting pathways. FTIR spectroscopy of the nanocomposite showed a peak at 1400 cm^{-1}, which confirmed the polymerization of carbazole on MWCNT. The peak at 2919 cm^{-1}represented the N-H bond stretching in PCz.The wrapping of PCz on MWCNT was also evident from a shift in the peak position from 263 nm to 283 nm in the UV-vis spectra.

References:

[1] Salleo,A.;Wong,W.S. (Ed.);Flexible Electronics: Materials and Applications, Electronic Materials: Science & Technology,Volume 11 **2009,**ISBN: 978-0-387-74362-2.

[2] Boudreault,P-L T.;Beaupre,S.;Leclerc,M.; Polym. Chem. **2010**, 1, 127–136.

[3] Lu, X.; Hlaing, H.;Germack,D.S.; Peet, J.,Won, H.J.; Andrienko, D.; Kremer, K.; OckoB.M.. Nature Comm. **2012**, 3, 795(1-7).

[4] Gupta, B.;Joshi,L.; Prakash, R.;Macromol. Chem. Phys. **2011**, 212, 1692-1699.

Rheological, Mechanical and Morphological Characterizations of HDPE/Sepiolite Based Nanocomposites

Vishwa Pratap Singh[1], Veena Choudhary[1*], K. K. Vimal[2],
G. S. Kapur[2], and Shashikant[2]
[1]Centre for Polymer Science and Engineering,
Indian Institute of Technology, New Delhi, India 110016
[2]Indian Oil Corporation Ltd. Research & Development Centre,
Sector 13, Faridabad, Haryana, India 121007

In the present study, high density polyethylene (HDPE)-based composites containing different amounts of sepiolite [1-10 wt %] and different types of compatibilizers, PE-g-MAH [Optim and Fusabond] were prepared by melt compounding in a corotating twin screw extruder. These composites were prepared through masterbatch route containing 20% sepiolite with HDPE. The effect of sepiolite loading and compatibilizer type on morphological properties using scanning electron microscopy [SEM], transmission electron microscopy [TEM] and X-ray diffraction [XRD], rheological studies using Rheotens set up and convergent flow analysis using capillary Rheometer and mechanical properties as per ASTM D638, D790 and D256 were examined. Thermal performance of nanocomposites was inspected using thermogravimetry [TGA] and differential scanning calorimetry [DSC].

SEM and TEM results revealed that the sepiolite distribution appears to be uniform across the specimens upto 5wt% sepiolite loading while some aggregates and cavities were found in the 10% sepiolite filled uncompatibilised nanocomposites and the interface is very sharp. The typical basal diffraction peak of sepiolite clays was observed at smaller angles for all the nanocomposite samples in WXRD pattern implying that the d-spacing increases and that intercalation occurred. The composition containing higher percentage of sepiolite exhibited enhancement in mechanical properties. About 40% in tensile modulus and about 50% improvement in flexural modulus were observed with 10wt% sepiolite content. High shear viscosity increased upon increasing filler content with slight decrease in onset of melt fracture at 10% sepiolite loading. On the other hand, incorporation of compatibiliser reduced the shear viscosity and increased the onset of melt fracture. Incorporation of varying amounts of sepiolite enhanced the melt strength, drawability and extensional viscosity. It was observed that Tm and Tc of the HDPE did not altered and the composition containing 5wt % sepiolite showed the highest decomposition temperature.

References:

[1] Muhammad S., Tariq Y., Shaukat S. Journal of Applied Polymer Sci., **2012**, 123, 1718–1723.
[2] Benlikaya, R.; Alkan, M.; Kaya, I. Polym Compos. **2009**, 30,1586.
[3] Huang, N. H.; Chen, Z. J.; Yi, C. H.; Wang, J. Q. eXPRESS Polym Lett. **2010,** 4, 227.
[4] Bokobza, L.; Burr, A.; Garnaud, G.; Perrin, M. Y.; Pagnotta, S. Polym Int. **2004**, 53, 1060.
[5] Zheng, Y.; Zheng, Y. J Appl Polym Sci. **2006**, 99, 2163.

Bisphenol A removal from water by magnetically guided guar benzoate films.

Md. Farooque Abdullah, Rajesh Shaw, Sumanta Kr Ghosh,
Arup Mukherjee
*Department of Chemical Technology, University of Calcutta,
92, A.P.C. Road, Kolkata-700009, West Bengal, India
** E-mail: arupm1234@gmail.com*

This work is pursued to design some paramagnetic iron oxide nanoparticles entrapped in newer guar benzoate (GGBA) matrix. The functionalized biopolymer films were applied for adsorption and removal of bisphenol A (BPA), a potent endocrine disrupting chemicals (EDCs) from water bodies. Paramagnetic iron oxide nanoparticles were synthesized following a bottom up co-precipitation method. Subsequently, the hydroxyl groups on nanoparticles surface were covalently modified with zwitterionic DOPA by mussel adhesive anchor reactions in ammoniacal water medium. Transmission electron microscopy (TEM) studies revealed an average size of 20-30 nm for the functionalized iron oxide nanoparticles. SQUID analysis further confirmed magnetic behaviour close to that of superparamagnetic materials. New functionalized magnetic nanoparticles were highly stable in water environment as observed in DLS and zeta analysis. Modified magnetic particles were homogeneously dispersed in GGBA matrix in DMSO solution in an ultrasonic reactor. The final composite was then cast as a nano-bio-composite film. The composite films were experimented for selective adsorption of BPA in synthetic aqueous solutions. Adsorption kinetics was followed at different pH conditions and quantified in HPLC - PDA detectors. Molecular associations and probable mechanism of adsorption were additionally evidenced in FT-IR analysis. New catechol functionalized iron oxides nanoparticles entrapped in GGBA biopolymer film can be a promising tool in bioremediation of EDCs like BPA from water bodies.

Surface-Quenching Induced Cell Opening Technique in Extrusion of Thermoplastic Foamed Sheets

Abhishek Gandhi, Naresh Bhatnagar*
Mechanical Engineering Department, Indian Institute of Technology,
Delhi, Hauz Khas, New Delhi 110016, India
*E-mail: narbhat@hotmail.com

In this article, a new technique has been developed to manufacture open cell extruded thermoplastic foamed sheets with the aid of extrudate surface-quenching phenomenon. As the extrudate foam exits the die, its surface is rapidly quenched which results in freezing of cells on the surface, while the cells at the core continue to grow and leads to development of open-cellular microstructure at the core. Influence of chill roll temperature was found to be extremely significant in developing porous morphological attributes. Subsequently, synergistic effect of blowing agent content and chill roll temperature was examined for their expansion ratio and open-cell microstructure. Further, chill roll rotating speed was also found particularly substantial in achieving open-cellular foam structures. This study intends to enhance the understanding of researchers working in the area of open-cell foam processing.

Keywords: Foams, Porous materials, Morphology, Composite, Microscopy, Open-cell foams

Synergetic effect of expanded graphite (EG) and multiwall carbon nanotubes (MWCNT) for reduction of electrical percolation threshold in the PMMA/HDPE/EG/MWCNT Nanocomposites

Ilamathi V, Avinash Raulo, and B. B. Khatua*
Materials Science Centre
Indian Institute of Technology Kharagpur, Kharagpur 721302, India

Hear we demonstrate a simple method to prepare highly conducting hybrid polymer nanocomposite composed of poly(methyl methacrylate) (PMMA)/high density polyethylene (HDPE) filled with multiwalled carbon nanotube (MWCNT) and expanded graphite (EG) . The EG used in this study was prepared by simple chemical exfoliation of graphite flakes and characterized by spectroscopic as well as morphological analysis. An industrially feasible melt mixing process was employed for the preparation of the nanocomposites through sequential heating protocol. The judicious control of temperature during mixing revealed a highly co-continuous structure of HDPE throughout the PMMA matrix and thus the percolation of the (75/25 w/w) PMMA/HDPE/bi-filler nanocomposites was achieved at 0.07 wt% loading of MWCNT. An extensive analysis revealed that the selective dispersion of the conductive bi-filler in the minor HDPE phase helped in the reduction of the percolation threshold through MWCNT-EG-MWCNT networking. The high barrier effect of the fillers was explained to be the prime in yielding co-continuous morphology in a highly asymmetric ratio (75/25 w/w) of the blend constituents.

References

[1] Linares, J. C. Canalda, M. E. Cagiao, M. C. Garcia-Gutierrez, A. Nogales, I. Martin Gullon, J. Vera, and T. A. Ezquerra, *Macromolecules,* **41**, 7090 (2008).

[2] N. K. Shrivastava, S. Suin, S. Maiti, and B. B. Khatua, *Ind. Eng. Chem. Res.,* **52**, 2858 (2013).

[3] Q. Wu , Y. Xu , Z. Yao , A. Liu, and G. Shi, *ACS Nano*, **4**, 1963 (2010).

[4] N. K. Shrivastava and B. B. Khatua, *Carbon*,**49**, 4571 (2011).

Fabrication of high performance composites based on MWCNT/poly (ether-ketone) and their thermal, mechanical and electrical properties

Sampat Singh Chauhan and Veena Choudhary*
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India
*veenach@hotmail.com

Composites of novel high performance multi-wall carbon nanotubes (MWCNT) /poly(ether-ketone) (PEK) containing 0 to 5 % [w/w] of MWCNTs were prepared by melt blending method followed by injection moulding to prepare the test specimens. The effect of MWCNTs content tensile properties, impact strength, electrical conductivity and electromagnetic shielding effectiveness [EMI] of PEK was evaluated. Tensile modulus and tensile strength increased with increasing amounts of MWCNTs. Impact strength of PEK decreased with increasing amounts of MWCNTs. Electromagnetic interference (EMI) shielding effectiveness (SE) of these composites investigated in the frequency range of 8.2–12.4 GHz (X-band) showed a significant increase [17 dB] upon incorporation of MWCNTs. Shielding mechanism was studied by resolving the total SE into absorption (SE_A) and reflection loss (SE_R). The effect of MWCNTs on thermal stability, crystalline behavior and mechanical properties has also been investigated. The overall increase in mechanical and electrical performance with light weight of such multifunctional nanocomposites materials make them suitable for their use in fields of telecommunications, electronics, and aerospace etc industries.

Refrences:

1. Rong C, Ma G, Zhang S, Song L, Chen Z, Wang G. Effect of carbon nanotubes on the mechanical properties and crystallization behavior of poly(ether ether ketone). Composites Science and Technology 2010;70:380–6.
2. Wang H, Wang G, Li W, Wang Q, Wei W, Jiang Z. A material with high electromagnetic radiation shielding effectivenes fabricated using multi-walled carbon nanotubes wrapped with poly(ether sulfone) in a poly(ether ether ketone) matrix. Journal of Materials Chemistry 2012;22:21232-37.

Development of a new polymeric composite from shellac-zirconium for efficient removal of fluoride

SimpiBhawna Patel[1], Sanjaya Kumar Swain[2], Tanushree Patnaik[3], R.K.Dey[1]*
[1]Centre for Applied Chemistry, Central University of Jharkhand, Ranchi
[2]Department of Chemistry, BIT, Mesra, Ranchi
[3]Department of Chemistry, Stewart Science College, Cuttack, Odisha
*rkdey@rediffmail.com

Fluoride contamination of water bodies is a major problem worldwide [1,2]. The development of new fluoride selective polymeric material for efficient removal of fluoride from drinking water is a scientific as well as technological challenge. In this investigation, a new polymeric composite from the combination of shellac and zirconium was successfully prepared and characterized by FTIR, SEM, XRD, TGA, BET and zeta-potential measurement studies. The fluoride adsorption was studied by batch method with variation of solution parameters. A number of factors such as molecular interaction and bonding between shellac and zirconium plays a major role in stability of the material. Almost 99% of fluoride could be removed from drinking water spiked with 10 mg L^{-1} fluoride by using an optimum adsorbent dose of 0.15g/L at pH of 6.8 and temperature 28^{o}C. The adsorption followed pseudo-second order reaction kinetics and Freundlich adsorption model (Fig.1). Computation of enthalpy, entropy and activation energy for the anion-adsorbent interaction in solution was evaluated to be 51.04kJ mol-1, 0.251kJ mol-1K^{-1} and 49.5kJ mol^{-1}, respectively. Temkin isotherm model shows the adsorption controlled by intra-particle diffusion control process. Column studies shows the break through volume as 280 with fluoride spiked water. The result demonstrated the potential and promising application of new polymeric composite material for efficient fluoride removal from drinking water.

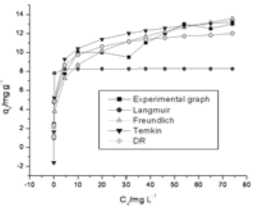


Fig.1: Application of adsorption model

References:

[1] Cheng, J.; Meng, X; Jing, C.; Hao, J.J.Hazard. Mater.**2014**, 278, 343 – 349.
[2] Chai, L.; Wang, Y.; Zhao, N.; Yang, W.; You, X.Water Res.**2013**, 47, 4040-4049.

Surface modified cellulose nanoparticles with silanes as reinforcement in composites

With increasing global concern over depletion of non-renewable fossil fuel and rising price for petroleum and petroleum derived products, present and future demands materials that are eco-friendly (with minimum waste disposal), having light weight, high durable with mechanical properties greater than or equal to those of traditional petroleum based materials. Natural cellulose based materials (wood, hemp, cotton, linen, etc.) have been used by our society as engineering materials for thousands of years, but cannot compete with high performance materials.

By extracting cellulose at the nanoscale, the majority of the defects associated with the hierarchical structure can be removed, and a new cellulose based ‘‘building block’’ (Cellulose nanoparticles (CNs)) can be obtained as the next generation of cellulose based composites. But one drawback is the hydrogen bonds present in CNs tend the fibres to agglomerate into bundles and unevenly distribute throughout the non-polar polymer matrix during compounding processing; resulting a weak interfacial adhesion. Therefore fiber treatment is beneficial towards improving the water resistance and wettability of the fiber surface by polymers and enhances interfacial adhesion. A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix. Mainly organosilanes are efficient coupling agents and they have been extensively used in composites. The hydroxyl groups present on the surface of the cellulose nanofibres is allowed to condense with the hydroxyl groups formed insitu during the hydrolysis of the silicates under alkaline or acidic pH conditions.

In this present work CNs were prepared from various sources like cotton, paper, baggase etc and insitu surface treatment with tetraethyl orthosilicate (TEOS) was also done. The properties of surface modified cellulose fibres are characterized by PXRD, SEM, TEM, TGA and FTIR. These reinforcement fillers were used in composites and the properties enhancement were studied.

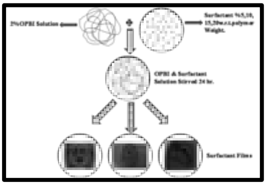
References:

1) Robert, J. M.; Martini, A.; Nairn, J.; Simonsenf, J.; Youngblood, J. *Chem. Soc. Rev*., **2011**, *40*, 3941–3994.
2) Abdelmouleh, M.; Boufi, S.; Salah, A.; Belgacem, M. N.; Gandini, A. *Langmuir*, **2002**, *18*, 3203-3208.
3) Yanjun Xie, Callum A.S. Hill , Zefang Xiao , Holger Militz , Carsten Mai . Silane coupling agents used for natural fiber/polymer composites: A review *Composites*: Part A 41 (**2010**) 806–819

Polybenzimidazole composite with acidic surfactant like molecules: An unique approach to develop PEM for the use in fuel cell

Balakondareddy Sana, Shuvra Singha, Tushar Jana
School of chemistry, University of Hyderabad, Hyderabad, India
Email: tusharjana@uohyd.ac.in

An ether linked polybenzimidaole (PBI) like oxypolybenzimidazole (OPBI) composite membranes are prepared by the addition of acidic surfactants with OPBI. The acidic surfactants used here are camphor sulfonic acid (CSA), paratoulene sulfonic acid (PTSA), mono dodecyl phosphate (MDP). Composites are made with respect to OPBI polymer weight in four different percentages (5%, 10%, 15%, 20% wt). The WAXD studies represent that the composite membranes have crystalline nature. The FT-IR, SS-NMR studies indicate the interaction between OPBI polymer and the surfactant in the composite membranes. The TGA studies proved the phosphoric acid (PA) doped OPBI/CSA, OPBI/PTSA, and OPBI/MDP composite membranes exhibits high thermal stability than pure OPBI. In all the three cases scanning electron microscopy (SEM) cross-sectional studies show that the membranes morphology affected the composite membranes properties. Mechanical properties of the composite membranes are quite high as obtained from the dynamic mechanical analyser (DMA) studies. PA doping level, water uptake, swelling ratio are carried out in both phosphoric acid and water medium. The PA doped composite membranes display higher proton conductivity than the conductivity of the PA doped OPBI. Higher percentage of the OPBI/CSA and OPBI/MDP composite membranes proton conductivities are found 2.82 × 10^{-1} S/cm and 1.43 × 10^{-1} S/cm temperature at 180^0C but OPBI/PTSA composite membrane conductivity as found to be 1.76 × 10^{-1} S/cm at 160^0C. All these results indicated that more promising candidates for the used as high temperature proton exchange membrane in fuel cell.



References:

[1] Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463-1502
[2] Kerres, J. *J. Membr. Sci.* **2001**, *185*, 3-27.
[3] Ghosh, S.; Sannigrahi, A.; Maity, S.; Jana, T. *J. Mater. Chem.* **2011**, *21*, 14897–14906.
[4] Singha, S.; Jana, T. *polymer* **2014**, *55*, 594-601.
[5] Carrette, L.; Friedrich, K. A.; Stimming, U. *ChemPhysChem* **2000**, *1*, 162-193.

Assessment of 'Agglomerated' versus finely dispersed Multiwalled Carbon Nanotubes in Polypropylene matrix: An investigation through Crystallization kinetiCS

Joyita Banerjee[1], Arup R. Bhattacharyya[1]*and Ajay S. Panwar[1]
[1]Department of Metallurgical Engineering and Materials Science,
Indian Institute of Technology Bombay, Powai, Mumbai - 400076, India
** E-mail: arupranjan@iitb.ac.in*

The state of dispersion of multiwalled carbon nanotubes (MWNTs) in polypropylene (PP) matrix was investigated through crystallization behavior of PP matrix using differential scanning calorimetric (DSC) analysis. PP/MWNTs composites (of 1-5 wt% of MWNTs content) were prepared via melt-blending, wherein two different MWNTs viz., NC3100 (Nanocyl SA, Belgium; hereafter, it would be denoted as N-MWNTs) and D-MWNTs (DMSRDE, Kanpur, India) were utilized. TEM observation had indicated differences in terms of 'agglomerated' structure, ordered graphitic content, purity and average diameter associated with respective MWNTs. Non-isothermal DSC analysis has indicated an increase in crystallization temperature (T_c) with increase in MWNTs content with respect to pure PP (115 ˚C). This observation was found to be more significant in PP/N-MWNTs composites (121 ˚C) as compared to PP/D-MWNTs (117 ˚C) composites at 4 wt% of MWNTs content. Heterogeneous nucleation ability of MWNTs has resulted in a decrease in half time of crystallization ($T_{½}$) from ~ 40 mins for pure PP to ~ 8 mins for PP/N-MWNTs and ~ 11 mins for PP/D-MWNTs composites at 1 wt% of MWNTs at 132 ˚C. Overall rate of crystallization (k) has significantly increased to 3.4 $x10^{-1}$ $min^{-1}$for PP/N-MWNTs composites as compared to 5.6 $x10^{-2}$ min^{-1} for PP/D-MWNTs composites at 1 wt% of MWNTs at 132 ˚C. PP/N-MWNTs composites have shown higher 'n' values of 1.5-1.9, which indicate a transition from 'rod' to 'disc' shaped crystal growth of PP. On the contrary, PP/D-MWNTs composites have exhibited 'n' values of 1.2-1.3, which manifest in a restricted crystal growth of PP. The rate of crystallization and 'n' value suggest a finer dispersion of MWNTs in PP/N-MWNTs as compared to PP/D-MWNTs composites, which may possibly be due to the higher extent of 'entanglements' associated with D-MWNTs as compared to N-MWNTs. This observation was further supported by scanning and transmission electron microscopic analyses.

Characterization of glyoxal modified SPI/ HLD fabric biocomposites

Palakshi Reddy* and Jeevan Prasad reddy
Sree Vidyanikethan Engineering College, Sree Sainath Nagar,
Tirupati, A.Rangampet, Andhra Pradesh – 517102
*palakshireddy@gmailcom

In this work, biocomposites were prepared using Hildegarida natural fabric (HLD) and a glyoxal modified soy protein isolate (GSPI) matrix. The effect of fabric loading on the mechanical properties (tensile and flexural) was investigated. GSPI/HLD biocomposites exhibited improved mechanical performance as compared to pure GSPI composites. The effect of chemical surface treatments (alkali and silane) of HLD fabrics on the mechanical properties, chemical resistance, and interfacial bonding was studied. It is evident that the strength and modulus of these composites with untreated fabric were increased by 1200% and 400 % respectively over those of the matrix. When alkali treated fabrics were used, these values got increased by 1200% and 600%. Morphological studies indicated improvement of interfacial bonding by alkali and silane coupling agent treatments of the fabrics. The chemical resistance of GSPI/HLD biocomposites was studied and found that the GSPI and GSPI/HLD biocomposites were not resisting in HNO_3 and NaOH.

References:

[1] Lodha, P.; Netravali, A.N. J. Mater. Sci. **2002**, 37, 3657–365.
[2] Luo, S.; Netravali, A.N. Polym. Degrad. Sta. **2003**, 80, 59–66.

Nanosilica filled PDMS/EVA hydrophobic nanocomposite for high voltage insulatior

Dipankar Ghosh, Prosenjit Ghosh, Tapan Kumar Chaki, Dipak Khastgir
Rubber Technology Centre, Indian Institute of Technology Kharagpur
Kharagpur-721302, West Bengal, India
ghoshdipankar2@gmail.com

The effect of modified hydrophobic nanosilica (MNSi) as one of the fillers on properties of high voltage insulator made from polydimethyl siloxane (PDMS)/ ethylene vinyl acetate (EVA) blends (60/40 wt%) was investigated. Composite samples with different nanosilica content in a blend of PDMS/EVA were subjected to aging under boiling water, dry heat, and UV radiation for the specific time duration. The changes in properties like surface resistivity, volume resistivity, dielectric properties, hydrophobicity and morphology were evaluated for these composites. The changes in various properties as mentioned above were found to be marginal when samples were treated with boiling water and dry heat. The recovery of hydrophobicity , after aging under dry heat, is appreciable for samples with higher nanosilica loading compared to samples with low nanosilica loading and it is found to be the best for 6 phr nanosilica loading. However when all samples were subjected to UV radiation there is an increase in hydrophobicity. Dry heat treatment and treatment of boiling water also increases the hydrophobicity. Addition of nanosilica marginally increases the dielectric constant and loss factor.

References:

[1] M.A. Pradeep, N. Vasudev, P.V. Reddy, D. Khastgir, Journal of Applied Polymer Science, 2007, 104 3505-3516.
[2] J.P. Reynders, I.R. Jandrell, S.M. Reynders, Dielectrics and Electrical Insulation, IEEE Transactions on, 1999, 6, 620-631.
[3] B. Shanshan, S. Jayaram, E.A. Cherney, Dielectrics and Electrical Insulation, IEEE Transactions on, 2013, 20, 185-193.
[4] J.V. Vas, B. Venkatesulu, M.J. Thomas, Dielectrics and Electrical Insulation, IEEE Transactions on, 2012, 19, 91-98.
[5] A. Milionis, R. Ruffilli, I.S. Bayer, RSC Advances, 2014, 4, 34395-34404.
[6] H. Homma, T. Kuroyagi, K. Izumi, C.L. Mirley, J. Ronzello, S.A. Boggs, Dielectrics and Electrical Insulation, IEEE Transactions on, 1999, 6, 370-375.
[7] J. Jin, S. Chen, J. Zhang, Polymer Degradation and Stability, 2010, 95, 725-732.
[8] G. Camino, S.M. Lomakin, M. Lazzari, Polymer, 2001, 42, 2395-2402.

An approach for Lowering the Percolation Threshold Value of Multiwall Carbon Nanotubes (MWCNTs) in the PP/HDPE/MWCNT Nanocomposites Using Styrene-b-Ethylene-co-Propylene-b-Styrene (SEPS) Co-polymer

Sarbaranjan Paria, Supratim Suin, Avinash Raulo and B. B. Khatua*
Materials Science Centre,
Indian Institute of Technology Kharagpur, Kharagpur 721302, India

Now a day's huge portion of research is going on to develop conducting polymer composites (CPCs) because of their immense applications in our daily life. Here, we developed a ternary polymer blend of PP, HDPE and SEPS in which the MWCNTs are located only in SEPS phase by simple industrially feasible melt blending method. The use of a tri-block copolymer SEPS helps to localize the CNTs at the interface of the PP and PE phase leaving the respective polymer phases to be CNT excluded. To engage almost all of the CNTs in the SEPS phase and form three dimensional networks along the blend interface required for low percolation threshold value, CNTs were premixed with SEPS, which is continuous throughout the whole matrix at the interface of the blend. The prepared nanocomposites have been electrically characterized by both DC and AC conductivities and dielectric properties. The obtained DC conductivity (1.3×10^{-3} Scm^{-1}) results have been correlated with the theory of percolation to attain the percolation threshold value and the underlying factors responsible for the high electrical conductivity. Thus, the percolation of MWCNT was obtained with a remarkably low CNT content at 0.12wt% in PP/HDPE/MWCNT nanocomposites where CNTs are used without modification.

Keywords: SEPS, MWCNT, Conductivity, PP, HDPE

References

1. Bhagat, N. A.; Shrivastava, N. K.; Suin, S.; Maiti, S.; Khatua, B. B. Polym. Compos. 2013, 34, 787-798.
2. Wu, D.; Zhang, Y.; Zhang, M.; Yu, W.; Biomacromolecules. 2009, 10, 417–424.
3. Lu, L.; Zhou, Z.; Zhang, Y.; Wang, S.; Zhang, Y. Carbon. 2007, 45, 2621–2627.

Diffusion of nanoparticles in ultra-thin polymer films: an in-situ study

Nafisa Begam, Sivasurender Chandran, Nupur Biswas and J K Basu*
Department of Physics,Indian Institute of Science, Bangalore-560012
*basu@physics.iisc.ernet.in

We report the *in-situ* X-ray scattering measurements vindicating the evolution of the dispersion of polymer grafted gold nanoparticles (PGNPs) dispersed in homopolymer matrixwithin a thin film during annealing[1]. Electron density profiles (EDP) in out-of-plane direction have been extracted from X-ray reflectivity profile with three layer model- *surface, bulk, interface*[2,3]. The resultant volume fraction of PGNPs(φ_{Au}) in three layers with time is shown in Fig. 1. Figure 1a reveals initially segregated un-annealed film becomes homogeneous during annealing. The average diffusion coefficient turns out to be 0.014 Å^2/s - two order of magnitude slower than corresponding bulk diffusion.

The in-plane diffusion characteristics of the PGNPs was probed with x-ray diffuse scattering (XDS) measurements. Figure 1b shows time evolution of the mean square displacement (MSDζ) varying as a power law with an exponent > 1, indicating a super-diffusive motion along the lateral direction. This slow out-of-plane and superdiffusivein-plane motion simultaneously helps it to make a homogeneously dispersed film. A schematic of the dispersion of PGNPs during annealing is shown in Fig. 1c.

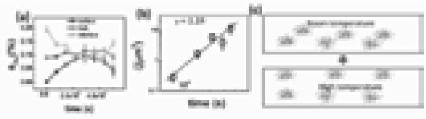


Fig. 1: (a) Time evolution of dispersion of PGNPs (φ_{Au}vs time) for different layers within PNC film (time zero points and end points correspond to room temperature data). (b) Evolution of MSD with time. (c)Schematic shows homogenization of distribution of PGNPs with temperature.

References:
[1] S. Chandran,J. K. Basu and M. K. Mukhopadhyay, J. Chem.Phys.,138,014902, (2013).
[2] N. Begam, S. Chandran, N. Biswas, and J. K. Basu, Soft Matt. *submitted* (2014)
[3] S. Chandran, N. Begam, V. Padmanabhan and J. K. Basu, Nat. Comm., 5, 1–9, (2014)

Effect of space filler and functional fillers on the friction and wear behavior of NBR powder modified Phenolic resin composite

Prosenjit Ghosh[1], Soumya Mondal[1], D. Khastgir[1], T. K. Chaki[1]*
[1]Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302
*tapan@rtc.iitkgp.ernet.in

Wear and friction properties of a polymer based friction composite are greatly affected by the interactions and synergistic effects among the multiple components used during composite fabrication. Both space fillers and functional fillers viz. abrasives, lubricants have due reasons to be used as an active multi-ingredient in polymer friction composite system. Different types of abrasives and lubricants have been fabricated in various possible combinations by both academia and industries over the last few years. Fibrous ingredients, which are the key reinforcing part of a conventional friction composite material, have been eliminated from the designed formulation to understand the effect of different filler functions on wear and friction behavior of the composites. Barytes has been taken as a space filler, whereas calcined petroleum coke and graphite powder have been adjusted as an abrasive and solid lubricant, respectively in the NBR powder modified Phenolic resin based formulation. Effect of individual fillers on the friction as well as wear characteristics has then been investigated separately on a pin on disc type of tribometer at room temperature. Subsequently, it has been found that the graphite based composites have depicted better wear characteristics, whereas the calcined petroleum coke based formulation has reported stable frictional coefficient among these three. Finally, the surface morphology of the friction composites has been studied by scanning electron microscopy (SEM) before and after friction and the results corroborates the tribological observations.

References:

[1] Mukesh Kumar, Jayashree Bijwe. Wear 269 (2010) 826–837.
[2] Zhencai Zhu, Lei Xu *, Guoan Chen Materials and Design 32 (2011) 54–61
[3] Mukesh Kumar, Jayashree Bijwe Wear 270 (2011) 269–280

Carboxymethyl cellulose based polymeric nanocomposites for transdermal drug-delivery

Barun Mandal and Sagar Pal*
Polymer Chemistry Laboratory, Department of Applied Chemistry,
Indian School of Mines, Dhanbad – 826004
Email-id: barunmandaliitd@gmail.com

Herein, we synthesized a carboxymethyl cellulose/MWCNT based polymeric nanocomposites for transdermal drug-delivery.MWCNT is ultrasonically dispersed in different weight percent aqueous carboxymethyl cellulose in different concentrations (with respect to CMC) to form the hybrid nanocomposites. The prepared nanocomposite has been characterized by using FTIR, XRD, FESEM and rheological analyses. Finally, we have also also used the nanocomposite for transdermal drug delivery application.

Room temperature processable, conformal ablative composites: Thermal and mechanical characteristics

Temina Mary Robert[1], Sunitha K.[1], Neeraj Naithani[2], Dona Mathew[1],
C. P. Reghunadhan Nair[1]
[1]Polymers and Special Chemicals Group, VSSC, Trivandrum
[2]Analytical, Spectroscopy and Ceramics Group, VSSC, Trivandrum

Polymer matrix composites offer a unique balance of properties which lend themselves attractive in structural and thermal insulation applications. These composites exhibit high specific strength, thermally stability, fatigue resistance, thermal cycling tolerance, etc making them suited for high performance aerospace applications. The present work describes development of a room temperature curable, silica reinforced ablative composites. State-of-the-art ablative composites are based on thermosetting matrices such as resole phenolics, poly benzoxazines, pthalonitriles, etc. which warrant high temperature curing (>150°C), making their processing time and energy intensive. Moreover, they need to be moulded or machined further to the required application contours. Present work describes room temperature processable, 'cure –in-place', self-extinguishing silica reinforced composites. The matrix is based on an epoxidizednovolac resin filled with glass microballoons (0-20% by weight) and cured using an equivalent ratio of amine based curing agent to tune the cure characteristics as well as the physical, thermo physical and thermo mechanical properties of the resultant composite. Prepreg tapes were processed by impregnating silica cloth/tapes with the matrix. The tapes were wound to required shape or contour and cured at RT for 24hrs. Extent of cure was monitored by FTIR, DSC thermograms and rheometry and cure completion was ensured. The cured composites exhibited inter laminar shear strength (ILSS) in the range of 20-23MPa, Flexural strength in the range of 100- 120MPa. The composite started to decompose above 250°C and its Limiting oxygen index (LOI) was found to be in the range of 30-40%. Coefficient of thermal expansion (CTE) was of the order of 10-5/°C, thermal conductivity in the range 0.4-0.45 W/m.K. The composites were pyrolysed at 700°C under inert atmosphere and char strength of the pyrolzed composites were determined to assess the composite as an ablative material. Dimensional stability of the composites was also evaluated by monitoring the shrinkage of the charred specimens. All the properties evaluated were correlated to the composition of the matrix system.

$R\text{-}NH_2$

Scheme1: Reaction between epoxy novolac and amine

References:

[1] Fried J R, Polymers in aerospace applications, SmithersRapra technology, Shawbury, 2010.

Multicomponent Magnetic Nanocomposites for Bone Tissue Engineering Applications

Arundhati Bhowmick[1], Nilkamal Pramanik[1], Manas Das[2] and Patit Paban Kundu[1]*
[1] Department of Polymer Science and Technology, University of Calcutta,
92 A.P.C. Road, Kolkata-700009, India
[2] Department of Chemical Engineering, University of Calcutta,
92 A.P.C. Road, Kolkata-700009, India.
*ppk923@yahoo.com

Development of scaffolds plays a vital role in tissue engineering in order to repair, regenerate, or create tissues and organs by mimicking of natural extracellular matrixes.[1] Scaffolds should have the suitable mechanical properties and the surface functionality to favor the cell adhesion, proliferation and differentiation[2]. Considering that bone is a composite of minerals and proteins[3,4], it is preferred to develop a composite that mimics natural bone. We have fabricated bone-like multicomponent magnetic nanocomposites (MMN I-III) simply by blending bio-compatible and bio-degradable natural polysaccharide of chitosan, polymethylmethacrylate-co-2-hydroxyethylmethacrylate (PMMA-co-PHEMA), and nano-hydroxyapatite-Fe_3O_4. The physiochemical, morphological and mechanical properties of the prepared nanocomposites were studied and significant improvement in mechanical properties (e.g. tensile strength, Young's modulus and stiffness) of the nanocomposites was observed. Swelling study indicates high water uptake ability in MMN I-III. Antimicrobial activities revealed that MMN I-III have excellent antimicrobial property which is necessary for practical applications. Thus, these materials should be a potential material for bone tissue engineering.

References:

[1] Langer, R.; Vacanti, J.P. Science **1993**, 260, 920
[2] Zhong, Z.K.; Sun, X.Z.S. Polymer **2001**, 42, 6961.
[3] Du, C.; Cui, F.Z.; Zhang, W.; Feng, Q.L.; Zhu, X.D.; Groot, K.D. J. Biomed. Mater. Res. A, **2000**, 50, 518.
[4] Kikuchi, M.; Itoh, S.; Ichinose, S.; Shinomiya, K.; Tanaka, J. Biomaterials **2001**, 22, 1705.

MWCNT/$CuFe_{10}Al_2O_{19}$/PolyanilineNanocomposite for Microwave Absorbing Applications

Pallab Bhattacharya[1, *],Chapal Kumar Das[1]
[1]Materials Science centre, Indian Institute of technology,
Kharagpur-721302, West Bengal, India.
E-mail: pallabcm@gmail.com

The formation of a MWCNT based nanocomposites and their structural characteristics were discussed thoroughly with their necessity on the field of microwave absorbing applications. Development of microwave absorbing material is a growing field of research in both the commercial and defense sector, and also to enrich the field of stealth technology. The recent work is attentive to the preparation of nanocomposite based on acid modified MWCNT, hexagonal shaped magnetic M-type hexaferrite ($CuFe_{10}Al_2O_{19}$) and polyaniline. $CuFe_{10}Al_2O_{19}$ was prepared by a facile chemical co-precipitation method. An in-situ approach was hired for the coating of polyaniline on MWCNT/$CuFe_{10}Al_2O_{19}$nanocomposite. The final fabrication of these nanocomposites for microwave measurements was done suitably in the matrix of thermoplastic polyurethane with 10% filler content. The prepared nanocomposites exhibited an outstanding and remarkable microwave absorption property in the X-band (8.2-12.4 GHz) region. The nanocomposites showed higher reflection loss with a broad absorption range in contrast to the pristine MWCNT and $CuFe_{10}Al_2O_{19}$. Addition of PANI improves the microwave absorption property of the nanocomposites. The thermal stability of the prepared nanocomposites is also high enough for the use of it in various high temperature applications.

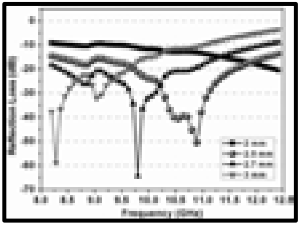


Figure 1: Reflection loss vs frequency plot of prepared nanocomposites at different thicknesses.

Polybezimidazole–CuBTC Composites: Effects of polymer structure on gas permeation of composite membranes

Anand Bhaskar[1], Rahul Banerjee[2] and Ulhas Kharul[1]
[1]Polymer Science and Engineering Division,
[2]Physical and material Chemistry Division, National Chemical Laboratory, Pune – 411008
Email: uk.kharul@ncl.res.in

Metal organic frameworks (MOFs) are a new class of ordered porous materials with tremendous diversity in their chemical structure and porosity.[1] They are rapidly perused as next generation membrane materials for the energy efficient gas separation application.[2] CuBTC is one of the most thoroughly studied MOFs as membrane material for its potential applicability in gas separation. It is usually fabricated as a continuous polycrystalline film on porous support or by mixing with polymers to enhance their permeation performance.[3, 4] Pristine CuBTC films normally show poor selectivity due to the inter crystalline defects. On the other hand, polymer based composites face compatibility issues. Lack of good compatibility between CuBTC filler particles and polymer adversely affects the gas permeation. Thus; there is need for further investigations with better compatible blends of a polymer and CuBTC for improvement in gas permeation properties.

We have studied effects of polymer structure variation on the gas permeation of the composite membranes, viz. CuBTC@PBI-BuI. This work demonstrates the critical role of polymer structural architecture on governing gas permeation properties of the composite material.

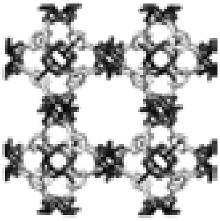


Fig. 1 Chemical structure of the CuBTC.

References:

[1] Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M.; Science, ***2013***, 341, 974-988.

[2] Li,J. R.; Sculley, J.; Zhou, H. C.; Chem. Rev. ***2012***, 112, 869–932.

[3] Qiu, S.; Xue, M.; Zhu, G.; Chem. Soc. Rev.*,* ***2014***, 43, 6116--6140.

[4] Jeazet, H. B. T.; Staudt, C.; Janiak, C.; J. Membr. Sci., ***2010***, 362, 478.

Understanding the Mechanism of Controlled Biodegradation of Polymer using Nanoparticles

Sunil Kumar[1] and Pralay Maiti[1]*
School of Materials Science and Technology IIT (BHU), Varanasi
**pmaiti.mst@itbhu.ac.in*

The main objective of this work is to develop an innovative process to control the degradation of polyesters using biological agent. The PCL PLA and PU are the widely used polyesters. Therefore, their mechanism of degradation was controlled on the basis of pH using three nanoclay 30B, 15A, C-18. Nanoclays act as strong nucleating agent that increased the filler dependency phenomena which was used to control the degradation rate. The degradation rate of polyesters were measured in term of depolymerase activity. The depolymerase activity of PCL and PLA by lipase was found maximum under alkaline zone at pH 7.7 and 7.2 respectively, while PU showed highest degradation at 6.5 pH. The pH of three nanoclay 30B, 15A, C-18 in deionized double distilled water was measured to be 7.8, 7.2 and 6.4, respectively. The respective pH of nanoclay were blended to corresponding depolymerase activity of polyester to monitor the biodegradation. The spectroscopic analysis of PCL suspension with 30B nanoclay showed maximum biodegradation through lipase while decrease rate with C-18 nanoclayin comparison to pure PCL suspension. The similar results were also observed with PLA and PU suspension with respective pH of nanoclay. PLA-15A nanocomposite film revealed 67% weight loss after 9 days in contrast to PLA-30B with 44% on treatment with lipase. The results were further supported by morphological studies.A model has been proposed for the controlled biodegradation of polymer induced by different nanoparticles.

Effect of poly (ethylene glycol) on thermal, mechanical and rheological properties of PLA/PEG biodegradable blends

Ranjana Nehra*, S. N. Maiti and Josemon Jacob
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New Delhi (India)
**ranju.nehra@gmail.com*

Poly (lactic acid) (PLA) is biodegradable aliphatic polyester which is obtained from renewable resources. PLA was plasticized with poly (ethylene glycol) (PEG) of molecular weight 4000 g/mol in varying concentration (0-30 wt %) using a twin screw extruder. Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) were used to analyze the thermal behaviour of PLA/PEG blends. DSC results reveal that crystallinity of PLA increased while significant decrease in glass transition temperature occurred with PEG content. The mechanical potential of these blends are explored using tensile and impact properties. Tensile strength and modulus decreased in a linear fashion with increasing PEG content. The impact strength of blends increased with PEG content, at 20 wt% PEG content the increase was by 60%. The Dynamic mechanical analysis (DMA) showed that as the PEG content increases, storage modulus and loss modulus decrease. The shear viscosity of PLA/PEG blends were lower than that of pure PLA and decreased considerably with increasing PEG content.

References:

[1] Z. Kulinski, E. Piorkowska, Polymer, **2005**, 46, 10290–10300.

[2] Isabelle Pillin, Nicolas Montrelay, Yves Grohens, Polymer, **2006**, 47, 4676–4682.

[3] Guralp Ozkoc, Sebnem Kemaloglu, Journal of Applied Polymer Science, **2009**, 114, 2481–2487.

Synthesize of nanocellulose from bio-waste and it's utilization for interfacial adhesion enhancement

Suma K.K.[1], Anmiya Peter[1], Vinod A.G.[1], Sinto Jacob[2*]
[1]Department of Chemistry, Maharajas College, Ernakulam, Kerala, India
[2]Department of Chemistry, St. Aloysius College, Elthuruth, Thrissur, Kerala, India
*sumarobin@yahoo.co.in

The bio-waste 'coconut pith' is an agro-industrial lignocellulosic residue generating as the by-product in coir industry. Resistance to natural degradation and leaching of polyphenols to the environment makes coconut pith a severe threat to the ecosystem. Extraction of cellulose from coconut pith is an effective way of utilization of coconut pith and thus to increase the income of farmers. Delignification by oxidation and the mechanical treatments helped to extract cellulose and its conversion to nanocellulose from coconut pith by cost effective way. TEM analysis showed the size of extracted cellulose in nanometer scale. Rubber blends are used for the preparation of commodity goods to speciality products. But the easy blending of polar and non polar rubber is very difficult. Synthesised cellulose is used for the enhancement of interfacial interaction between polar-nonpolar rubber. Natural rubber [NR] (non-polar rubber) successfully blended with chloroprene rubber [CR] (polar rubber) by the incorporation of extracted cellulose from coconut pith. Master batch process was utilized for the preparation of NR/CR blend. Mechanical properties such as tensile strength, tear resistance, abrasion resistance, compression set, rebound resilience, heat build-up etc. are used for the blend evaluation and optimization of nanocellulose concentration for making good quality blend. The results were compared with the commercially available cellulose. It is found that the cellulose from coconut pith is effective to improve interfacial interaction of NR/CR blend compared to commercially available microcrystalline cellulose.

References:
[1] Martins, A.F.; Suarez, J.C.M; Visconte, L.L.Y.; Nunes, R.C.R.; Mater. Sci. **2003,** 38, 2415-2422.
[2] Wen Bai; Kaichang Li; Composites: Part A **2009**, 40, 1597–1605.
[3] Visakh, P.M.; Thomas, S; Oksman, K.; Aji P.M.; *JAPS* **2012**, 124, 1614–1623.

Nano titanium dioxide: Synthesis and its reinforcement with natural rubber

Sinto Jacob[1*], Aneena K.T.[2], Suma K.K.[2]
[1]Department of Chemistry, St. Aloysius College, Elthuruth, Thrissur, Kerala, India
[2]Department of Chemistry, Maharajas College, Ernakulam, Kerala, India
*sintojacob@rediffmail.com

Polymer products are widely using for the applications such as food packages, furniture, refrigerator etc. They are highly useful in the areas were antimicrobial and antipollution properties are required. The biopolymer natural rubber (NR) possess remarkable elasticity and undergoes long range reversible extension under relatively small applied force. Titanium dioxide (TiO_2) is very well known for its antibacterial activities, photocatalytic activities and environmental cleanup activities. Since natural rubber is susceptible to oxidation and other environmental factors, nano-TiO_2 incorporated natural rubber can show higher resistance to oxidation, increase biocompatibility and thus can widen the application area of rubber composite..

In rubber industry conventional TiO_2 is used as non-reinforcing filler as well as white pigment. The present study involves the preparation of nano TiO_2 and its evaluation as reinforcing filler in NR. Nano titanium dioxide prepared in colloidal form and is incorporated into natural rubber by latex stage mixing. The peculiarity of the study is the liquid stage incorporation of nano colloidal sol of TiO_2 with NR latex. The present study investigated the reinforcing nature of nanoTiO_2 in natural rubber by the evaluation of properties such as tensile strength, tear strength, abrasion resistance, compression set, solvent resistance etc. NR/nano TiO_2 composite prepared through latex stage mixing showed superior performance.

References:

[1] Cristina, V.; Luminita, A.; Anca, D; Journal of Nanoscience and Nanotechnology, **2009**, 9, 1–9.
[2] Stephen, S.O; Adriaan, S.L.; International Journal of Composite Materials: **2011**, 1(1), 7-13.
[3] Tatiane, M.A.; Katyuscya, V.L.; Antonio, G.F.; Polymer Testing, **2009**, 28, 490–494

Experimental Evaluation of Mechanical Properties of Cocos Nuci Fera L. Thick Leaf Sheath Woven Fibre Reinforced Polyester Composites

Nadendla Srinivasababu[1*], Thota Sailalitha
[1]Department of Mechanical Engineering, Vignan's Lara Institute of Technology and Science,
Vadlamudi-522213, Andhra Pradesh, India
[21]IV B.Tech Mechanical Engineering, Vignan's Lara Institute of Technology and Science,
Vadlamudi-522213, Andhra Pradesh, India
*cnjlms22@yahoo.co.in

In India utilization of potential bio mass exists for various applications is a significant task. Cocos Nuci Fera L. is the scientific name of coconut tree and it belongs to Arecaceae (palm family). Nearly eighty varieties of the coconut have been described in the literature (FAO,1970). Many of these are ecological type and are evolved as a result of adaptation to a certain environment. Intermediate forms will also occur due to hybridization. One of the ways of classification of the trees is based on color, size, shape, inflorescence, and size of the trunk whereas recent classification is due to genetic characteristics, mode of pollination. The coconut palm is a typical monocotyledon. It has many thousands of long narrow roots emerge from base of the swollen bole or stem.

In the present work an attempt is made to collect thick coconut leaf sheaths which are in woven form from the coconut trees in the field of N. Chennakesavaih located in Gorigapudi, Guntur Dt., and Andhra Pradesh and have twenty five years of life, are of pure-bred. The trees have moderate water supply in the year along with the regular annual rain fall. The composites are fabricated using Ecmalon 4413 unsaturated polyester resin and are tested according to ASTM standards. The obtained mechanical properties are compared with the values exist in the literature. Based on the reasonably good results, one finds application of the composites in the fabrication of automobile parts.

References:

[1] Brian E. Grimwood, "Coconut Palm Products: Their Processing in Developing Countries", Food and Agriculture Organization of the United Nations, Rome **1975**.
[2] Satyanarayana, K. G.; Pillai, C. K. S.; Sukumaran, K. J. Mat. Sci. **1982**, 17, 2453-2462.
[3] Obi Reddy, K.; Siva Mohan Reddy, G.; Umamaheswari, C.; Varada Rajulu, A.; Madhusudhana Rao, K. J. Fore. Res. **2010**, 21, 53-58.
[4] Winowlin Jappes, J., T.; Siva, I. Poly.-Plas. Tech. Engg. **2011**, 50, 1600–1605.
[5] Siva, I.; Winowlin Jappes J. T.; Sankar, I.; Amico, S., C.; Ravindran, D. J. Mfg. Engg. **2013**, 8, 060-063.
[6] Senthil Kumar, K.; Siva, I.; Rajini, N.; Jeyraj, P.; Winowlin, J. T. J. Rein. Plast. Comp. **2014**, 33, 1802-1812.

How Intellectual Property (IP) sparks academic-industrial research partnership?

Dr. Asim Pattanayak, Aditya Chakravarti, Mahalakshmi Ganesh,
Dr. Raghunadh Vajjula, Dr. Ganesh Sathyamurthy & Dr. Arup Ghosh
Legal Affairs – Intellectual Property Analysis Team,
SABIC Technology Center, Bangalore, India

Universities and industry have been collaborating for over a century, but the rise of a global knowledge economy has intensified the need for strategic partnerships that go beyond the traditional funding of discrete research projects. Further, with ever increasing cost of capital, uncertainty in global consumer demand - industry is increasingly looking at leveraging the “intellectual” infrastructure of academic institutes to remain competitive while academic institutes look at overcoming reduced Governmental funding by partnering with industry.This paperdiscusses the use of Patent Information to initiate the hunt for the right partner to take the Industry-Academia relationship forward. The importance of Patent Landscape studies and role of licensing, Joint Disclosure Agreements (JDA) & technology transfer are discussed.

References:

[1] Making University-Industry Partnership Work –The Science| Business Authors.

Performance of Shear Thickening Fluid Treated p-Aramid Fabric Composites

Animesh Laha*, Abhijit Majumdar, B. S. Butola,
Akash Gupta, and Rachit Agarwal
[1]Department of Textile Technology, Indian Institute of Technology Delhi,
*ttz138210@textile.iitd.ac.in

Soft body armours are used by police personnel and soldiers to protect them from the attack of hand gun or pistol. In order to facilitate their body movements, it is desired that the armour should be light and flexible. Recently, shear thickening fluid (STF) treated p-aramid (Kevlar) woven fabric composites are used as one of the potential material for this kind of application. In this work, STF was prepared using silica nano particles and polyethylene glycol (PEG) of different molecular weight (MW). Rheological studies of STF conducted with a parallel plate stress controlled rheometer have shown an abrupt increase in viscosity after a critical shear rate. This effect was found to be more prominent with increasing the MW of PEG. Kevlar fabrics were treated with the prepared STF. Yarn pull-out, yarn extension and yarn rupture are the three major modes of energy absorption during impact testing of STF treated fabric composites. So, yarn pull-out test was carried out using universal tensile tester to evaluate the performance of STF treated Kevlar fabric composites. Various configurations of yarn pull-out test were tried using a newly fabricated jaw. Test results clearly show that more yarn pull-out force is obtained in case of STF treated fabrics than the untreated fabrics. Yarn pull-out force also increases with the increase in MW of PEG. The normalized yarn pull-out force increases in a nonlinear manner with the increase in number of yarns taken in the pull-out study.

References:

[1] Kirkwood, K. M., Kirkwood, J. E., Young, S. L., Ronald, G. E. J., Wagner, N. J., Wetzel, E. D., T. R. J. **2004,** 74, 920-928.
[2] Majumdar, A., Butola, B. S. Srivastava A., Mater. Design. **2013**, 51, 148-153.
[3] Carr, D. J. J. Mat. Sci. Lett. **1999,** 18, 585-588.
[4] Bilisik, K. Composites: Part A. **2011,** 42, 1930-1942.

Investigation on sodium benzoate release from poly(butylene adipate-co-terephthalate)/ organoclay/ sodium benzoate based nanocomposite film and their antimicrobial activity

Dibyendu Mondal[1] Biplab Bhowmick[1] & Dipankar Chattopadhyay[1]*
[1]Department of Polymer Science and Technology,
University of Calcutta, Kolkata-700009, India
*dipankar.chattopadhyay@gmail.com

Antimicrobial film containing poly(butylene adipate-co-terephthalate) (PBAT) / organoclay (CMMT) / sodium benzoate (SB) was made by a solution mixing process. Cation exchange technique has been employed for modification of montmorilonite (MMT) to get CMMT using cetyl trimethylammonium bromide (CTAB) and confirmed through FTIR, TGA and XRD studies. PBAT/CMMT nanocomposite film showed higher barrier properties against water vapor compared to the virgin PBAT film. The release of sodium benzoate from PBAT and its nanocomposite film was measured and data were fitted in the Weibull model. Bacterial inhibition studies were evaluated against two food pathogenic bacteria like *Bacillus subtilis* and *Staphylococcus aureus* using the inhibition zone method and growth curves of bacteria. Those experiments established that PBAT/CMMT/SB showed better antimicrobial activity compared to PBAT/SB film. Therefore, the PBAT/CMMT/SB nanocomposite film can be used for food packaging application as it showed good barrier properties and antimicrobial activity against food pathogenic bacteria.

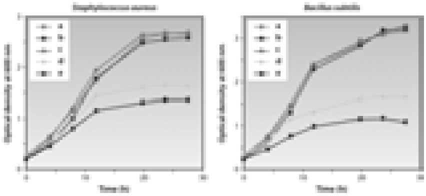


Figure: Growth curves of Bacillus subtilis and Staphylococcus aureus in the Nutrient broth containing (a) control medium, (b) PBAT, (c) PBAT/SB, (d) PBAT/4wt% CMMT and (e) PBAT/4wt% CMMT/SB at 37°C.

Synthesis and Characterization of Transparent Erbium Doped Polymer Nanocomposites: A Promising Candidate for Active Polymer Optical Fiber

Ipsita Chinya, Chandra Khatua, Ranjan Sen and Anirban Dhar*
Academy of Scientific and Innovative Research, CSIR-CGCRI
Fiber Optics & Photonics Division, CSIR-Central Glass & Ceramic Research Institute
196 Raja. S. C. Mullick Road, Jadavpur, Kolkata-700 032, India
*anirband@cgcri.res.in

Rare-earth (RE) doped polymer optical fiber (POF) attracts increasing research interest due to their technological cutting edge over glass fibers, in terms of easy handling, flexibility and cost effectiveness which make them suitable for short-distance communication [1]. Among different RE ions, erbium (Er) is the most important due to their potential application as amplifier and sensor. In compare to conventional inorganic RE salts, RE-chelates provides higher solubility in a polymer matrix without appreciable concentration quenching effects [2]. A sharp refractive index increase at the interface of the particles and polymer matrix results strong scattering and optical clarity of the composite system rapidly diminishes [3]. Accordingly, doping of RE ion in polymer matrix maintaining optical transparency is a real challenge. Here, we report synthesis and characterization of polystyrene (PS) and poly methyl methacrylate (PMMA)-grafted Er_2O_3 colloidal nanocomposite particles using a simple technique which will be a potential material for active POF. Nano erbium oxide (Er_2O_3) particles were synthesized by mixing Erbium nitrate ($Er(NO_3)_3{\cdot}5H_2O$) and urea ($CO(NH_2)_2$) in dimethyl formamide (DMF) following optimized reaction condition. The synthesized particle is then en-capsulated using 3-methacyloxypropyltrimethoxy silane (MPS) followed by drying in a vacuum. In-situ polymerization of MMA was performed using benzoyl peroxide as initiator in toluene medium and blended with PS using tetrahydrofuran as a solvent prior to coating on glass slide. UV-vis spectroscopic measurement revealed optimum particle size (15-35 nm) to achieve optical transparency. The Shape of particle and their sizes were evaluated from FESEM, SEM are in good agreement with the particle size analysis data. XRD of synthesized particle and film confirms presence of Er_2O_3 nano-crystal while refractive index of the film measured by prism coupler indicates RI > 1.5 at 589 nm wavelength. All observed result indicates synthesized material is a potential candidate for active core material in fabrication of POF.

References:

[1] Kobayashi,T; Nakatsuka, S; Iwafuji ,T; Kuriki, K; N Imai , Nakamoto,T,;Claude, C. D.;Sasaki, K; and Koike,Y; Okamoto,Y. Applied Physics Letters. **1997**, 71, 2421-2423.
[2] Koeppen, C.; Yamada, S.; Jiang, G.; Garito, A. F.; Dalton,R.L. J. Opt. Soc. Am. **1997**,14, 155-162.
[3] Hanemann,T;Szabó,V.D.Materials **2010**, *3*, 3468-3517.

Mechanical Investigations of Polypropylene based composites

Manoj Kumar[1], S. K. Srivastava[2] and Vikas Gupta[1]
[1] IFTM University Moradabad U.P.
[2]CeNSE IISc, Bangalore
**mkchauhan13@gmail.com*

Polypropylene based composites are getting better attention by research community because of sturdiness and tailorable mechanical properties. The mechanical properties, such as, tensile properties of polypropylene (PP) based SEBS copolymer are investigated with varied concentration of SEBS-g-MA copolymer from 0 to 20 wt%. It was observed from the stress strain curve that the pure polypropylene showed rubbery deformation. It was also observed that Young's modulus decreases with increasing wt% of SEBS, which may be due to flexible nature of copolymer. The area under the curve increases with increasing wt% of SEBS, which indicates the enhancement of energy absorption properties of the composites. The effect of salt spray on Young's modulus was also investigated to study the degradation properties.

Preparation and Characterization of Phosphonium Modified Organoclay used as a Potential filler for the development of exfoliated and optically transparent polymethylmethacrylate/clay nanocomposite

Dr. B. B. Khatua[1], Prajesh Nayak[2]*
Material Science center Indian Institute of Technology, Kharagpur

We report the preparation and properties of optically transparent polymethylmethacrylate (PMMA)/clay nanocomposites through the conventional methods of nanocomposites preparation (melt blending and solution blending) leading mainly to the exfoliation of thermally stable phosphonium modified organoclay. The organic modification of the sodium montmorillonite (Na-MMT) was done by the inclusion of (Methoxymethyl)triphenylphosphonium chloride (MOMTPPC) ion inside the layer spacing of Na-MMT clay through ion exchange reaction. The resulting quaternary phosphonium modified organoclay showed outstanding stability against thermal degradation in isothermal TGA analysis at the processing temperature of PC (190_C). Wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) studies revealed that the MMT layers were well exfoliated at lower loading (0.5 phr) of MOMTPPC-MMT, whereas, presence of a mixed clay morphology of exfoliation with minor intercalation was obtained at higher loading (1 phr) of the clay in both the melt and solution blended PMMA/MOMTPPC-MMT nanocomposites. The tensile strength and Young modulus were increased, whereas, elongation at break was decreased with increase in clay loading in both the melt and solution blended MOMTPPC-MMT nanocomposites. The thermo-mechanical properties of the nanocomposites were superior to that of the neat PC in both the glassy and rubbery regions. The optical transparency of PC was retained without development of any colour in the PMMA/MOMTPPC-MMT nanocomposites.

Keywords: PMMA, Na-MMT, Nanocomposites, Transparent, Thermal Stability.

References

[1] Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym **Sci 2003**;28: 1539–641.
[2] Usuki A, Hasegawa N, Kato M. Polymer-clay nanocomposites. Adv Polym Sci **2005**; 179:135-95.
[3] Pavlidoua S, Papaspyrides CD. A review on polymer-layered silicate nanocomposites. Prog Polym Sci **2008**; 33:1119–98.
[4] Chen TK, Tien YI, Wei KH. Synthesis and characterization of novel segmented polyurethane/clay nanocomposites. Polymer **2000**; 41:1345–53.
[5] Najafi N, Heuzey MC, Carreau PJ. Polylactide (PLA)-clay nanocomposites prepared by melt compounding in the presence of a chain extender. Compos Sci Technol **2012**; 72:608–15.
[6] Cho J W, Paul DR. Nylon 6 nanocomposites by melt compounding. Polymer **2001**; 42:1083–94.
[7] Dalir H, Farahani RD, Nhim V, Samson B, Levesque M, Therriault D. Preparation of highly exfoliated polyester-clay nanocomposites: process-property correlations. Langmuir **2012**; 28:791–803.
[8] Messersmith PB, Giannelis EP. Synthesis and barrier properties of poly(e-capro1actone)-layered silicate nanocomposites. J Polym Sci Polym Chem **1995**;33:1047–57.

Polyphenylene sulfide based conducting hybrid composites: effect of aspect ratio of second conducting filler on the electrical percolation

B.T.S. Ramanujam[1*], S. Radhakrishnan[2]
1. School of Engineering and Technology, Navrachana University, Vadodara, Gurajat
2. Research, Innovation center, Maharastra Institute of Technology, Pune, Maharashtra
*ramanujambts@nuv.ac.in

Electrically conducting polymer composites are being focused due to their demand in various applications such as Fuel cell bipolar plates[1], EMI shielding devices[2] etc. As polymer based composites offer excellent flexibility due to easy processing, light weight, reduced cost, they are in high demand as alternatives for conventional materials. Every application demands certain level of electrical conductivity along with other properties such as mechanical and thermal, the required level of electrical conductivity is obtained by careful selection of fillers. Conducting fillers such as graphite, metal fibers etc. can be added to insulating polymer matrix to make the resulting composite electrically conducting. In binary composites, at a particular loading of conducting filler known as percolation threshold (φ_c), the electrical conductivity shoots up to many orders. The electrical percolation threshold depends on filler particle size, aspect ratio, orientation, processing routes along with the characteristics of the polymer matrix. For easy processing, it is advisable to keep the percolation threshold as minimum as possible. In this regard nanofillers such as carbon nanofiber, carbon nanotubes, graphene etc. are being focused.

Polyphenylene sulfide (PPS) is a high temperature semicrystalline thermoplastic which exhibits better dimensional stability, creep resistance etc. Powder mixed PPS-graphite binary composites exhibits percolation threshold at 7 wt% graphite loading. In PPS-7 wt% graphite, second conducting fillers such as carbon black, sonicated expanded graphite and carbon nanofibers were mixed to make conducting hybrid composites. The electrical percolation threshold was reduced with respect to the aspect ratio of the second conducting filler. It has been found that the second conducting filler occupies inter graphite space and hence the barrier for the charge transport has been reduced considerably. Hence detailed analysis of electrical properties of these hybrid composites along with the corresponding binary composites will be presented.

References:

[1] Radhakrishnan, S; Ramanujam B. T. S.; Adhikari A.; Sivaram S. J. Power Sources **2007**, 163(2), 702-707.

[2] Al-Saleh M. H.; Sundararaj U. Carbon **2009,** 47, 1738-1746.

Photoinduced energy transfer in dye encapsulated polymer nanoparticle–CdTe quantum dot light harvesting assemblies

Simanta Kundu, Bipattaran Paramanik, Bikash Jana,
Dipankar Bain, and Amitava Patra*
Department of Materials Science,
Indian Association for the Cultivation of Science, Kolkata 700 032, India

Here, we have designed organic–inorganic light harvesting assemblies in which highly efficient resonance energy transfer occurs from CdTe quantum dots (donors) to Nile Red dye (acceptor) encapsulated polymer nanoparticles. Our motivation is to develop an assembly where the quantum dots (QDs) will absorb visible light as an antenna material, followed by the funnelling of the exciton to an acceptor molecule (the Nile Red dye), which is confined in polymer nanoparticles in order to enhance their energy transfer efficiency. An ionic liquid is used to prepare the positively charged Nile Red (NR) dye encapsulated poly(methyl methacrylate) (PMMA) polymer nanoparticles. Then, the negatively charged thioglycolic acid capped CdTe QDs are attached to the surface of the polymer nanoparticles by electrostatic interaction. The drastic quenching of the photoluminescence (60%) and the shortening of the decay time of the CdTe QDs imply an efficient energy transfer (73%) from the CdTe QDs to the NR dye doped PMMA nanoparticles. Time resolved anisotropy decay measurements reveal the rotational motion of the dye molecules inside the PMMA nanoparticles. Interesting findings reveal that the efficient energy transfer in the organic–inorganic assemblies may open up new possibilities for the design of an artificial light harvesting system for future applications.

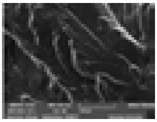
References:

[1] Kundu S.; Bhattacharyya S.; Patra A. Mater. Horiz.**DOI:** 10.1039/C4MH00138A.

Optimization of the Processing Parameters via Statistical Methods for the Thermoplastic Vulcanizate Nanocomposites

Aruna Kumar Barick*
Department of Chemistry, Veer Surendra Sai University of Technology (VSSUT),
Burla, Sambalpur – 768018, Orissa, India
**akbarick@gmail.com*

Statistical approaches including Taguchi design of experiments (DOE), analysis of variance (ANOVA), and multiple linear regression analysis were taken to evaluate the optimum processing conditions for the preparation of thermoplastic vulcanizate nanocomposite (TPVNC) based on thermoplastic polyurethane (TPU)/millable polyurethane (MPU) blend incorporated with Cloisite 30B (C30B) of composition TPU/MPU/C30B = 50/50/3 wt/wt/wt using an internal batch mixer. Total numbers of mixing layouts were designed by the application of Taguchi's orthogonal array (OA) methodology based on three parameters and three levels in the L_9 selector matrix model. Mechanical properties of all the runs were measured and fitted into the statistical software to determine the signal to noise (S/N) ratio. Ranks of the parameters were determined based on the delta statistics of the *larger is better* case of the S/N ratio. The ANOVA parameters were analyzed and percentage contribution of each factor, along with the correlation co-efficient of each variable was measured. The multiple linear regression models for each property were correlated with the parameters through mathematical equations. Fourier transform infrared (FTIR) analysis was performed to examine the existence of interfacial interactions between polyurethane matrices and organoclays. X-ray diffraction (XRD) analysis and field emission transmission electron microscope (FE-TEM) were employed to analyze the dispersion of organoclays in the polyurethane matrix. Field emission scanning electron microscope (FE-SEM) was employed to observe cryo-fractured morphology. Dynamic mechanical analysis (DMA) and dynamic shear rheometer (DSR) were used to investigate the dynamic mechanical properties and rheological properties of the trials, respectively. Based on all of these characterizations, an optimum processing condition was established.



FESEM
image of Run
1 (180 °C, 60 rpm, & 6 min)
(Left Side)
FETEM
image of Run
1 (180 °C, 60 rpm, & 6 min)
(Right Side)

References:

[1] Barick, A.K.; Jung, J.-Y.; Choi, M.-C.; Chang, Y.-W. J. Appl. Polym. Sci. **2013**, 129, 1405–1416.

[2] Barick, A.K.; Chang, Y.-W. J. Appl. Polym. Sci. **2013**, 130, 4014–4023.

[3] Barick, A.K.; Chang, Y.-W. High Perform. Polym. **2014**, 26, 609–617.

Hygrothermal aging effects on nano-carbon reinforced epoxy adhesive joints

P. Jojibabu[1], G.D. Janaki Ram[1], Srinivasa Rao Bakshi[1]*,
Abhijt P Deshpande[2]*
[1]Department of Metallurgical and Materials Engineering,
Indian Institute of Technology Madras, Chennai, India-600036.
[2]Department of Chemical Engineering,
Indian Institute of Technology Madras, Chennai, India-600036.
[1]sbakshi@iitm.ac.in, [2]abhijit@iitm.ac.in

Epoxy adhesives are largely used adhesive types for joining similar and dissimilar materials.In order to enhance the strength of epoxy adhesive joint, differentnanofillerssuch as carbon nanotubes (CNTs)[1], aluminum oxide (Al_2O_3), silica (SiO_2)[2]etc. have been used. In this present study, different types of carbon nanofillerssuch as multiwalled carbon nanotubes (MWCNTs), graphene nanoplatelets (GNPs) and carbon nanohorns (CNHs) of different amounts 0.2, 0.5, 1 and 2wt.% were dispersed using Brabender®Plasti-Corder®. Rheological studies were done to observe the effect of carbon nanofillersaddition on the viscosity of epoxy resin at different shear rates.The adhesive lap joints were tested using the ASTM standard test D1002. It was found that the lap shear strength of the adhesive bonded joints increased with increase incarbon nanofillercontent up to the level of extentconsiderd as optimum.Increase in the amount of the carbon nanofillersbeyond a certain weight fraction in the adhesive, reduced the strength of the joint. The effect of density and specific surface area of nanofillers on adhesive strength was studied. Dispersion of carbon nanofiller in epoxy matrix was studied using HRSEM and it was observed that the dispersion of the carbon nanofillers was poor at higher content. Amongthe three nanofillers, MWCNTs are found to be most effective at higher loading while GNPs were better at lower loading of the filler content. The mechanical properties of adhesive joints change with aging for long term durations at different temperatues and relative humidity conditions [3]. In this work, aging studies of the neat and 0.5 wt.% carbon nano-filled epoxy adhesive joints were carried out at elevated temperature and higher relative humidity conditions. The mechanical behavior of aged specimens were investigated and the failure mechanisms were also studied.

References:

[1] U. Vietri, L. Guadagno, M. Raimondo, L. Vertuccio, K. Lafdi, Composites Part B: Engineering, 61 (2014) 73-83.
[2] M. Mansourian-Tabaei, S.H. Jafari, H.A. Khonakdar, Journal of Applied Polymer Science, 131 (2014) n/a-n/a.
[3] F. Zhang, X. Yang, H.-P. Wang, X. Zhang, Y. Xia, Q. Zhou, International Journal of Adhesion and Adhesives, 44 (2013) 130-137.

Study the Topology of Styrene-Butadiene Copolymer Blends and Nanocomposites of Polypropylene

Amit M. Gawde[1], Prof. R. N. Jagtap[2]
Department of Polymer and Surface Engineering,
Institute of Chemical Technology, Mumbai
amitgawde89@gmail.com[1]

Polypropylene (PP), a member of Polyolefin's family is lightest amongst all. PP passes higher softening temperature, lower shrinkage and excellent environmental crack resistance. This versatile polymer is used for molded articles for house hold and medical application; however, largest applications are in films like Biaxial oriented polypropylene (BOPP) and automobile components. This chemically neutral polymer, gives edge of advantage in many applications, but poses serious limitation while decorating these objects. In order to alter the topology for improving the paint adhesion on this chemically inert material, surface preparation and treatment is necessary. However for bigger objects like automobile bumpers Chlorinated polypropylene (CPP) coat as primer is essential.

In this endeavour the extra step of surface treatment and surface preparation is eliminated which adds Volatile organic compound (VOC) in the atmosphere and may deteriorate the mechanical properties of the object. For this blend and nanocomposites of PP are made in order to alter the surface characteristics and with the help of advanced characterization tools like Atomic force Microscopy (AFM) and Contact angle measurement the properties are evaluated.

Key Words: Polyolefin, polypropylene, blend, nanocomposites, topology, paint adhesion.

Reference:

[1] M. Strobel, MC. Branch, M. Ulsh, RS. Kapaun, S. Kirk, CS. Lyons, "Flame surface modification of polypropylene film", J Adhe. Sci. and Tech., **1996**, vol. 10 n. 6, pp. 515-539.

[2] A. S. Athalye, Handbook of Packaging – Plastics, 1st ed., Multi-tech Publ., **1999**, pp.341-342.

[3] L. A. Utracki, Ed. Polymer Blends Handbook, Vols. 1 and 2, Springer, **2003**, pp. xi, 601-630.

[4] D. Nwabunma; T. Kyu, Eds. Polyolefin Blends, J. Wiley and Sons, **2008**, pp. xv–xvi, 3-17.

Rheology studies on capillary force induced UHMWPE gels

Sameer Huprikar, Ashish Orpe, Ashish Lele*
Complex Fluids and Polymer Engineering Group, CSIR- National Chemical Laboratory, Pune-411008

We study the suspension to gel transformation process caused due to addition of tiny amounts of a secondary, immiscible fluid. Suspensions of Ultra High Molecular Weight Polyethylene (UHMWPE) particles in a density matched medium show a dramatic change in its flowability characteristics upon addition of small amount of PDMS as a secondary fluid. These flowability characteristics, as determined using steady unidirectional and oscillatory rheology, point towards the formation of a gel. The strength of the gel, obtained in terms of moduli and yield stress, shows significant dependence on the suspension volume fraction and the amount of secondary liquid used. The driving force behind such gel formation is anticipated to be due to relative wettability of the primary and secondary liquid with respect to particle surface [1, 2].

References

[1] Koos, E. et al. *Science*. **2011**, *331*, 897-900
[2] Koos, E. et al. *Soft Matter*. **2012**, *8*, 6620-6628

Microwave assisted reduction of graphene oxide (GO) using blackberry seed extract and formation of complexes of the reduced graphene oxide with chitosan polymers

Amartya Bhattacharyya, Gunjan Sarkar & Dipankar Chattopadhyay*
Department of Polymer Science and Technology, University of Calcutta,
92 A.P.C. Road, Kolkata 700 009, India
E mail: dipankar.chattopadhyay@gmail.com.

In this work we demonstrate a new, efficient and environment friendly procedure of reduction of grahene oxide (GO), prepared by a standard laboratory procedure, the Modified Hummers' Method. The reducing agent used is the extract of blackberry seeds, prepared by boiling these dried and powdered seeds for two hours. When sonicated GO and the extract are mixed in a 1:1 ratio by volume and processed in a microwave oven for 16-20 minutes, completely reduced graphene oxide (RGO) is obtained. The product has been characterized using UV, FTIR and Raman spectroscopy as well as by X-ray diffraction, scanning electron microscopy and TGA. All these analytical techniques have provided conclusive evidence about the completeness of the reduction process. The resulting RGO is then mixed with chitosan solutions to form mixtures with different percentages of the polymer. These mixtures are then cast into films on Petri dishes. The mechanical properties of these films are then studied to find out the optimum composition in the mixture, for which the film, now actually a composite of graphene with chitosan shows the best mechanical properties.

Fabrication and Characterization of Chitosan/Hydroxyapatite composite for medical applications

Namrata Yadav[1], Pradeep Srivastava[2*]
[1,2]School of Biochemical Engineering, IIT (BHU), Varanasi
*pksrivastava.bce@itbhu.ac.in

Natural polymer based composite have shown significant role in bone tissue engineering with their properties being attributed to their origin and/or chemical modifications(1).They have been intensively studied for their contribution in the field of bone tissue engineering.Fabrication of a polymer based artificial graft enable regeneration of bone in defective cases. In this study, hybrid compositeswere successfully fabricated by biomimetic (2) approach from Hydroxyapatite (Ha)/ gelatin (Gel)/ chitosan (CS) in the pore-size ranging from ~200-500 µm. The effect of process parameters on the composite efficiency was determined by varying the same in order to assess their application in bone tissue engineering.

In order to verify the effectiveness of the composite, the prepared composite (CS/HA) was characterized in comparison to the conventional composite using SEM, FTIR,TGA, DSC and XRD analysis. Studies to determinemorphological, mechanical and thermal properties were done too. This study showed that apatite-coated CS composite hold the potential to be the prospective candidate osteogenicsystem for enhancing bone tissue regeneration applications. Bioactivity of the scaffolds was directly dependent on the content in the samples according to the results.Ha/CS containing polymericcomposites synthesised could be promising scaffolds for bone tissue engineering.

References:

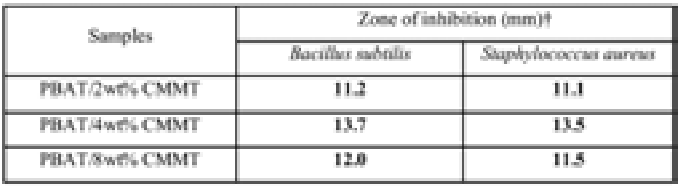
1. Laurencin CT, Ambrosio AM, Borden MD, Cooper JA. Tissue engineering: orthopedic applications. Annu Rev Biomed Eng. 1999;1:19–46.
2. Wu S, Liu X, Yeung KWK, Liu C, Yang X. Biomimetic porous scaffolds for bone tissue engineering. Mater Sci Eng R Reports [Internet]. Elsevier B.V.; 2014 Jun [cited 2014 Jul 14];80:1–36. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0927796X14000503
3. Li Z, Ramay HR, Hauch KD, Xiao D, Zhang M. Chitosan-alginate hybrid scaffolds for bone tissue engineering. Biomaterials [Internet]. 2005 Jun [cited 2014 Jul 25];26(18):3919–28. Available from: http://www.ncbi.nlm.nih.gov/pubmed/15626439

Effect of Clay on the Antimicrobial Activity and Biodegradation Behavior of Poly (butylene adipate-co-terephthalate) film

Nayan Ranjan Saha[1] & Dipankar Chattopadhyay[1]*
[1]Department of Polymer Science and Technology,
University of Calcutta, Kolkata-700009, India
*dipankar.chattopadhyay@gmail.com

Poly(butylene adipate-co-terephthalate) (PBAT) nanocomposites films are prepared by a solution intercalation process using natural montmorillonite (MMT) and cetyltrimethylammonium bromide (CTAB)-modified montmorillonite (CMMT). Cation exchange technique has been used for modification of MMT by CTAB and characterized by X-ray diffraction (XRD) studies. CMMT gives better dispersion in the PBAT matrix than MMT and is confirmed by XRD. Because of better compatibility of CMMT, water vapor transmission rate of PBAT decreases more in the presence of CMMT than MMT. The biodegradability of PBAT and its nanocomposite films are studied in compost and from the morphological analysis it is apparent that the PBAT/CMMT shows a lower biodegradation rate in comparison to the PBAT / MMT. The antimicrobial activity of PBAT and its nanocomposite films is tested by an inhibition zone method using two pathogenic bacteria such as *Bacillus subtilis* and *Staphylococcus aureus*.

Table: Zone of inhibition of those film samples against *Bacillus subtilis* and *Staphylococcus aureus*.



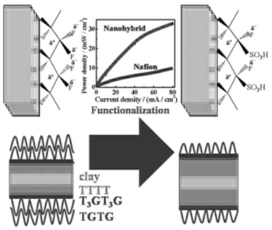
Samples	Zone of inhibition (mm)†	
	Bacillus subtilis	*Staphylococcus aureus*
PBAT/2wt% CMMT	**11.2**	**11.1**
PBAT/4wt% CMMT	**13.7**	**13.5**
PBAT/8wt% CMMT	**12.0**	**11.5**

Functionalized Poly(vinylidene fluoride) Nanohybrid for advanced Fuel Cell Membrane

Karun Kumar Jana and Pralay Maiti*

School of Materials Science and Technology,
Indian Institute of Technology (BHU), Varanasi 221 005, India
karun.jana@gmail.com

Functionalization of poly(vinylidene fluoride) (PVDF) nanohybrid has been performed in template system using two-dimensional layered silicate and superior fuel cell membrane has been demonstrated. Sulfonation of nanohybrid has been carried out at control condition to maintain the mechanical stiffness and toughness of the membrane using chlorosulfonic acid and the results have been compared with pure PVDF. The sulfonation and its relative extent have been confirmed through NMR, FTIR and UV-Vis measurements showing greater degree of functionalization in nanohybrid which arises from the specific arrangement of polymer chains on top of nanoplatelets. The structural change over from common crystallized form □ to piezoelectric □ phase in nanohybrid has been established and the amount of □ phase has been enhanced after sulfonation as evident from deconvoluted XRD patterns and DSC measurement. A plausible mechanism has been proposed for this improvement which led to the formation of smart membrane. Essential criteria of an ideal membrane have been verified through high water uptake, low permeability and hydrophilic nature by measuring contact angle. The molecular level clustering due to the attachment of sulfonate group in main chain has been explored which in turn explain the higher barrier property both for gas and liquid (fuel). Proton conductivity of functionalized nanohybrid has been found to be quite high along with significantly low methanol cross over as compared to standard Nafion membrane. I-V characteristics of the nanohybrid membrane show high potential at low current density with considerably lower value of slope. Membrane electrode assembly using functionalized nanohybrid exhibit significantly high value of current density and prove its worth for superior fuel cell membrane using common thermoplastic polymer.



References:

[1] Tiwari, V. K.; Prasad, A. K.; Jana, K. K.; Misra, M.; Prasad, C. D.; Maiti, P. Macromolecules. **2013**, 46, 5595-5603.

[2] Jana, K. K.; Vishwakarma, N. K.; Ray, B.; Khan, S. A.; Avasthi, D. K.; Misra, M.; Maiti, P. *RSC Adv*. **2013**, 3, 6147-6159.

[3] Jana, K. K.; Ray, B.; Avasthi, D. K.; Maiti, P. *J. Mater. Chem.* **2012**, 22, 3955-3964.

[4] Souzy, R.; Boutevin, B.; Ameduri, B. Macromolecules. **2012**, 45, 3145-3160.

[5] Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. J. Am. Chem. Soc. **2006**, 128, 1762-1769.

[6] Tashiro, K.; Tadokoro, H.; Kobayashi, M. Ferroelectric. **1981**, 32, 167-175.

Growth of Au Nanoparticles Surrounded Polythiophene Nanocore at Room Temperature

Mala Mukhopadhyay*, Ishani Roy, Satyajit Hazra
Saha Institute of Nuclear Physics, Kolkata
*mala.mukhopadhyay@saha.ac.in

Polythiophenes are an important class of conjugated polymers that are environmentally stable, structurally versatile and have found many applications in light emitting diodes, solar cells, memory devices, thin film transistors and chemical sensors. Conjugated polymeric films with metal nanoparticles have attracted much attention due to their enhanced catalytic, electrical, sensing and electrochemical properties. Several research groups have attempted to incorporate gold nanoparticles (AuNPs) into polymeric and polythiophene films because of their ease of synthesis and stabilization. Nicholson et al. synthesized composite poly (3-hexylthiophene)/dodecanethiolate protected AuNP LB films and observed a significant increase in the visible photoluminescence of the polythiophene.[1]Zhai and McCullough demonstrated a one-pot approach to assemble and wrap the polythiophene around AuNPs and their application in field effect transistors.[2]

We have tried to attach thiol-capped AuNps with poly (3-dodecylthiophene) (P3DDT) in a mixed solvent (good and poor) environment. P3DDT shows enhancement of the degree of crystallinity in mixed solvent.[3]At room temperature we have observed nice attachment of AuNps on the surrounding wall of P3DDT nanocores (coil-like or rod-like structures) by TEM (shown in fig.1). The UV-vis absorption spectra show the change in interaction due to incorporation of AuNps. This type of attachment will enhance the conductivity as well as luminescence of P3DDT.

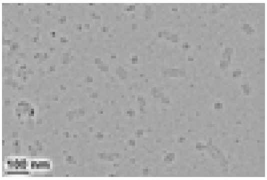


Fig.1: TEM Image

References:

[1] P. G. Nicholson et al.; Phys. Chem. Chem. Phys., **2006**, 8, 5096–5105.

[2] L. Zhai and R. D. McCullough, J. Mater. Chem., **2004**, 14, 141–143.

[3] I. Roy and S. Hazra, *RSC Adv.*, **2014**, 4, 00000.

Preparation, structure and properties of multiwalled carbon nanotubes based poly vinylidene fluoride composites

Tridip Baishya[1], Arup R. Bhattacharyya[1]
[1]Department of Metallurgical Engineering and Materials Science,
Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

State of dispersion of organically (sodium salt of adipic acid, Na-AA) modified multiwalled carbon nanotubes (m-MWNTs)was investigated in poly (vinylidene fluoride) (PVDF) matrix. Various characterization techniques viz., transmission electron microscopic (TEM) observation and Raman spectroscopic analysis were employed to compare the extent of dispersion of as received (MWNTs) as well as m-MWNTs in the aqueous medium. PVDF/MWNTs composites were prepared in a conical twin-screw micro-compounder. The dispersion extent of m-MWNTs in the PVDF matrix was investigated using transmission electron microscopic (FEG-TEM) analysis. Composite films were prepared by compression molding machine. Crystallization studies indicated that MWNTs could act as hetero-nucleating agent for developing β -crystalline phase in PVDF film. Initial stretching of the film was carried out using Universal Testing Machine (UTM), however,a significant extent of stretching could not be achieved. To develop piezoelectric property, the film samples were polled in the silicon bath and simultaneous stretching was carried out in a stretching device, which was developed in-house. The influence of MWNTs on the crystal structure and the crystallinity ofPVDF/MWNTs composites were investigated. Wide angle X-ray diffraction analysis and FTIR spectroscopic analysis were carried out to determine the formation and the content of the β phase in the composite samples. Dielectric property of the composite samples was also investigated. An attempt has been made to correlate 'structure-property' relation studies in PVDF/MWNTs composites.

References:

[1] Kim, K. S.; Park, S. J. Macromol. Res. 2010, 18, 981 - 985.
[2] Shafee, E. E.; Gamal, M. E.; Isa, M. J. Polym. Res. 2012, 19, 9805–9813.
[3] Vijayakumar R. P.; Khakhar, D.V.; Misra, A. J. Appl. Polym. Sci. 2010, 117, 3491–3497

Influence of Methyl Ester of Styrene /Maleic Anhydride Copolymer an aromatic compound in compatibilizing PP and hypalon based TPV system

Ashis K. Mondal[1], Debabrata Chakrabarty[1] and Mahuya Das[2]*
[1]Department of Polymer Science , University of Kolkata, West Bengal
[2]Department of Chemistry, JIS College of Engineering, Kalyani, West Bengal
*d_mahuya@yahoo.com

The present work is focused to study the influence of an aromatic compound in compatibilizing PP and hypalon based TPV system. The compatibilizer used here is a copolymer of styrene & maleic anhydride in which some fragments of the maleic compound has been esterifies with methyl alcohol to incorporate some hydrocarbon fraction as methoxyl group and to reduce the hydrophilic nature so as to enhance the compatibility of PP and hypalon. The unvulcanized compounded HypalonVR was subsequently blended with PP and compatibilizer copolymer of styrene & maleic anhydride (PMES/MA) in different proportions (2.5, 5, 7.5, 10) at 170^{0}C for 10 min in a Brabender mixer with the help of two rotors housed in a case at the speed of 80 rpm.16 The HypalonVR -PP blend was collected as a lump form. The sheet form with required thickness of such blends was prepared from its lump in a two-roll mill. The TPV was then evaluated with respect to the physical, mechanical, and thermal properties in relation to their morphological and rheological properties and the same were compared to that of virgin PP and amongst themselves. The mechanical analysis of the prepared TPVs exhibited significant improvements in stress at 25% modulus, ultimate tensile strength (UTS), and hardness values. FTIR studies revealed that a chemical interaction had taken place between HypalonVR and functionalized compatibilizer during the process of dynamic vulcanization which led to an enhancement of interfacial adhesion between them. The two-phase morphologies were clearly observed by scanning electron microscopic studies. The Tg values of HypalonVR was modified in the TPVs as exhibited by differential scanning calorimetric studies. TGA studies indicated the increase in thermal stability of all TPVs with respect to the elastomeric HypalonVR . Rheological properties showed that the compatibilizer reduces the melt viscosity of TPVs and thus facilitates the processibility of such TPVs

References:

[1] Coran, A. Y.; Patel, R. Thermoplastics Elastomers, 3rd ed.; Hanser/Gardner, Cincinnati, OH, **2004**.
[2] Nakason, C.; Saiwari, S; Kaesaman, A. Polym. Eng. Sci. **2006**, 46, 594-600.
[3] George, J.; Neelakantan, N. R.; Varughese, K. T.; Thomas, S. J. Appl. Polym. Sci. **2006**, 100, 2912-2929.
[4] Thitithammawong, A.; Noordermeer, J.W. M.; Kaesaman, A.; Nakason, C. J. Appl. Polym. Sci. **2008**, 107, 2436-2443.

Studies on the mechanical, morphological and thermal properties of biocomposites based on Poly (lactic acid)/Jute fiber

Mohammad Tahir Zafar, Anup K. Ghosh, Saurindra N. Maiti
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New Delhi 110 016, India.
**E-mail: anupkghosh@gmail.com*

In this research work bio-composites based on Poly(lactic acid)(PLA)/Jute fibers were prepared using twin screw extruder. Prior to the compounding, Jute fibers were chopped properly in the average size of 1-3 mm and then surface modified using alkali (JFNA) and alkali followed by silane (JFNASI). These prepared biocomposites were characterized by various techniques e.g.- mechanical, morphological and thermal. Results shows that composites reinforced using JFNA and JFNASI shows improved mechanical, morphological and thermal properties then the composites reinforced using untreated jute fibers (UJF).

Key words: Biocomposites; Mechanical properties; Thermal properties

Studies on thermal, mechanical and thermo-mechanical properties of bio-composites based on poly(lactic acid)/lignin

Rajendra Kumar, S. N. Maiti, Anup K. Ghosh
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New Delhi, India - 110016
Email: rajendrasingla898@gmail.com

The present study focused on fabrications of bio-composites of PLA with varying concentration (0-30 weight %) of lignin using twin screw co-rotating extruder followed by test specimens' preparation using injection and compression molding. The thermal behaviour of bio-composites was studied from thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) while thermo mechanical properties were analysed by dynamical mechanical analyser (DMA) technique. Thermo-gravimetrical analysis results revealed that char percentage increased with increasing lignin contents. However, slight reduction in onset thermal degradation and final degradation temperatures were observed. DSC results narrated depression in glass transition temperature, reduction in crystallinity and increase in cold crystallisation temperature. FT-IR spectra indicate the existence of intermolecular interaction between PLA and lignin. Study of mechanical properties of the composites indicated increase in Young's modulus. However, the impact strength, the tensile strength and the elongation-at-break are slightly decreased. DMA measurements showed increase in storage modulus, decrease in loss modulus and lower side shift in glass transition temperature. These findings show that the PLA and lignin bio-composites are promising materials compared with other biodegradable polymers, because the thermal stability, mechanical properties and cost are at acceptable level.

Keywords: Poly(lactic acid), bio-degradable, crystallinity, composite.

References

1. Averous, L.; Le Digabel, F., Carbohydrate polymers 66, 480 2006.
2. Zhang, S.; Feng, X.; Zhu, S.; Huan, Q.; Han, K.; Ma, Y.; Yu, M., Materials Letters 98, 238 2013.
3. Yu, L.; Dean, K.; Li, L., Progress in Polymer Science 31, 576 2006.

Viscoelastic and melt rheological properties of PLA/PEG biodegradable blends

Ranjana Nehra*, S. N. Maiti and Josemon Jacob
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New Delhi (India)
*ranju.nehra@gmail.com

Polylactide (PLA) was plasticized with poly (ethylene glycol) (PEG) of molecular weight 4000 g/mol in varying concentration (0-30 wt %) by melt blending method. Viscoelastic properties were studied by dynamic mechanical analysis (DMA). DMA showed that as the PEG content increases, storage modulus and loss modulus decrease. Tenδ curve s show that with increase in PEG content glass transition temperature of PLA decrease. Capillary rheometry was used to analyse melt rheological properties of PLA and PLA/PEG blends. It shows that both PLA and PLA/PEG blends behaved as non-Newtonian fluids. The shear viscosity of PLA/PEG blends were lower than that of pure PLA and decreased considerably with enhancing PEG content.

References:

[1] Z. Kulinski, E. Piorkowska, Polymer, **2005**, 46, 10290–10300.
[2] Isabelle Pillin, Nicolas Montrelay, Yves Grohens, Polymer, **2006**, 47, 4676–4682.
[3] Guralp Ozkoc, Sebnem Kemaloglu, Journal of Applied Polymer Science, **2009**, 114, 2481–2487.

Green Composites from Styrene Butadiene Rubber and Chicken feather fiber

Rajesh C[1*] and Seena C[1]
[1]MES Keveeyam College Valanchery, Malappuram, Kerala, India
*rajeshvlcy@rediffmail.com

Fiber reinforced rubber composites are of immense importance both in the industrial field and in the area of research and development. The properties like tensile strength, elasticity, ductility, impact strength, abrasion resistance etc. of rubber can be improved by the incorporation of fibrous fillers. Short fibers obtained from agricultural resources are usually of lower density than inorganic fibers, environmentally friendly and relatively easy to obtain. Researchers have got momentum on the utilization of natural and biofibers as reinforcing agents in polymeric matrices for making composites for wide range of applications[1-3]. Chicken feathers are easily accessible fiber resource generated by poultry industry. The feathers are made of keratin, which contains ordered -helix or β-sheet structures and some disordered structures. Chicken feathers possess unique properties which could be used advantageously in a number of applications. Use of chicken feathers as reinforcing agents for polymers has been tried by various researchers [4]. Chicken feather fiber was used as reinforcing agent in styrene butadiene rubber (SBR). Fibers of almost similar length and diameter were mixed into SBR using a Two Roll Mixing Mill. The mechanical and thermal properties of the composites were analysed as a function of fiber loading. The results indicate that feather fiber improves the mechanical properties and glass transition temperature of the rubber. Scanning electron microscopy revealed some interaction between the rubbers and feather fiber.

Key words: *Composites ,SBR, chicken feather*

References

1. Shinoj S, Visvanathan R, Panigrahi S, Kochubabu M, *Industrial Crops and Products*, **33** (2011),7-22.
2. Fathima S, Mohanthy AR, *Applied Acoustics*, **72** (2011),108-114.
3. Jacob M, Thomas S and Varughese KT, *Compos. Sci. Technol.,* **64** (7) (2004) 955.
4. Hamoush S A, and El-Hawary M M., *Conc Int: Design Const*, **16** (1994), 33–5.

Electrical properties and DC conductivity modelling of polyvinylidene fluoride (PVDF)/multi-walled carbon nanotube (MWCNT) composites

Ranvijai Ram[1], M. Rahaman[2], D. Khastgir[1]
[1]Rubber Technology Centre, Indian Institute of Technology Kharagpur-721302, India
[2]Chemical Engineering Department, King Fahd University of
Petroleum and Minerals, Dhahran 31261, Saudi Arabia
*Email: khasdi@rtc.iitkgp.ernet.in

DC conductivity, AC conductivity, dielectric constant, and dielectric loss factor of PVDF–MWCNT composites increase with the increase in MWCNT concentration. There is sharp increase in DC conductivity at 1 wt% MWCNT loading thereafter the DC conductivity increases relatively slowly with further increase of MWCNT loading. The composites conductivity decreases with the increase in temperature, which indicates that these composites can be used as pyro-electric sensors. The relative DC conductivity for 1wt% MWCNT loaded composite is found higher to that of 5 wt% loaded composite. The heating-cooling cycle shows electrical hysteresis where there exist an electrical set. The semi-transparent composites can be used in aerospace industry as ESD materials. The predicted theoretical conductivity by Voet, Bueche, Scarisbrick, and Rahaman models is not in well agreement with their experimental conductivity results. However, the conductivity predicted by modified Scarisbrick and Rahaman models is found to be in well agreement with the present experimental results (PVDF–MWCNT composites) as well as with the conductivity results in published literature.

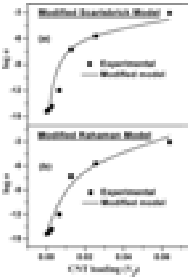


Figure: DC conductivity modelling (a) Modified Scarisbrick model (b) Modified Rahaman model

References:
[1] Tzeng SS, Chang FY. Mater Sci Eng A **2001**;302:258–267.
[2] Das NC, Chaki TK, Khastgir D. Adv Polym Tech **2001**;20:226–236.
[3] Wu J, Chung DDL. Carbon **2002**;40:445–467.
[4] Chung DDL. Carbon **2001**;39:279–285.

Mechanism of Impact Energy Absorption by Silica Nano-particle Based Shear Thickening Fluid Reinforced p-Aramid Woven Fabrics

Abhijit Majumdar, Bhupendra Singh Butola & Ankita Srivastava
Department of Textile Technology, Indian Institute of Technology, Delhi, India
E-mail: majumdar@textile.iitd.ac.in

Body armor designers and manufacturers face constant challenges for improvement with continuous increase in the velocity and profiled shape of projectiles. Reduction of weight and enhancing the flexibility of body armors have been the major concerns for the researchers. Body armor materials need to be developed to provide better impact resistance while maintaining its flexibility and reducing the weight. Treatment of shear thickening fluid (STF) on high performance textiles is one of the ways to achieve the same. Present paper deals with the analysis of impact energy absorption mechanisms by STF treated p-aramid (Kevlar) fabrics in dynamic impact testing. A comparative study of the mechanism was carried out for untreated and STF treated Kevlar fabrics. Three distinct zones of energy absorption were identified and were named as elastic zone, slippage/ breakage zone and failure zone. It is observed that in the case of untreated Kevlar fabrics, only primary yarns, which are engaged by the impactor, participate in energy absorption during impact and hence the amount of energy absorbed is low. The primary yarns form long loops but the rest of the fabric remains undisturbed. However, in case of STF treated Kevlar fabrics, the STF is transformed into a solid like material during impact. Therefore, the entire structure, which includes both the primary and secondary yarns, participates in energy absorption. It is found that as compared to untreated fabrics, STF treated Kevlar fabric absorbs almost double amount of the total energy during impact and shows a significantly improved impact resistance.

References:

1. Lee YS, Wetzel ED, Wagner NJ. The ballistic impact characteristics of Kevlar woven fabrics impregnated with a colloidal shear thickening fluid. J. Mater. Sci. 2003; 38:2825–33.
2. Majumdar A, Butola BS, Srivastava A. Optimal designing of soft body armour materials using shear thickening fluid. Mater. Des. 2013; 46:191–8.
3. Srivastava A, Majumdar A, Butola BS. Improving the impact resistance of textile structures by using shear thickening fluids: a review. Crit. Rev. Solid State Mater. Sci. 2012; 37:115–29.

Influence of synergistic / antagonistic mixtures of oligomeric stabilizers on the biodegradation of γ-sterilized polyolefins

Sameh. A. S. Alariqi
Department of Chemistry, Faculty of Applied Science, University of Taiz, Taiz, Yemen
E-mail: samehalariqi@yahoo.com

Our previous studies aimed to investigate the biodegradation of γ-sterilized polyolefins in composting and microbial culture environments at different doses and γ-dose rates. It was concluded from the previous studies that the pretreatment of γ-irradiation can accelerate the biodegradation of neat polymer matrix in biotic conditions significantly. A similar work was carried out to study the stabilization of γ-sterilized polyolefins using different mixtures of stabilizers which are approved for food-contact applications. Isotactic polypropylene (iPP), and ethylene-propylene (EP) copolymer have been melt-mixed with hindered amine stabilizers (HAS), phenolic antioxidants and hydroperoxide decomposers. Results were discussed by comparing the stabilizing efficiency, combination and consumption of stabilizers and the synergistic and antagonistic effects was explained through the interaction between the stabilizers. In this attempt, we have aimed to study the influence of the synergistic and antagonistic mixtures of oligomeric stabilizers on the biodegradation of the γ-irradiated polyolefins in composting and microbial culture. Neat and stabilized films of iPP and EP were irradiated under γ-radiation and incubated in compost and fungal culture environments. The changes in functional groups, surface morphology, mechanical properties and intrinsic viscosity in polymer chains were characterized by FT-IR spectroscopy, SEM, instron and viscometric measurements respectively. Results were discussed by comparing the effect of different stabilizers, stabilizers mixtures on the biodegradation of the γ-irradiated polyolefins. It was found that the biodegradation significantly depends on the components of stabilization system, mobility, interaction and consumption of stabilizers. It was concluded that the combination of different types of stabilizers can accelerate the biodegradation of γ-stabilized polymer matrix in biotic conditions.

Key words: Polyolefins, Biodegradation, γ- irradiation, Stabilization.

Synthesis of Low Molecular weight Compatibilizers (CA-26) for Preparation of Jute Based Biocomposites

D. P. Ray, L. Ammayappan, S. Debnath, R. K. Ghosh, D. Mondal,
S. Dasgupta, S. Chakroborty, Md. S. Islam
ICAR-National Institute of Research on Jute and Allied Fibre Technology
Indian Council of Agricultural Research, 12 Regent Park, Kolkata-700040

The modification of natural fibre is a foremost prioritized area of the research at present to obtain the durable natural fibre based composites. Jute is one of the most potential natural fibre which is being ventured for bio and green composites. It is often termed as the golden fibre not only because of it's golden luster but also due to its economic values. The use of natural fibre as a replacement to the non degradable synthetics is the major call of the day. The major drawback of the natural fibres is its water absorption property or hydrophilicity of which leads to the incompatibility between the fibre and the polymer matrix. This incompatibility is mainly due to the hydrophobic nature of polymer matrix, which in turn hinders proper interfacial bonding amid the matrix and the fibre. Therefore, an extensive study has been carried out for the synthesis of a suitable chemical compatibilizers which acts as a bridging agent between the polar jute fibre and the non polar polymer matrix thus inducing hydrophobicity in the composite materials. This chemical compatibilizer is basically combination of small molecules that reacts with the fibre surface improving the degree of cross- linking in the interface region. This improved bonding plays the major role in offering a perfect chemical bonding with the matrix material. This compound is generally characterized by being of dual or multiple functionality. Thus a chemical bridge between the fibre surface and the polymers matrix complements the formation of the jute based biocomposites. Thus a chemical compatibilizer was synthesized using a required ratio of an acid and a glycol (CA-26). Composites were prepared using jute fabrics treated at different ratio of the synthesized compatibilizers. The composites were tested at INSTRON for its mechanical properties. The tensile strength increased by nearly 30-35%, Flexural by nearly 25% and ILSS by nearly 17-20%.

Keywords: Jute, Bio Composites, Hydrophilicity, Hydrophobicity, Compatibilizer, INSTRON

Characterization of polymers using thermal techniques.

Sujatha Ramesh
Sujatha.ramesh@netzsch.com

Polymers both synthetic and natural, due to their broad range of properties play an essential role in everyday life. Polymers especially thermoplastics possess distinct thermal properties which help us to classify them and more importantly to study the influence of one or more impurities or additives. This paper highlights some of the application examples using established techniques such as Differential scanning calorimeter (DSC) and simultaneous thermal analyzer (STA).

Key word: glass transition, melting, crystallization, oxidative stability, decomposition.

Conducting polymer supported silver nanocomposite (mPANI/Ag): A new efficient and reusable nanocatalyst for acylation of amines, alcohols and thiophenols under solvent free condition

Usha Mandi, Md. Mominul Islam, Mita Halder,
Susmita Roy and Sk. Manirul Islam*
Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India

A mesoporous polyaniline/silver (mPANI/Ag) nanocomposite has been prepared using mesoporous conducting polymer polyaniline with silver nitrate via radical polymerization of aniline monomer in the presence of hydrochloric acid. The mPANI/Ag nanocomposite has been characterized by powder XRD, TEM, EDX, FT-IR and UV-vis.

Nanocomposites formed by metal nanoparticles (NPs) dispersed in electrically conducting polymer, polyaniline, are expected to display several synergistic properties between the polymer and the metal nanoparticles, making them potential candidates for application in several fields such as catalysis and others. Polyaniline (PANI) is a conducting polymer of particular interest, due to its ease of preparation, high conductivity and good environmental stability. The choice of Ag in our work is mainly guided by its highest electrical conductivity among all the metals as well as its enhanced catalytic activity [1].

So, in our study, we attempt to use mPANI/Ag as a potential catalyst for various organic reactions like acylation of amines, alcohols and thiophenols using acetic acid as acylating agent. This catalyst can be easily separated by using a simple filtration technique and can be reused five times without significant loss of catalytic activity [2].

References:

[1] Salam, N.; Sinha, A.; Roy, A.S.; Mondal, P.; Jana, N.R.; Islam, S.M. *RSC Advances*, **2014**, 4, 10001-10012.

[2] Salam, N.; Sinha, A.; Mondal, P.; Roy, A.S.; Jana, N.R.; Islam, Sk. M. *RSC Advances*, **2013**, 3, 18087-18098.

Studies on non-isothermal crystallization kinetics of PP/SEBS-g-MA/Teak Wood Flour composites

Rishi Sharma, S. N. Maiti
Centre for polymer science and engineering, IIT Delhi

The study of non-isothermal crystallization kinetics of PP/SEBS-g-MA/Wood Flour composites was done by differential scanning calorimetry at four different cooling rates 10, 15, 20 and 30^0 C/min. The crystallization properties were analysed by Avrami, Jeziorny and Liu models. Primary and secondary crystallization processes were described by Avrami equation. The Avrami equation describes about primary and secondary crystallization processes. Avrami model showed that all types of shapes grow from small dimensions during primary crystallization. However, three dimensional crystal growth was observed during secondary crystallization process. The composites was not nucleated by wood flour. Augis-Bennet, Kissinger and Takhore models have been used to calculate activation energy, ΔE, during non-isothermal crystallization process. The value of ΔE decreased with wood flour up toΦ_f=0.08 which showed chains of PP not hindered by wood flour. However, a$\Phi_f \geq 0.15$ ΔE increased due to phase adhesion.

Activated Graphene Quantum Dots for Enhanced Photo-Electrochemical Performance

Vincent Gomes* and Mahbub Hassan
School of Chemical Engineering, The University of Sydney, Australia
**Vincent.gomes@sydney.edu.au*

Graphene quantum dots (GQDs) with their edge-bound nanometer-size present extraordinary characteristics due to quantum confinement and edge effects. We report an ultrasonic approach with chemical activation to prepare activated GQDs enriched with both free and bound edges. Compared to GQDs, the aGQDs we synthesized had enhancement of BET surface area by a factor of six, photoluminescence intensity by five-fold and electro-capacitance by a factor of two.

Unlike their non-activated counterparts, the new GQDs with enhanced edge states emit intense luminescence and exhibit electrochemical double layer capacitance greater than that of graphene and activated graphene. They hold significant potential for use in supercapacitors and biomedical applications. Though deviations in capacitance are observed due to the increase of charge transfer resistance and the slower ion diffusion in the thicker electrode, the capacitance values are of similar magnitude.

The hierarchy in capacitance values for all samples (aGQDs> aFLGs> GQDs> FGs), both thin and thick films were maintained. These results indicate that chemically activated graphene quantum dots with lower mass loading could be beneficial for applications for the next generation of miniaturized energy storage devices such as electrochemical micro-supercapacitors. The outstanding photoluminescence is useful for applications in bio-imaging, light-emitting diodes and optoelectronics.

References:

[1] M. Hassan, K. R. Reddy, E. Haque, A. I. Minett and V. G. Gomes, *J.Coll. Interf. Sci.*, **2013**, *410*, 43.

[2] Liu, M.-H. Jang, H. D. Ha, J.-H. Kim, Y.-H. Cho and T. S. Seo, *Adv. Mater.*, **2013**, *25*, 3657.

[3] J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, L. Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaipparettu, A. A. Marti, T. Hayashi, J.-J. Zhu and P. M. Ajayan, *Nano Lett.*, **2012**, *12*, 844.

[4] K. Lingam, R. Podila, H. Qian, S. Serkiz and A.M Rao, *Adv. Funct. Mater.*, **2013**, *23*, 5062.

[5] M. Hassan, K. R. Reddy, E. Haque, A. I. Minett and V.G. Gomes, *RSC Nanoscale, 2014 (in press)*.

Electrode-active Polymers for Lithium-ion Battery Applications

Gouri Cheruvally*
Lithium-ion and Fuel Cell Division, VSSC, Thiruvananthapuram
*gouri_cheruvally@vssc.gov.in

Lithium-ion batteries (LIBs) have taken the lead position among the various energy storage devices being used in consumer electronics including portable gadgets. The high capacity variants of LIBs are the preferred secondary power source for satellites. They are also emerging fast as the power sources for electric and hybrid-electric vehicles. LIBs gained wide spread acceptance for such varied applications because of their unique properties including high specific energy (both in terms of mass and volume), low self-discharge, high calendar life, high cycle life and high-power capability. The LIB technology is based on the shuttling of Li^+ ions between the electrodes during charge-discharge reactions through the ion-conducting separator. The performance of LIB is decided mainly by the properties of cathode, anode, electrolyte and separator. Polymers play a crucial role in LIBs. Different polymers are used as cell components such as separator, binder, electrolyte, electrode-active material, insulating material and pouch packing material. Thus, several new developments in LIB originate from the advancements achieved in polymer science and technology. The scope of electrode-active polymers for LIB is highlighted in this lecture.

Functionalized polymers have been developed and found promising as electrode-active materials for LIBs in place of the conventional inorganic materials. Polymers as active materials impart light weight, flexibility and processability to the electrodes and help to realize ultrathin batteries. Electrically conducting polymers with π-conjugated skeleton structures, such as polyaniline, polypyrrole, polythiophene, and their related derivatives, have been explored as electrode-active materials. However, the success of these π-conjugated polymers is limited by their insufficient doping levels, resulting in low redox capacities and fluctuation of the cell voltage through the doping/de-doping process. Redox-active radical polymers are emerging electrode-active materials. Polymers with pendent nitroxide radicals such as tetramethylpiperidineoxyl (TEMPO) derivatives and the oxygen radicals such as phenoxyls and galvinoxyls are typically examined as electrode-active materials. The radical polymers allow fabrication of flexible thin-film batteries with excellent rate performance which allows instant full charging. Polymer-Carbon nano tube composite electrodes are also emerging candidates as electrodes.

Effect of graphene-silica in polyanilineelectrode material in supercapacitor performance

M. Umashankar, U. Susmitha and S. Palaniappan*
Polymers& Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India
* *palaniappan@iict.res.in*

Ternary composites of graphene-silica-polyaniline (GSP) are prepared by chemical polymerization of aniline using ammonium persulfate oxidant with various amounts of graphene–silica (GS). In the GSP composite, nano fibrous form of polyaniline (PANI) is intercalated in the graphene layers and also covered the GS. In order to improve the stability of pseudocapacitance properties of polyaniline, conductive and mechanically stable GS is used to modify the polyaniline material. The symmetric supercapacitor cell is fabricated in CR2032 coin cell with GSP composite as electrode and its electrochemical performance is evaluated from cyclic voltammetry, charge-discharge and electrochemical impedance spectroscopy. GSP composite yielded higher capacitance and lower equivalent series resistance compared to that of its individual components, PANI and GS. The energy density of the composite is found to be 10 W h Kg^{-1} at a power density of 2310 W Kg^{-1}. Furthermore, over 75.2% of the original capacitance is retained after 6000 galvanostatic charge–discharge cycles with a columbic efficiency of 99-100%.

Acknowledgements:
We thank the Department of Science & Technology, New Delhi for funding under the project (DST/TSG/PT/2011/179-G). We are thankful to Dr. M. Lakshmi Kantam, Director and Dr. K.V.S.N. Raju, CSIR-IICT for their support and encouragement. We also thank Dr.Vijayamohanan K Pillai, Director, CSIR-CECRI for his valuable discussion. UM is thankful to CSIR, India and SU is thankful to UGC, India for financial assistance.

References:

[1] Y. Zhu, Y.; Murali, S.;Cai, W.; Li, X.; Suk, J.; Potts, J.; Ruoff, R. Adv. Mater. 2010, 22, 3906-3924.

[2] Sydulu, S.; Palaniappan, S.; Srinivas, P.Electrochim.Acta 2013, 95, 251-259.

Impact of Surface Energy on the Efficiency of Bulk Heterojunction Solar Cells

Kothandam Krishnamoorthy
Department of Polymers and Advanced Materials Laboratory, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India
k.krishnamoorthy@ncl.res.in

PEDOT-PSS has been the work horse of bulk heterojunction solar cells. The surface energy of PEDOT-PSS is high and the photoactive materials are low, hence there is incompatibility between these two materials. Despite this incompatibility, high efficiency organic solar cells (OSCs) have been fabricated using PEDOT-PSS as hole transport layer (HTL). We hypothesized that a low surface energy HTL would facilitate better interaction between the photoactive and HTL materials. Furthermore, the low surface energy HTL can induce crystallization of the photoactive materials and improve the charge transport to the electrodes. We used a transparent low surface energy HTL to fabricate P3HT-PCBM OSCs with efficiency as high as 4.5%. The HTL is based on our previous work on polymer-surfactant interaction.[1] The important features of this cell are (1) no additives were used and (2) the ratio of P3HT:PCBM was 1:0.4. The decrease in the PCBM quantity is expected to improve the device stability and decrease the cost of the cells.

The orientation of PCBM with respect to the donor (polymer and small molecule) is crucial. PCBM should be close to the electron poor component of the donor polymer. To achieve such an orientation, we designed and synthesized electron rich-electron poor-electron rich small molecules. The electron rich segment was designed in such a way that the PCBM is unlikely to come closer, instead move closer to the electron poor segment. The electron poor segments are *i*-indigo[2] and BODIPY[3]. As a first step, we measured the charge transport properties of these materials and found that μ_h is as high as 0.5 cm^2/Vs. OSCs using these donors and PCBM as acceptors have been fabricated.

References:
[1] Das, C.; Krishnamoorthy, K. Chem. Commun. **2014**, 50, 5905.
[2] Dharmapurikar, S. S.; Arulkashmir, A.; Das, C.; Muddellu, P.; Krishnamoorthy, K. ACS Appl. Mater. Interfaces **2013**, 5, 7086.
[3] Singh, S.; Venugopalan, V.; Krishnamoorthy, K. Phys. Chem. Chem. Phys. **2014**, 16, 13376.

Novel Donor–Acceptor p-Type Copolymers Based on Dioxoring-Annelated [*c*]Thiophene Units for Bulk-Heterojunction Organic Photovoltaics

Jianming Huang[1], Yutaka Ie[1,2], Makoto Karakawa[1]and Yoshio Aso[1]*
[1]The Institute of Scientific and Industrial Research, Osaka University,Osaka, Japan
[2]Japan Science and Technology Agency (JST)-PRESTO, Saitama, Japan
*aso@sanken.osaka-u.ac.jp

Organic photovoltaic devices (OPVs) have been attracted great attention for their advantages of low cost, light weight, and large-area manufacturability. The most important breakthrough in OPVs is based on the concept of bulk-heterojunction (BHJ) structure in organic active layer, which comprises a blend of a π-conjugated polymer as an electron donor (p-type) and a fullerene derivative as an electron acceptor (n-type). It is generally accepted that the donor–acceptor (D–A) π-conjugated copolymers are an important class of p-type OPV materials.

We have developed novel D–A π -conjugated copolymerscontaining alkyl-substituteddioxocyclopenta[*c*]thiophenes or naphtho[2,3-*c*]thiophene-4,9-diones as electron-accepting units (Figure 1) and dithienosilole or dibenzothiophene as electron-donating units *via*Stille coupling polymerizations between the brominated acceptor unit and the distannylated donor unit.1,2) These copolymers exhibited amorphous nature in the solid state. The BHJ photovoltaic devices based ondihexyldioxocyclopenta[*c*]thiophene–dithienosilole copolymer and phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) showed a power conversion efficiency (PCE) of 5.17%under the air mass 1.5 simulated solar illumination. On the other hand, a blend of naphtho[2,3-*c*]thiophene-4,9-dione–dithienosilole copolymer and $PC_{71}BM$exhibited PCE values up to 5.21%. To further improve the performances, we optimized the alkyl groups attached to the acceptor unit, the synthesis of the copolymers, and active-layer fabrication, and successfully achieved a high PCE value up to 7.85%with an open-circuit voltage of 0.86 V, a short-circuit current of 14.39 mA cm^{-2}, and a fill factor of 0.64.

Fig. 1.New acceptor units for D–A copolymers.

References:

[1] Ie, Y.; Huang, J.;Uetani, Y.;Karakawa, M.;Aso, Y. *Macromolecules***2012**, 45, 4564–4571.

[2] Huang, J.;Ie, Y.;Karakawa, M.;Aso, Y. *J. Mater. Chem. A*,**2013**, 1, 15000–15009.

Tailoring Semiconductor Polymers and Block Copolymers towards Functional Control in photovoltaics

M. Hufnagel, D. Heinrich, P. Reichstein, J. C. Brendel, M. Thelakkat*
Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth
**mukundan.thelakkat@uni-bayreuth.de*

Nanostructured charge percolation pathways for electrons and holes with about 10 nm size domains hold great promise for exciton dissociation, charge transport in organic/hybrid solar cells. The self-assembly principle of block-copolymers is often viewed as an efficient way to generate and control such microdomains which are in equilibrium. We demonstrate this in fully functionalized donor-acceptor block copolymers to obtain well-ordered self-assembled morphologies as shown below.

The concept has been recently extended to fullerene-grafted block copolymers.In this contribution, examples of macromolecular design and structural control are given, which extend this concept of organic systems towards self-assembled hybrid devices. For this purpose, we developed amphiphilicblockcopolymers such as PTPD-b-PSS, P3HT-b-P4VP, etc. in which P4VP or PSS segments can preferentially interact with inorganic materials. Once the domain size control is achieved, the next step is the desired vertical orientation of the microdomains. Using PTPD-b-PSS, we demonstrate the vertical alignment of microdomains using solvent vapor annealing method. Thus we demonstrate that the tuning of domain size as well as the alignment of the nanostructures in a desired vertical direction are feasible with the self-assembly approach using semiconductor block copolymers.In a recently developed hybrid perovskite system, we show how the self-assembled crystallization from the components/precursors leads to reproducible and highly crystalline perovskite solar cells exhibiting high power conversion efficiency of 13%.

References:

[1] Hufnagel, M.; Muth, M. A.; Brendel, J. C.; Thelakkat, M. Macromolecules, **2014**, 47, 2324–2332.

[2] Brendel, J. C.; Liu, F.;Lang, A. S.;Russell, T. P.;Thelakkat, M. ACS Nano, **2013**, 7 (7), 6069–6078..

[3] Lohwasser, R. H.;Gupta, G.;Kohn, P.;Sommer, M.;Lang, A. S.;Thurn-Albrecht, T. Macromolecules, **2013**, 46, 4403–4410.

[4] Lohwasser, R. H.;Thelakkat, M. Macromolecules, **2012**, 45, 3070-3077.

Smart Polymers, Elastomers and Nanocomposites: Energy harvesting applications for Defence sector

Dipak K. Setua
Defence R&D Organization, Min. of Defence, Govt. of India
Defence Materials & Stores Research & Development Establishment,
DMSRDE (PO), G.T. Road, Kanpur-208013, India

Confluence of innovative technologies in every field of science has resulted in the development of smart materials and structures. Conventional materials have found a passage to functional, then to smart and intelligent materials encompassing information science into material's structure. These materials can respond to external stimuli such as temperature, pH, light, electric and magnetic field etc. and the responses are manifested through changes in one or more of the characteristics of the materials e.g., shape and size, structure, molecular characteristics, self-assembly and phase transformation etc.

Stimuli-sensitive polymers (SSPs) have attractive aspect of reversibility with respect to change of temperature, pH, light etc. For example, polythiophene can act as a photo-responsive, chitosan as a pH responsive and poly (n-isopropylacrylamide) as a temperature responsive polymers. R & D works related to development of sensors using these materials have been perused. The stimuli sensitive fibres and fabrics may be developed by grafting or coating of SSPs on them. They find interesting applications in clothing for army personnel in Defence for detection, stealth and camouflage applications. Micro-encapsulation is a process of enveloping microscopic size droplets or particles of PCMs in a shell material. MPCM coated fabrics used in clothing can help buffer/ maintain human skin temperature against abruptly changing climatic conditions besides being protective to nuclear, biological and chemical (NBC) warfare agents.

The interest in the field of Dielectric elastomer (DE) has also grown continuously over the last two decades. They have been found promising for applications as actuators, heel-strike generator, and other inexpensive mode of power generation by energy harvesting of human movement, ocean wave or wind flow which can offer clean power-generation possibilities. Development of Magneto-rheological (MR) elastomer, shape-memory elastomers and nano-fluids based elastomer nanocomposites has extended the usage of rubbers far beyond their traditional use in tyres and other non-tyre products.

References:

[1] Setua, D. K.. "Smart Elastomers" in Current Topics in Elastomer Research, Ed. A.K.Bhowmick, Taylor & Francis Gr. LLC, CRC Press, USA, 2008, Ch.10, 277-296.

[2] Setua, D. K.. "Emerging Technology: Polymer Coated Textiles & Fabrics with Smart, Intelligent and Nano-structured Fibres and Fabrics" in Advances in Polymer Coated Textiles, Ed. Guneri Akovali, Smithers/Rapra Tech. Ltd., UK, 2012, Ch.7, 315-367.

[3] Sahu, R. K.; Pramanik, B.; Patra, K.; Bhaumik, S.; Pandey, A. K.; Setua, D.K. Special Issue on "Nanotechnology for Biomimetics and Nano-Biomaterials", J. Nanoscience and Nanotechology, 2014, 14(10), 7439-7444.

Polymers as active elements in molecular and polymeric solar cells

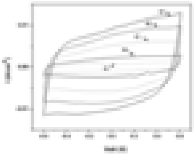
Jayant Kumar
Physics & Applied Physics, Center for Advanced Materials, Nanomanufacturing Center of Excellence, University of Massachusetts, Lowell, USA

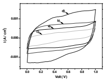
Some polymeric materials investigated during the course of our research on dye sensitized solar cells (DSSC's) as well as polymeric solar cells (OPV's) shall be discussed. Charge transport characteristics in these materials were characterized using time of flight technique as well as CELIV (charge extraction by application of a linear voltage) method. Photovoltaic devices incorporating conjugated polymers in conjunction with lead perovskites have also been investigated. These devices have yielded fairly high efficiencies. However, device stability under ambient conditions is an issue which needs to be addressed.

Conducting Polymer Based Metal Oxide Nanocomposites as Efficient Supercapacitor

Pintu Sen[a] and Amitabha De*[b]
[a]Variable Energy Cyclotron Centre, 1/AF Bidhannagar, Kolkata 700064, India
[b]Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India
*E-mail: amitabha.de@saha.ac.in

A nanocomposite material comprising of nanaoparticles of inorganic transition metal oxides and conducting polymer like poly 3,4-ethylenedioxythiophene (PEDOT) and Polyaniline (PANI) can act as very efficient supercapacitor with enhanced specific capacitance value due to synergistic effect. Here we used nanaoparticles of two different metal oxides i.e. nickel ferrite ($NiFe_2O_4$) and manganese dioxide (MnO_2) to combine separately with PEDOT or PANI to form nanocomposite electrodes to investigate their electrochemical behavior as supercapacitor. Nanocrystalline nickel ferrite was synthesized by sol-gel method from stoichiometric amount of their nitrates and α - MnO_2 nanorod by redox reaction between stoichiometric quantities of $MnSO_4$ and $KMnO_4$ in aqueous medium. Reverse micro emulsion polymerization in n-hexane medium was adopted for PEDOT nanotube formation using different surfactants. The PANI–MnO_2 nanocomposite was chemically synthesized by oxidative polymerization of aniline using $FeCl_3$ under controlled conditions in presence MnO_2 nanorod. Structural morphology and characterization for the nanocomposites were studied using XRD, SEM, TEM, IR and XPS. Their electrochemical performances were tested using cyclic voltammetry at different scan rates (2-20mV/s) and galvanostatic charge-discharge at different constant current densities in acetonitrile containing 1M $LiClO_4$ electrolyte. Both the Nanocomposite electrodes showed higher specific capacitances; for PEDOT- $NiFe_2O_4$ (251 F/g) in comparison to $NiFe_2O_4$ (127 F/g) and PEDOT (156 F/g) and for PEDOT-MnO_2 (315 F/g) compared to MnO_2 (158 F/g) where morphology of the pore structure plays a significant role over the total surface area. AC impedance measurements were done to ascertain contribution of pseudocapacitance in the frequency range 10kHz to 10 mHz with a potential amplitude of 5mV.





Typical cyclic voltammogram of (a) PEDOT-Aq (b) PEDOT-Org (c) Nano $NiFe_2O_4$ and (d) PEDOT-$NiFe_2O_4$ composite electrodes in acetonitrile containing 1 M $LiClO_4$ electrolyte at a scan rate 2mV/s in a potential range between 0 to 1V.

Cyclic voltammogram of PEDOT–MnO_2 composite in acetonitrile containing 1M $LiClO_4$ electrolyte at a scan rate (a) 2mV/s, (b) 5mV/s, (c) 10 mV/s (d) 15 mV/s and (e) 20 mV/s in a potential range between 0.6 and –0.6 V.

Bulk Heterojunction Polymer based Solar Cells – Status and Roadmap

K.S. Narayan
Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore

Solution processed bulk-heterojuction solar cells have been intensely pursued with the key selling points being " low-cost, flexible and scalability to large-area" . The talk will address the status of this photovoltaic technology based on bulk heterojunction polymer semiconductors. Ongoing strategies in our laboratory will be highlighted. Issues ranging from material design, charge generation mechanisms, charge transport and extraction bottlenecks, morphology and microstructure, and stability issues will be discussed.

Applications of Cyanocopolymers in Electrochemical Sensors

Kailash C Gupta
Polymer Research Laboratory, Department of Chemistry, I.I.T. Roorkee - 247 667 India
Email:guptakc03@yahoo.co.in

Most of the ions selective electrodes (ISE) reported in literature are based on polyvinyl chloride membranes. These studied have suggested that polyvinyl chloride used in fabrication of ISE are able to control the activity and selectivity of electroactive agents encapsulated for sensing and quantitation of the ions in the solution. But it is interesting to note that no systematic attempts have been made to analyze the influence of the properties of the polymers on the activity and selectivity of the electrodes and to prevent the application of anions excluders and plasticizers in the electrode membranes. The high molecular weight polyvinyl chloride is routinely used in fabrication of ion selective electrodes for different cations and anions but these electrodes have shown significant deviations in their sensitivity with time due to the leaching of employed anions excluders other constituents. These drawbacks associated with polyvinyl chloride based ions selective electrodes have clearly indicated that there is a need to modify the properties of the polymers for fabrication of ions selective electrodes so that electrodes with high sensitivity and selectivity might be prepared without using leachable anions excluders and plasticizers. Currently the high molecular weight polyvinylchloride is used in fabrication of the ISEs, which essentially needs 60-70 wt % of plasticizer to achieve optimum polymer flexibility and diffusivity of the analyte in the membranes to generate voltaic signal for its detection but it reduces the overall life of the electrodes. To overcome these problems of polyvinyl chloride based ions selective electrodes and to exploit the chemical diversity of polymers in sensing applications, efforts have been made to develop ion selective electrodes using cyanocopolymers of suitable size, composition and conformations. The sensitivity cyanocopolymer based electrodes has been evaluated as a function of electrode compositions and the structure of the cyanocopolymers. In addition to contribution of cyanocopolymers in ions selective electrodes, the role of imprinting, conducting and conjugated polymers to develop various kinds of sensors would also be discussed to provide structure properly relation in sensing application of the analytes.

Polymer based sensor for the detection of Nitro-aromatic Compounds

Neelotpal Sen Sarma*
Physical Sciences Division, Institute of Advanced Study in Science and Technology,
Guwahati, Assam, India

Explosive sensors are substances capable of detecting specific chemicals used in explosives and transforms chemical information into an analytically useful signal. Non-destructive detection of nitroaromatic explosives is very essential for protection and criminal investigations, minefield remediation, military applications, ammunition remediation sites, homeland security applications and chemical sensors plays a vital role in the detection of such chemicals. Nitroaromatic compounds viz. picric acid, TNT, DNT are regarded as explosive chemical due to its very high volatility. These chemicals upon initiation undergo highly exothermic reactions yielding gaseous products. Besides, these chemicals also causes soil and water pollution. In this endeavor, we have developed a Layer by Layer polymer detector for efficient detection of nitro-aromatic chemical and picric acid is considered as the model nitroaromatic chemical.

Two polymers are synthesized and characterized to develop the sensor system namely, co-polysulfone of cholesterol methacrylate with 1-hexane (PCHMASH) and co-poly 2-vinyl pyridine with acrylonitrile (P2VP-Co-AN). To fabricate the Layer by Layer detector, P2VP-Co-AN was placed in between two layers of PCHMASH and sandwiched in between the SS mesh. The detection process is based on very fast decrease in the impedance of the detector in presence of the vapor of picric acid. The thickness of the individual polymer layers plays a vital role towards the sensing efficiency of the detector. The detector with thinner outer layers undergoes a very steep decrease in impedance within 10 seconds. This sensitivity increases with the increase in the concentration of the vapor of the picric acid. In addition, selectivity of the detector for picric acid, reversibility and the interference of common chemical towards the detection of picric acid are also investigated. A general mechanism is proposed in support of the sensing process by the trilayer polymer detector.

References:

[1] Hulanichi, A.; Geab, S.; Ingman, F. Pure and Applied Chemistry. **1991**, 63, 1247–1250.

[2] Toal, S.J.; Trogler, W.C. Journal of Materials Chemistry. **2006**, 16, 2871–2883.

[3] Sohn, H.; Sailor, M.J.; Magde, D.; Trogler, W.C. Journal of the American Chemical Society. **2003,** 125, 3821–3830

[4] Sohn, H.; Calhoun, R. M.; Sailor, M. J.; Trogler, W. C. Angewandte Chemie International Edition. **2001**, 40, 2104–2105.

Polymers for High Energy Materials (HEMs) application

Dr. A. K. Sikder
High Energy Materials Research Laboratory, Pashan, Pune-41121, India

In the last two decades, there have been dramatic changes in material science and related technology. In the context of these materials, polymers have emerged as a multidimensional product In the area of defence and aerospace, polymeric materials play very important role either as an insulator or as a conducting material or as an adhesive. Many smart polymers based on polyimide etc. have been developed for defence, aerospace and electronic applications which can sustain even at high temperature up-to 600 ^{O}C.

The advent of advanced explosive and propellant technology has laid emphasis on the use of ingredients that impart enhanced performance and reduced vulnerability. Emergence of novel propellants having unique combination of high energy and low vulnerability has led to emergence of energetic polymers in case of binders and plasticizers. Prepolymers having exothermically decomposing azido groups or oxygen-rich facile nitro/nitrato groups offer formulations with superior performance at relatively lower solid loading levels of solid oxidizers culminating in superior structural integrity. The first polymer to be developed in this category was glycidyl azide polymer (GAP), which came into prominence during early 90's. Subsequently, a series of poly azido oxetanes emerged on the scenario. Energetic thermoplastic elastomers (ETPE) viz. BAMO- THF, BAMO-AMMO and BAMO- NIMMO copolymers are also emerging as a new class of potential binder system. These ETPEs are attractive binder system for solid propellants due to their inherent ability to recycle, recover and reuse the propellant ingredients. All the polymers and copolymers have been found to be insensitive to impact and friction stimuli and have wide defence applications as a binder for insensitive munitions (IMs) whose formulations are being used in rocket propellant, gun propellant and plastic bonded explosives (PBXs). The resultant munitions with these polymers have comparable energy with desired structural integrity and reduced sensitivity over the current non- IM counterparts.

Energetic polyphosphazenes, a new class of polymer, are of special interest as binder for energetic formulations. Polyphosphazenes consist of an inorganic phosphorous-nitrogen backbone and reactive pendant side groups that may be organic, organometallic or inorganic in nature. Polyphosphazenes are having low glass transition temperatures, thus providing good low temperature properties, because of the flexibility of the polyphosphazene backbone.

The performance of polymers, in terms of their mechanical properties, adhesion, storage life, flame retardancy etc. can further be enhanced by making Nano-composites. Recently, many polyurethane Nano-composites using nano clay / carbon nano tubes have been reported which shows 40 -60 % increase in their mechanical properties i.e. tensile strength and % elongation. Energetic Nano-composites based on energetic polymers like GAP, PolyNIMMO etc. have also been prepared to be used as a coating material for desensitization of HEMs and also for binder applications. These energetic Nano-composites will not only have better mechanical properties but also have enhanced shelf life of the compositions. Clay based Nano-composites of inert polyols or epoxy resins are also being made for rocket propellant Inhibitors, Liners, insulators etc. The advantage of these Nano-composites are high mechanical properties, light weight because of low filler content (3 – 5 % as compared to 15 – 25 %), flame retardancy and better storage life.

Actuation and Sensing of IPMC based Devices

Debabrata Chatterjee
Chemistry & Biomimetics Group, CSIR-Central Mechanical Engineering Research Institute,
M. G. Avenue, Durgapur-713209, India
dchat57@hotmail.com

The emerging bio-inspired technologies are potentially key technologies of the future, and in this regard there has been immense research interest in the field of Electro Active Polymers (EAP) which is also viewed as part of the field of Biomimetics. In this lecture our capability towards developing IPMC (ionic polymer metal composites) based micro-devices using EAP that actuates under external stimuli, biological action potential generated by nerve cells, and could sense human pulse bits.

In the present lecture include the preparation of IPMC through surface electroding of the ion-exchange polymer, fabrication and mechano-electrical behaviour of a robotic mini-hand that actuated under very low under operating voltage +2.0 V,[1] and development of IPMC based wrist-band that senses the human pulse bits (Figure 1) are presented and discussed. Exploratory works with regard to development of Heart & BP monitoring devices are in progress in association with a cardiologist.

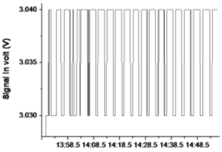


Figure 1: Sensing of human pulse bits by IPMC sensor

Acknowledgments
This work was carried out under CSIR SINP Project (No. ESC 0203). Author is thankful to Prof. P Pal Roy, Director, of this institute for his encouragement to this work.

References:
[1] D Chatterjee, N. Hanumaiah, Y. Bahramzadeh and M. Shahinpoor. *Adv. Mat. Res*. 740, 2013, 492-495.

Lithium Ion Conductivity in Polymer Nanocomposite Solid Electrolytes

Satyabrata Si* and Jagdeep Mohanta
School of Applied Science (Chemistry) & Center of Industrial Technology, KSBT Building,
Campus 11, KIIT University, Bhubaneswar – 751 024
Email: satyabrata.si@gmail.com

Making efficient use of energy mostly relies on rechargeable batteries, which has been creating major technological challenges in the entire consumer market worldwide. Rechargeable lithium-ion battery (LIB), in particular, is very popular in consumer electronics, which generally uses liquid electrolytes due to better Li^+ ion conductivity at room temperature. But due to various limitations of liquid electrolytes, such as, transport, storage etc. composite polymer electrolyte is another option as an electrolyte for Li^+ ion battery due to their solid state nature. In spite of solid nature, most of them are not much useful due to their very low ionic conductivity. Thus, these are being modified to form nanocomposite polymer electrolytes (NCPE) by incorporating various inorganic nano-fillers for enhancing the Li^+ ion conductivity as well as to improve their mechanical, thermal, chemical and electrochemical stability. Moreover, materials in the nano-scale exhibit new and improved properties compared to their bulk counterparts due to the reduced phase dimensions of the inorganic and the organic matrix, which helps in the enhancement of Li^+ ion conductivity. A wide range of nano-scale materials are being used for the construction of novel NCPE systems, which includes ceramics and metal oxides nano-materials. The current work comprises a brief discussion of the basic of Li^+ ion conductivity in composite polymer electrolytes as well as my own group activities and their perspectives.

Aqueous solubility of thermoresponsive PNIPAM-PS block co-polymers from molecular simulations

Rahul Singh[1], Sanket Deshmukh[2], Subramanian Sankaranarayanan[2],
Ganesh Balasubramanian[1]*
[1]Department of Mechanical Engineering, Iowa State University
[2]Center for Nanoscale Materials, Argonne National Laboratory
*bganesh@iastate.edu

The structural properties of PNIPAM (poly-N-isopropylacrylamide), which is a thermosensitive polymer, have been investigated by copolymerizing it with hydrophobic monomeric units of polystyrene (PS). We employ molecular dynamics (MD) simulations to examine aqueous solutions of PNIPAM and PNIPAM-PS co-polymer chains across a temperature range below and above the LCST of pure PNIPAM to understand the fundamental physics underlying the coil-to-globule transition in PNIPAM and in consequence on the LCST. The thermoresponsive solubility of PNIPAM can be controlled by copolymerizing it with PS, and such changes in the aqueous solutions of the polymers are accompanied by conformational alterations that are dependent on potential models employed, chain lengths simulated etc. We prepare a number of copolymers with different chain lengths of the hydrophobic units and observe the lowering of the LCST of the modified PNIPAM by computing the radius of gyration and end-to-end distances across the temperature range, in addition to examining the variation in diffusion coefficients of the polymers and the layering of water in the neighborhood of these chains. Our results show that the temperature sensitive properties of the water-soluble polymers can be tuned by copolymerizing them with varying lengths of hydrophobic block polymers. Our work demonstrates the controllability of PNIPAM solubility in aqueous solutions and recommends strategies to design complex programmable polymers that have wide-ranging applications in several biomedical and industrial processes.

Novel functionalized polymeric materials for fuel cell applications

Santoshkumar D. Bhat
CSIR-Central Electrochemical Research Institute-Madras Unit,
CSIR Madras Complex, Chennai-600 113

In our recent research studies, carbon nanotubes and fullerenes are functionalized and incorporated in Nafion and sPEEK matrices to study the impact of ionic conductivity and methanol crossover behaviour of PEM in DMFCs. Sulfonic acid functionalization is done for carbon nanotubes and fullerene to enhance their dispersion in the polymer matrices and to impart the additional ionic conductivity. Composite membranes of sPEEK-PSSA-CNTs, Nafion-sulfonated fullerene and sPEEK-Sulfonated fullerene were fabricated and studied for their properties like water uptake, proton conductivity and methanol crossover which are critical for successful operation of DMFCs. All the composite membranes show improved water uptake, proton conductivity and reduced methanol permeability through the membrane by partially blocking the micropores of the membrane [1]. Anion exchange membrane electrolytes are also developed for its use in alkaline fuel cell. The introduction of quaternary ammonium cation is carried out on the aryl carbon hitherto on benzyl carbon in the preparation of anion exchange membrane from engineering plastics namely poly(2,6-dimethyl-1,4-phenylene oxide) via chloromethylation followed by a pre-functionalization methodology for quaternization. The influence of several parameters such as amount of chloromethylating agent, polymer concentration, reaction temperature, reaction time etc., were investigated and optimized. The chloromethylated PPO (CPPO) was further quaternized by homogeneous amination, in which PPO is directly converted to ionic form and is distributed over the polymer matrix. Membrane intrinsic properties such as ion exchange capacity, water uptake and ionic conductivity were evaluated. The membrane electrolyte (AEM) exhibited an enhanced performance in comparison with the state-of-the-art commercial membrane [2].

References:

[1] Gutru Rambabu; Bhat, S.D. Chem. Eng. Journal. 2014, 243, 517-525.
[2] Hari Gopi, K. *et al*. Int. J. Hydrogen Energy. 2014, 39, 2659-2668.

Towards Designer Acceptor for Solar Cell: Click Copolymerization on thiophene-based functionalized fullerene

Munusamy Krishnamurthy, [1, 2] P. Murugan, [1] Debasis Samanta*, [1] Asit Baran Mandal*[1,3]
[1]Polymer Division, [3]Chemical Laboratory
CSIR-Central Leather Research Institute, Adyar, Chennai - 600 020
[2]Academy of Scientific & Innovative Research, New Delhi
Email. abmandal@hotmail.com

Fullerene-polymer conjugates have attracted significant attention owing to their applications in different fields such as material science, biomedicines, and molecular electronics. Especially thiophene-based conjugated polymer –fullerene systems are important for their potential applications in organic photovoltaic device fabrications. So far, various synthetic strategies have been reported for fullerene funtionalization in addition to polymerization. Most of the synthetic approaches have certain drawbacks such as, multistep reactions with drastic reaction conditions, formation of undesired side products, etc. In this context, we used click chemistry approach that has been proven to be effective and attractive route to prepare well-defined conjugates for different applications.

In this presentation, we will discuss about our recent results on copolymerization of fullerene-based compounds using “click” reaction conditions. The synthetic methodology for the preparation of precursor organic molecules and functionalization of fullerene derivatives will be described. We will also discuss about the results of click polymerization reactions on those materials. The study of the materials using SEM, TEM, and AFM techniques will also be highlighted. Finally, our attempts to prepare photovoltaic device components using the materials will also be discussed.

Reference

[1] Stephen Z. D.; Cheng, Macromolecules, **2008**, 41, 515.
[2] Samanta, D.; Amitabha Sarkar, Chem. Soc. Rev. **2011**, 40, 2567–2592
[3] Samanta, D.; Murugan,P.; Somanathan,N.; Jaisankar,S.N.; Mandal,A.B; Chem. Commun. **2012**, 48**,** 12068.

Synthetic Analogue and Conjugated Polymer of Fluorene for Sensing Application

Manas Kumar Bera, Ketaki Samanta and Sudip Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata-700032

Now-a-days the field of chemical sensing is becoming ever more dependent upon novel materials. Fluorene based small molecule and conjugated polymers (CPs) become very much useful as signal-transducing materials for sensory applications because of their versatility in their molecular design and signal amplification properties.[1] A typical optical chemosensor contains a receptor (the recognition site), linked to a fluorophore (the signal source), which translates the recognition event into the fluorescence signal (Fig. 1).

Fig. 1. Schematic representation of our designed

In this consequence, functional derivative of fluorene and its copolymers have been designed and synthesized. All compounds are highly air stable. The functional derivative that has been used as a cyanide sensor, detects cyanide from water at very low level concentration (0.06 ppm). The presence of cyanide in cellular environment is also judged by this moiety. On the other hand, three stereo chemically different copolymer based on the above fluorene derivative have been synthesized. Among the polymers, two are achiral and third one is chiral. We have studied metal ion sensing ability of the polymers. From this study we see that the two achiral polymers have no selectivity towards any particular metal ion but the chiral polymer is highly selective towards zinc ion. We have also performed theoretical calculation of the polymer with metal ion. The result suggests that zinc ion is perfectly fitted in the cavity of the chiral polymer. Thus, chiral polymer can be used as a fluorescent sensor for selective detection of zinc ion from water.

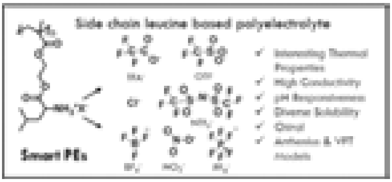
References:

[1] Thomas, S. W.; Joly, G. D.; Swager, T. M. Chem. Rev. **2007**, 107, 1339-1386.
[2] De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T. A.; Huxley, T. M.; McCoy, C. P.; Rademacher, J. T. and T. E. Rice, Chem. Rev., **1997**, 97, 1515-1566.
[3] Bera, M. K.; Chakraborty, C.; Singh, P. K.; Sahu, C.; Sen, K.; Maji, S.; Das, A. K.; Malik. S.; J. Mater. Chem. B, **2014**, 2, 4733-4739.

Effect of counterions on the thermal, pH-response and electrochemical properties of the side-chain leucine based chiral polyelectrolytes

Amal Narayanan, Bhuban Ruidas and Priyadarsi De*
Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur – 741246, Nadia, West Bengal, India
*p_de@iiserkol.ac.in

Polyelectrolytes (PEs) are polymers with ionizable repeating units along the polymer chain. Framing electrochemical membrane, electroactive devices, microwave-absorbing material with polyelectrolytes of high ionic conductivity is at state of the art. Keepingpoly (NH_3^+-L-leucine methacryloyloxyethyl ester) cation, we varied the associative counteranionastrifluoroacetate (TFA^-), bis(trifluoromethylsulfonyl)imide (NTf_2^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), trifluoromethanesulfonate (OTf^-), chloride (Cl^-) and nitrate (NO_3^-) by anion exchange reactions.A novel library of PEs with vibrant thermal, pH responsiveness, chiroptical and electrochemical behavior were achieved. In contrast with neutral polymer, a three time increase in glass transition temperature (T_g) was obtained when PF_6^- acted as the associative counterion. The difference in co-ordinating ability of anion resulted in capricious thermal stability. An amassed effect of counterion condensation resulted in variable solubility of PEs.High solution conductivity of 2.1 mS/cm was obtained for the PE with Cl^- anion. The validity of Arrhenius and Vogel-Fulcher-Tammanmodels in conductivity were investigated. The circular dichroism (CD) spectroscopy gave hint about the ability of NTf_2^- and OTf^- to facilitate intrachain hydrogen bonding sincethose PEs showed higher ellipticity value in methanol. The high solution conductivity, thermal stability and expected biocompatibility enables these smart PEs fit for applying in electrochemical membrane technology.



References

[1] Dobrynin,A. V.; Rubinstein, M. Prog. Polym. Sci.**2005**, 30, 1049–1118.

[2] Bauri, K.; Roy, S. G.; Pant, S.; De, P. Langmuir**2013**, 29, 2764–2774.

Phosphonium Based Poly(ionic liquid) and Its Copolymers with Tunable Thermoresponsive Behaviour

Yajnaseni Biswas and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India
**psutkm@iacs.res.in*

Thermoresponsive polymers are of interest in several biological contexts such as tissue engineering and drug delivery. These responsive polymers often exhibit a lower critical solution temperature (LCST) above which polymer chain collapse into a globular state in solution.[1] In contrast, the polymers showing phase separation in solution due to chain collapsing below an upper critical solution temperature (UCST) are relatively rare. In this context, poly(ionic liquid)s (PILs) have attracted considerable attention to the research community as fascinating water soluble polymer materials whose solution properties can easily be tuned via external stimuli such as temperature, pH and ionic strength of solution.[2,3] This prompted us to design new PILs having interesting solution phase behaviour. Thus, in this study, a novel PIL, poly(triphenyl-4-vinylbenzylphosphonium chloride) is synthesized by conventional free radical polymerization of a phosphonium-based ionic liquid monomer triphenyl-4-vinylbenzylphosphonium chloride. This newly designed PIL exhibits tunable UCST-transition behaviour in aqueous solution upon addition of different inorganic salts. The phase transition behaviour of this PIL in aqueous solution is then studied in detail in terms of polymer concentration, nature of added salts and the ionic strength of the solution. Interestingly, upon copolymerization of this IL monomer with 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) respectively, the resulted copolymers also show tunable UCST behaviour in water and as well as in other solvents. Such tunable temperature responsiveness enriches the toolbox of thermo-responsive polymers by introducing a strong polyelectrolyte type candidate, therefore broadening the scope of designed smart materials.

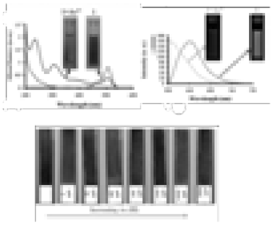
References:

(1) Aoshima, S.; Oda, H.; Kobayashi, E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, 30, 2407– 2413.
(2) Men, Y.; Li, X.-H.; Antonietti, M.; Yuan, J. *Polym. Chem.* **2012**, *3*, 871-873.
(3) Men, Y.; Schlaad, H.; Yuan, J. *Acs Macro Letters* **2013**, *2*, 456-459.

“In field” sensing and removing of As (III) by norbornene based homopolymer

Sourav Bhattacharya and Raja Shunmugam*
Polymer Research Centre ,DCS, Indian Institute of Science Education and research Kolkata, Mohanpur-741252
E-mail: sraja@iiserkol.ac.in

Arsenic is a well-known toxic metal and is present mainly as oxyanion compounds in groundwater. Arsenite (As^{III}) interferes with the function of enzymes by bonding to the -OH and -SH groups leading to the inactivation of the enzymes. Sensing As (III) is very tedious process because no such traditional chelating group is present which can bind to As(III). Norbornene derived rhodamine (Nor-Rh) shows colorimetric as well as fluorimetric response against As(III) in the presence of potassium iodate and hydrochloric acid which is monitored through UV-visible and fluorescence spectroscopy. Sensing properties of the Nor-Rh monomer towards As(III) are explored in presence of KIO_3 and HCl. The observed colorimetric as well as fluorometric changes are attributed to the redox reaction involved in the unique design. Cyclic voltammogram measurements confirm the oxidation of As(III) to As(V) during the sensing event. This novel design is able to sense ppb levels of As(III) very selectively in an aqueous environment. Since As(III) has specific affinity towards thiol functionality we have prepared Nor-Th monomer & it’s corresponding polymer through ROMP polymerization technique. Here protected thiol has been chosen to avoid cross linking during polymerization which is deprotected after the polymerization. As (III) is trapped when the water is passed through a column containing Nor-Th polymers.



References:
[1]. Vickaryous, W. J.; Herges, R.; Johnson, D.W. *Angew.Chem. Int. Ed.* 116 (**2004**) 5955.
[2]. Bhattacharya , S.; Sarkar, S.; Shunmugam, R. *J. Mater. Chem. A* 1 *(***2013**) 8398.

Fabrication Of A Highly Stable AChE Biosensor Through Electro entrapment In Polypyrrole And Its Application To Organophosphate Detection

Rekha Rani Dutta (1), Himadri Borah (1), Panchanan Puzari (2)*
1,2Department of Chemical Sciences, Tezpur University, Tezpur-784028, India
*pancha@tezu.ernet.in

We describe here a novel way of fabrication of an amperometric acetyl cholinesterase (AChE) biosensor and its application to detect organophosphate (OP) pesticide ethion using thiocholine oxidation at a low potential of 0.2V. AChE was electro entrapped in polypyrrole (Ppy) using low amount (0.02M) of supporting electrolyte (KCl) followed by cross linking with gluteraldehyde and porcine skin gelatin [1]. The sensor thus obtained showed a storage stability up to 4 months and a high operational stability with intra state precision 0.742%. We observed that thiocholine oxidation on PPy surface occurs at 0.1V while the same occurs at 0.2 V when PPy is doped with gelatin and gluteraldehyde. Based on this observation, the low potential workability of the sensor was tested taking ethion as the sample OP pesticide. Ethion could be detected down to 0.15 ppb in a solution in 5% acetonitrile using 0.2V applied potential for substrate oxidation. The sensor could be used up to eight repeated measurements after reactivating every time using 0.5% NaF solution. The work has demonstrated that (i) electro entrapment procedure can be used for effective fabrication of amperometric AChE biosensor (ii) Gelatin-gluteraldehyde combination can impart enhanced stability to electro entrapped AChE biosensors (iii) Polypyrrole entrapped AChE biosensors can be used for low potential detection of thiocholine (iv) Lower concentration of supporting electrolyte is necessary for the stability of electrochemical response of electro entrapped enzyme biosensors.

Key-words: Acetylcholinesterasebiosensor, Conducting polymer, Electroimmobilization, Ethylparaoxon, Organophosphates, Organocarbamates.

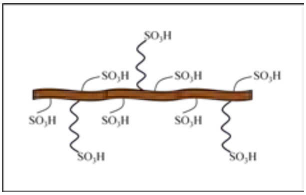
Reference:

[1] Dutta, R. R. and Puzari, P. Biosensors and Bioelectronics 52, 166-172, 2014.

High proton conducting fluorinated sulfonated poly(arylene ether sulfone)s copolymers with side chain grafting

Rajdeep Mukherjee[1], Susanta Banerjee[1]*
[1]Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
*susanta@matsc.iitkgp.ernet.in

A series of new copolymers HPPQSH-XX PS were synthesized from there preformed sulfonated ionomers HPPQSH-XX in order to get high proton conductivity along with excellent other properties. They were prepared by direct copolymerization of bisphenol HPP with two bishalides, QBF and SDCDPS. Again the copolymers were post-sulfonated using 1,3-propanesultone in presence of NaH and were analysed by spectroscopic techniques. The random copolymers HPPQSH-XX with different statistical distribution of $-SO_3H$ moiety showed very small ionic clusters (5–10 nm) whereas the grafted copolymers showed larger ionic domains (60–100 nm) on their TEM images. All ionomer membranes exhibited good mechanical properties, high oxidative and dimensional stability with low water uptake and swelling ratios. IECs (weight and volume based) were also calculated to explain a better correlation with water uptake and proton conductivity (14-125 mS/cm at 80 °C and 15-142 mS/cm at 90 °C under fully hydrated condition) of the membranes.



References:
[1] Tsai, J-C.; Lin, C-K. J. Power Sources. **2011**, 196, 9308-9316.
[2] Li, Z.; Ding, J.F.; Robertson, G.P.; Guiver, M.D. Macromolecules. **2006**, 39, 6990-6996.
[3] Kim, D.S.; Robertson, G.P.; Guiver, M.D. Macromolecules. **2008**, 41, 2126-2134.
[4] Li, N.; Wang, C.; Lee, S.Y.; Park, C.H.; Lee, Y.M.; Guiver, M.D. Angew. Chem. Int. Ed. **2011**, 50, 9158-9161.
[5] Mukherjee, R.; Mohanty, A.K.; Banerjee, S.; Komber, H.; Voit, B. J. Membr. Sci. **2013**, 435, 145-154.

Poly(Dimethyl siloxane) supported Zeolitic imidazolate frameworks with improved water stability for gas chromatographic separations

Manju Roy[1,2], Prasun,[1] and Arunachalam Ramanan[2]
[1]Centre for Fire, Explosive and Environment Safety, DRDO, Delhi-110054
[2]Department of Chemistry, Indian Institute of Technology Delhi, New Delhi-110016

Metal–organic frameworks (MOFs) are new class of crystalline materials, exhibiting various structures and enthralling porosity. These crystalline porous frameworks not only demonstrate novel performances but because of their tunable pore size, and controllable host guest interaction feature offer numerous opportunities in the field of adsorption and separation technology. The availability of in-pore functionality and possibility of outer-surface modification allows interactions based on both “molecular sieving” as well as “chemical affinity”, which in turn render these materials extremely interesting for gas/liquid mixture separation. In this paper we propose a simple and economically viable method to develop core shell PDMS- metal organic frameworks microspheres. Core-shell poly (dimethylsiloxane) (PDMS)-ZIF 8 microspheres were prepared by directed crystallization of ZIF 8 on thermally stable PDMS beads. The core-shell microspheres were evaluated for their potential use as stationary phase for gas-chromatographic separation of permanent gases and liquids, where the issues associated with pressure drop were circumvented which permitted separation of gas and liquid mixtures in conventional gas chromatographic packed columns. In view of the exceptional water stability of ZIF 8, the column could be used for the effective separation of aqueous mixtures. The simple and versatile methodology widens the scope for large-scale application of MOFs.

References

[1] H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, 341.
[2] S. L. James, *Chem. Soc. Rev.*, 2003, 32, 276-288.
[3] P. K. Roy, Manju, A. Ramanan and C. Rajagopal, 2013. Indian Patent Filed (Appl Number: 2766/DEL/2013)
[4] Manju, P. K. Roy, A. Ramanan and C. Rajagopal, *RSC Advances* 2014, *4*, 17429-17433.

Polyaniline-$BaTiO_3$ nanocomposite revisited : Synthesis and application to humidity sensing

Sunil Patil[1], Sharada Thakur[2] and Pradip Patil[2]*
[1]Department of Physics, Sathaye College, Vile Parle-(E), Mumbai-400 057, India
[2]Department of Physics, North Maharashtra University, Jalgaon 425 001, India
*pnmu@yahoo.co.in

This contribution reinvestigates synthesis of polyaniline-$BaTiO_3$ (PANI- $BaTiO_3$) nanocomposite with regards to its exclusive formation and feasibility for application in humidity sensing. In the present work, PANI- $BaTiO_3$ nanocomposite was synthesized first time, by an in situ chemical polymerization of aniline in the presence of $BaTiO_3$ nanoparticles of 25-40 nm in diameters. The resulting nanocomposite was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM). The characterization results confirmed an exclusive formation of PANI-$BaTiO_3$ nanocomposite. Humidity sensing characteristics such as relative humidity (RH)-impedance property, humidity hysteresis, response and recovery times and reproducibility of PANI– $BaTiO_3$ have been investigated. The nanocomposite with 10 wt% $BaTiO_3$ exhibited better humidity sensing properties than pure PANI, such as good sensitivity, fast response, rapid recovery, hysteresis within 2% and excellent repeatability. We have also compared the results of this study with a previous report of PANI- $BaTiO_3$ composite [1], which reports the formation of $BaSO_4$ in the composite due to the leaching of Ba^{2+} ions from the surface of $BaTiO_3$ particles in HCl medium.

Acknowledgement
One of us (ST) is thankful to University Grants Commission (UGC), New Delhi, for awarding the Rajiv Gandhi National Fellowship.

Reference :

[1] Patil, P.; Lee, J. M.; Seo, Y. K.; Hwang, Y. K.; Kwon, Y. K.; Jhung S. H. and Chang, J. S. J. Nanosci. Nanotechnol., 2009, 9, 318

Development of Highly Sensitive Sensor Strip for Organophosphate Pesticides Using Polypyrrole - Ionic Liquid Combination

Himadri Borah (1), Rekha Rani Dutta (1), Panchanan Puzari (2)*
[1,2]Department of Chemical Sciences, Tezpur University, Tezpur-784028, India
* *pancha@tezu.ernet.in*

The work presented here describes the electro synthesis of a highly stable and highly conducting polypyrrole film using a room temperature ionic liquid 1-butyl-3-methyl immidazolium bromide and utilization of the same for quantitative estimation of organophosphate pesticides. Doping the film with different oxidising agents such as copper sulphate and N-bromosuccinimide, selected organophosphate pesticides were oxidised and the change in conductivity of the film at the time of oxidation was correlated with the amount of pesticide present. The organophosphate pesticides ethion and parathion could be detected down to 0.2 ppb and 1.8 ppb respectively. Characterization of film properties such as variation of conductivity with temperature, effect of humidity and storage stability were investigated.

Key-words: Conducting polymer, Ionic liquid, Organophosphates

References:

[1] Pringle, J.M.; Patrick, J; Howlett, C; Efthimiadis, J; MacFarlane, D.R.; Chaplin, A.B; Hall, S.B.; Officer, D.L; Gordon G. Wallace, G.G; Forsyth G.G; Forsyth, M. Polymer.**2004**, 45, 1447 - 1453.

A rapid room temperature LPG sensor using poly(o-methoxyaniline)-CeO_2 nanocomposite

Sharada Thakur, and Pradip Patil*
Department of Physics, North Maharashtra University, Jalgaon, India
*pnmu@yahoo.co.in

Over the last decade, considerable attention has been focused on the development of suitable sensing materials for the fabrication of low cost, rapid and selective gas sensors operating at room temperature [1,2]. Different conducting polymer-metal oxide nanocomposites have been synthesized and based on these nanocomposites gas sensors, humidity sensors, biosensors have also been developed by few research groups. Here we report a rapid and selective room temperature liquefied petroleum gas (LPG) sensor using poly(o-methoxyaniline)-cerium oxide (POMA-CeO_2) nanocomposite. The POMA-CeO_2 nanocomposites have been synthesized by an in situ chemical oxidative polymerization of o-methoxyaniline in the presence of pre-prepared CeO_2 nanoparticles. The techniques of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) were used to characterize the resulting POMA-CeO_2 nanocomposites. The sensor based on POMA-CeO_2 nanocomposite with proper weight percentage of CeO_2 showed better LPG sensing properties than that of pure POMA. Upon exposure to 3.4% LPG, the nanocomposite with 30 wt% CeO_2 exhibited an improved response (~2.06%), very fast response (~3-4 s), full recovery within 20 s in air and most notably, enhanced selectivity at room temperature. Thus, the combination of the CeO_2 nanoparticles and POMA endows an attractive selective sensing performance to LPG at room temperature with fast-response / recovery rate.

Acknowledgement
One of us (ST) is thankful to University Grants Commission (UGC), New Delhi, for awarding the Rajiv Gandhi National Fellowship.

Reference :
[1] Comini, E. Anal. Chim. Acta 2006, 28, 568-
[2] Zhang, F.; Zhu, A.; Luo, Y.; Tian, Y.; Yang, J. and Qin, Y. J. Phys. Chem. C 2010, 114, 19214-

High performance sPEEK-sPOPblend membranes for polymer electrolyte membrane fuel cells (PEMFCs)

Rambabu Gutru, S. Gouse Peera, S. D. Bhat* and A. K. Sahu
CSIR-Central Electrochemical Research Institute-Chennai Centre, CSIR Madras Complex, CSIR Campus, Taramani, Chennai 600113,India

Membrane electrode assembly (MEA) is the heart of the fuel cell in which polymer electrolyte membrane (PEM) plays a major role whereinNafion is the widely used membrane for PEMFCs due to its superior proton conductivity and high mechanical strength. However Nafion has its own disadvantagesviz, limited operational temperature window and the cost hindering its commercial applications [1]. In the present study, acid-base blend membranes were fabricated to imply as electrolytes in polymer electrolyte membrane fuel cells. Poly(bis(phenoxy)phosphozene) (POP) was sulfonted with sulfuric acid[2], to impart the ionic conductivity and then blended with sulfonated poly(ether ether ketone) (sPEEK). The blend membranes were fabricated by varying the sPOP content from 2 to 4 wt.% in relation to sPEEK. The resultant blend membranes (sPEEK-sPOP) were characterized in terms of AFM and SAXS to determine the change in the ionic domains and then studied in PEMFCs.The strong hydrophobic backbone of POP improves the mechanical strength of the membrane; incorporation of sPOP in sPEEK matrix enhances the dimension of the ionic clusters in turn promoting the proton transport. The blend membranes exhibit superior electrochemical properties and peak power density of 986mW/cm^2 in comparison with735mW/cm^{2}for pristine sPEEKmembrane.

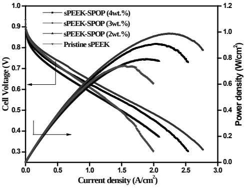


Fig.1 PEMFC performance of pristine sPEEK and sPEEK-sPOP blend membranes

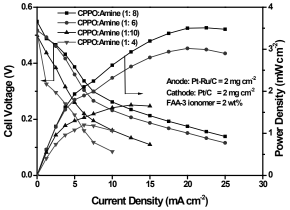
Reference :

1. L. Wang, B.L. Yi, H.M. Zhang, Y.H. Liu, D.M. Xing, Z.-G. Shao, Y.H. Cai, J. Power Sources, **2007**, 164, 80–85.
2. R. Wycisk, J. K. Lee and P. N. Pintauro, *J. Electrochem. Soc.* **2005**, 152, A892-A898.

Quaternized poly (2,6-dimethyl-1,4-phenylene oxide) anion exchange membrane for alkaline direct methanol fuel cells (DMFCs)

K. Hari Gopi, Santoshkumar D. Bhat*, Akhila Kumar Sahu
CSIR-Central Electrochemical Research Institute- Chennai centre, CSIR Madras Complex,
Taramani, Chennai- 600113, India.
**sdbhatcecri@gmail.com*

A series of anion exchange membranes containing quaternary ammonium groups are fabricated from poly(phenylene oxide) for application in alkaline DMFCs (ADMFCs). In the first step, poly(phenylene oxide) (PPO) was chloromethylated by substituting chloromethyl groups in the aryl position of polymer. The impact of reaction time on the chloromethylation reaction was studied and optimized from the degree of substitution calculated from ^{1}H NMR spectra. In the second step, the chloromethylated PPO (CPPO) was further homogeneously quaternized and then ion-exchanged to form an anion exchange membrane (AEM)[1]. The successful introduction of functional groups on the polymer backbone was confirmed by ^{1}H-NMR and FT-IR spectroscopy. From the second step, a series of AEMs are prepared by varying the molar ratio of amine with respect to CPPO. The prepared membranes are also characterized in terms of their ion-exchange capacity, water uptake and ionic conductivity. Finally, the fabricated QPPO membranes are subjected to cell polarization studies in alkaline DMFCs, wherein CPPO: amine ratio of 1:8 exhibited a higher peak power density of 3.51 mW cm^{-2} among the four ratios as represented in Fig. 1. The variation of metal loading in the catalyst layer on either sides such as 2 mg, 1 mg and 0.5 mg cm^{-2} were also studied for its performance in ADMFCs.



Reference:

[1] Hari Gopi, K. *et al.,* Int. J. Hydrogen Energy. 2014, 39, 2659-2668.

Polymer nanocomposites with Carbon and Silver nanoparticles as efficient sensing materials for Nitroaromatic explosives

Priyanka Dutta[1], Neelotpal Sen Sarma[1,*]
[1]Polymer Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, PaschimBoragaon, Garchuk, Guwahati – 781 035, Assam, India
E-mail: priyanka_2600@yahoo.com

Nowadays, the development of highly sensitive sensory materials for the detection of trace explosives is a very challenging area of research. Recently chemical sensors with high sensitivity for the detection of principal explosive ingredients such as RDX, TNT, PA, etc. have found immense applications in public security and environmental pollution problems. Herein we attempt to develop conducting polymeric nanocomposites for sensing nitroaromatic explosive ingredients such as TNT, DNB, PA etc. by PL methods. PVA-thiophene composite and their nanocomposite were prepared by incorporating carbon and silver nanoparticles in it. The nanocomposites showed enhanced fluorescent behaviour after the loading of nanoparticles as compared to the undoped ones. All these materials prove to be highly efficient sensors for nitroaromatic compounds. The polymeric nanocomposites are electron rich species and they act as electron donors while the analytes behaves as electron acceptors forming a donor-acceptor complex. The fluorescence of highly explosive nitroaromatic compounds such as TNT and PA are reduced effectively with a quenching efficiency of about 95-99% in case of the polymer nanocomposites. The sensing of nitroaromatic compounds occurs through Photoinduced Electron Transfer (PET) mechanism which is established by zeta potential and CV measurements.

References:

[1] Gole, B.; Shanmugaraju, S.; Bar, A. K.; Mukherjee, P. S. Chem. Commun. **2011**, 47, 10046 – 10048.
[2] McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem. Rev. **2000**, 100, 2537– 2574.
[3] Yang, J. S.; Swager, T. M. J. Am. Chem. Soc. **1998**, 120, 11864– 11873.
[4] Cavaye,H.; Shaw, P. E.; Wang, X.;Burn, P. L.; Lo, S.-C.; Meredith, P. Macromolecules **2010**, 43, 10253 – 10261.

Polycurcumin acrylate and polycurcumin methacrylate: Novel bio-based polymers for nitroaromatic chemical sensor

Bedanta Gogoi and Neelotpal Sen Sarma*
Physical Sciences Division, Institute of Advanced Study in Science and Technology, Guwahati, Assam, India

Non-destructive detection of nitroaromatic explosives is very essential for protection and criminal investigations, minefield remediation, military applications, ammunition remediation sites, homeland security applications and chemical sensors plays a vital role in the detection of such chemicals. In this work, we developed a very simple chemical sensor for nitroaromatic compound from a couple of novel bio-based polymers polycurcumin methacrylate (PCUMA) and polycurcumin acrylate (PCUA). The polymers exhibit purely electronic conduction and is confirmed by Wagner polarization technique. Sensitivities of the polymers are observed by monitoring the change in the impedance response (Z) with time and the current–voltage characteristics in presence of the vapor of picric acid and nitrobenzene. The sensitivity of PCUMA for these analyte is higher than that of PCUA. It showed one order decrease in log Z values within 10 minutes and 90.44% increase in current density in current–voltage characteristics in presence of the vapor of the analyte. The polymers selectively interact with picric acid and the interference of varying humidity, other nitroaromatic chemicals, $CO_2$and common solvents is negligible. The sensitivity of the polymer is reversible in nature and the sensor system is statistically accessible with significant inter and intra assay precession.

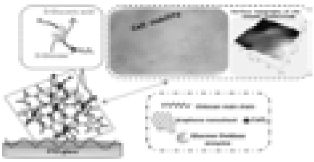
References:

[1] Hulanichi, A.; Geab, S.; Ingman, F. Pure and Applied Chemistry. **1991**, 63, 1247–1250.
[2] Toal, S.J.; Trogler, W.C. Journal of Materials Chemistry. **2006**, 16, 2871–2883.
[3] Sohn, H.; Sailor, M.J.; Magde, D.; Trogler, W.C. Journal of the American Chemical Society. **2003,** 125, 3821–3830

Synthesis of electrochemically active nano-CeO_2 decorated graphene based green nanohybrid and property evaluation of their suitability for enzymatic biosensing platform

Sriparna De[1], Smita Mohanty[1,2], Sanjay Kumar Nayak*[1,2]
[1]Central Institute of Plastics Engineering and Technology (CIPET), Chennai, India
[2]Laboratory for Advanced Research in Polymeric Materials (LARPM),
CIPET,Bhubaneswar,India
*sriparna.de2@gmail.com

A candid approach to analyze the prospects and study the biocompatibility of synthesized nano-CeO_2 decorated exfoliated graphene nanohybrid reinforced green polymeric nanocomposite as electrochemical sensing material has been presented in this communication. CeO_2 nanoparticles were successfully grown on graphene sheet in the presence of cationic surfactant (HTAB) followed by facile hydrothermal treatment. The effective growth of synthesized CeO_2 nanocrystals on graphene was evident from X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. Glucose oxidase (GOx) was employed on the green polymer nanocomposites modified FTO electrode, which was confirmed from topographical study (AFM). The electrocatalytic and electroanalytical response of the GOx/nano-CeO_2-GR/CS/FTO bioelectrode towards electrooxidation of glucose analyte was investigated by electrochemical impedance (EIS) and cyclic voltammetry (CV) study. The variation of current response as a function of pH, applied potential and GOx concentration was also monitored. The results obtained indicate that compare to bare CeO_2 nanoparticles and graphene, the nano-CeO_2/graphene nanohybrid shows significant electrochemical activity and provides an adequate microenvironment for effective enzyme immobilization due to the excellent synergistic effects between the CeO_2 nanoparticles and graphene sheet.

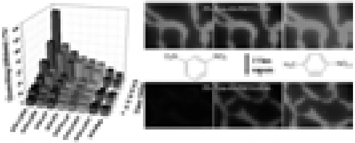


References:
[1] Jha, S. K.; Kumar,C.N.Electrochimica Acta. 2014, 120, 308–313
[2] Srivastava, M.; Das, A.K. J. Mater. Chem. A, 2013, 1, 9792-9801
[3] Wang,Y.;Guo, C. X. Dalton Trans., 2011, 40, 6388–6391
[4] Jiang,L.; Yao,M. J. Phys. Chem. C, 2012, 116, 11741−11745

Solid State Multicolor Emitting Polystyrene Microbeads for Sensing of Nitroaromatic Compounds

Swapnil L. Sonawane[1] and S. K. Asha[1]*
[1]Polymer Science and Engineering Division,
National Chemical Laboratory, Pune-411008
*sk.asha@ncl.res.in

Solid state multicolor emitting material have great demand due to their potential applications as light emitting materials, bio-imaging, bio-labeling, optical sensing and optoelectronics. Pyrene and Perylene bisimide (PBI) chromophores have high absorption coefficient, high quantum yield, good photo and thermal stability. The chromophores were used as a acrylate monomer and cross-linker respectively for making fluorescent polstyrene microbeads. The solid state multicolor emitting, lightly cross-linked, thermally stable polystyrene material were developed by dispersion polymerization and well characterized by NMR, GPC. The morpholgies and solid state fluorescence was measured by SEM and fluorescence microscopy respectively. The fluorescent microbeads were used for the sensing of the nitro aromatic compounds such as TNT, 1,3-DNB, 2,4-DNT, 4-NT, 2,6-DNT, Picric acid 4-NP and 2,4-DNP. The ethanol dispersion of monodisperse multicolor emitting PS microbeads were spin coated on the quartz plate. The spin coated films were kept in the closed tubes saturated with nitro aromatic molecule vapors. Time dependant fluorescent measurement showes the rapid decrease in the intensity of Pyrene emission without effecting the PBI emission indicating selective sensing of Pyrene chromophore in the PS backbone. The material can be used for the dual application as an optical sensor and a green-red emitting material.



References:

[1] *Beyazkilic, P.; Yildrim, A.; Bayinder, M.; ACS Appl. Mater. Interfaces,* ***2014****, 6, 4997–5004*.

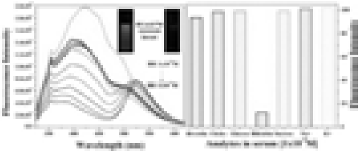
[2] Sonawane, S. L.; Asha, S. K. *J. Phys. Chem. B,* ***2014****, 118, 9467–9475*.

[3] Sonawane, S. L.; Asha, S. K. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12205−12214.

Glucuronic acid appended Polyfluorenes for selective sensing of Bilirubin in Human serum

T. Senthil kumar[1], and S. K. Asha[1]*
[1]Polymer Science and Engineering Division, National Chemical Laboratory, Pune - 411008
*sk.asha@ncl.res.in

Water soluble conjugated polymers have received great research interest in biosensing applications. D-glucuronic acid appended polyfluorenes was designed and successfully used to demonstrate the selective naked-eye detection of bilirubin in human serum. D-glucuronic acid was appended to fluorene unit which upon polymerization resulted in water soluble polyfluorenes. The favorable spectral overlap between the polymers and bilirubin facilitated forster resonance energy transfer (FRET) to occur from polymer to bilirubin. Upon addition of bilirubin, the fluorescence of the polymer was quenched with gradual reduction in the fluorescence lifetime of the polymers and also increases in the lifetime of bilirubin indicative of energy transfer. There was a fluorescence color change of the solution from blue to green upon addition of the bilirubin to the polymers. The new polymers showed high selectivity and visual sensitivity towards free bilirubin in human serum in presence of interference from hemoglobin, biliverdin, glucose, cholesterol, as well as metal ions. The role of the combined effects of energy transfer, non-covalent interaction and entrapment by self-assembly highlights the potential of the new polymer design for highly selective visual detection of free bilirubin in human serum.



References:

[1] McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, 100, 2537-2574.

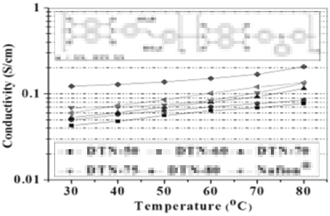
[2] Senthilkumar, T.; Asha, S. K. Macromolecules **2013**, 46, 2159-2171.

[3] Liu, B.; Bazan, G. C.; J. Am. Chem. Soc. 2004, 126, 1942-1943.

Triphenyl Amine Containing New Sulfonated Aromatic Polyimide Proton Exchange Membranes

Anaparthi Ganesh Kumar, Debaditya Bera, Ershad Ali Mistri,
Susanta Banerjee*
Materials science centre, Indian Institute of technology, Kharagpur 721302, India
**susanta@matsc.iitkgp.ernet.in*

In the past few decades proton exchange membrane fuel cells (PEMFCs) have emerged as an alternative clean energy conversion devices [1-3]. The electrolytes developing aspect in the field of proton exchange membrane fuel cells is high proton conductivity [2]. A series of new sulfonated co-polyimides **(**co-SPI**)** were prepared via polycondensation reaction route, with a various combination of diamines. The low molecular weight diamine 4,4'-diaminotriphenylamine (DATPA) were used to increase the ion exchange capacity (IEC_w) along with another diamine 4,4'-diaminostilbene-2,2'-disulfonic acid (DSDSA) and dianhydride 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). These copolymers have shown good solubility and given flexible membranes. Morphological observation through transmission electron microscopy (TEM) revealed the micro phase separated morphology with well-dispersed hydrophilic (around 5-100 nm) and hydrophobic domains. The well connecting hydrophilic domains were responsible for the higher proton conductivity. The SPI membrane DTN-80 (80% degree of sulfonation) with IEC_w = 2.74 mequiv g^{-1} shown significantly higher proton conductivity (207 mS cm^{-1}) at 80 °C in water as compared to perfluorinated Nafion® 117 (135 mS cm^{-1}) under similar experimental condition. All these co-SPI membranes shown higher fuel efficiency compared to Nafion. Lower oxygen permeability were observed for these co-SPI membranes (for DTN-80, P_{O2} = 0.9 barrer) than Nafion® 117 (P_{O2} = 3.6 barrer).



References:

[1] Park, C. H.; Lee, C. H.; Guiver, M. D.; Lee, Y. M. Progress in Polymer Science, **2011**, 36, 1443-1498

[2] Li, N.; Guiver, M. D. Macromolecules,**2014**, 47, 2175-2198.

[3] Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Macromolecules, **2002**, 35, 6707-6713.

Synthesis and characterization of Carbazole and Triphenylamine based novel photo emissive polymeric materials for optoelectronics applications

V. Ramkumar T. Vandana and P. Kannan*
[1]Department of Chemistry, Anna University, Chennai - 25
*pakannan@annauniv.edu

Photo-emissive materials are mainly based on the fluorophores were present in a molecule. We have designed and synthesized twocarbazole and triphenylamine based polymeric materials. The synthesized materials confirmed by standard characterization techniques such as FT-IR, ^{1}H- NMR analysis. Optical behaviors of these materials were evaluated by UV-visible and fluorescence spectrophotometer. Solvent effect of these synthesized materials was tested from high polar to low polar solvents.There was a considerable red shift in absorption spectra and drastic red shift in emission spectra with differentpolarity of the solvents. These solvent effects are may be due to the various factors such as dipole moment, free energy of solvation, reorganization energy. The thermal properties of the materials were studied by TGA and DSC analysis. The surface morphology of the materials was analyzed using SEM analysis. Cyclic Voltametry analysis used to analyses the electrochemical behavior of the materials.

From these results, the synthesized both materials were well efficient fluorophores adopted for optoelectronics applications.

References:

[1] Leriche P, Frere P, Cravino A, Aleveque O, Roncali J, J. Org. Chem. **2007**, 72, 8332.
[2] T. Sano, Y Nishio, Y. Hamada, H. Takahashi, T. Usuki and K Shibata. J. Mater. Chem.**2000,** 10, 157.
[3] Y. T. Tao, E. Balasubramaniam, A. Danel, B. Jarosz, and P. Tomasik, Chem. Mater. **2001**, 13, 1207.
[4] Lei Y, Liao Q, Fu H, Yao J. J. Phys. Chem C., **2009**, 113, 10038-10043.

Simultaneous unzipping and sulfonation of multi-walled carbon nanotubes through hydrothermal route to form sulfonated graphene nanoribbons: sPEEK-sGNRs composite membranes for polymer electrolyte fuel cells (PEFCs)

Avanish Shukla, Santoshkumar D. Bhat*
CSIR-Central Electrochemical Research Institute-Chennai Centre, CSIR Madras Complex,
Taramani, Chennai-600113

Simultaneous unzipping and sulfonation of multi-walled carbon nanotubes (MWCNTs) through hydrothermal synthesis route is carried out to form sulfonated graphene nanoribbons (sGNRs) [1]. TEM analysis confirms the formation of sGNRs. The increase in width of unzipped MWCNTs shown in Figure 2 in comparison with the width of MWCNTs as seen in Figure 1 indicates the formation of GNRs. The required amount of sGNRs viz., 0.05, 0.1, 0.15 and 0.2 wt.% is incorporated to sPEEK to form composite membrane electrolytes by solution casting method. The proton conductivity, ion exchange capacity (IEC), water uptake and swelling ratio of composite membrane electrolytes is comparatively better than pristine sPEEK as shown in Table 1. Further studies are in progress to evaluate these electrolytes in PEMFC applications.

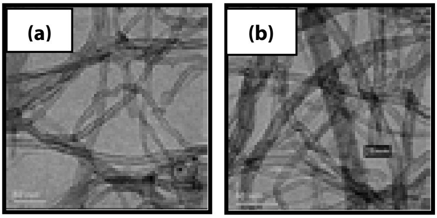


Figure 1- (a) MWCNTs (5-10 nm) and (b) sGNRs (5-25 nm)

S.No.	Membrane type	IEC (meq./gm)	Proton Conductivity (mS/cm)	Water Uptake (%)	Swelling Ratio
1.	Pristine sPEEK	1.48	35	30.5	1.30
2.	sPEEK-sGNRs (0.05 wt%)	1.51	39	32.2	1.32
3.	sPEEK-sGNRs (0.1 wt%)	1.52	81	32.8	1.33
4.	sPEEK-sGNRs (0.15wt%)	1.61	48	35.3	1.35
5.	sPEEK-sGNRs (0.2 wt.%)	1.55	63	39.1	1.39

Table 1- Physicochemical properties of composite membranes

Reference:

[1] Dhanraj B. Shinde, Mainak Majumder, Vijayamohanan K. Pillai, Scientific Reports 4, 2014, 4363

Impact of Polymeric Gate Dielectric Materials and Deposition Temperatures on Structure, Morphology and Mobility of CuPc Thin Films

Sumona Sinha[1*], Tanusree Samanta[1], C.-H.Wang[2],
M. Mukherjee[1] and Y.-W. Yang[2]
[1]Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata – 700064, India
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan, R.O.C.

The study of semiconductingsmall molecules like Copper (II) Phthalocyanine (CuPc) for applications in organic thin film devices has received considerable attention, due to their capability to form ordered films with virtuous electrical properties.The uses of polymeric dielectrics are attractive due to their ease in processing,flexibility and tunablesurface properties;indeed, the great promise of organic electronics is based on the idea of using flexible polymeric substrates.The smart temperature sensors can be made by using the change of polymeric properties at their glass transition temperature (T_g). Motivated by such interesting issues, we have investigatedofthe impact of polymeric gate dielectric materials and deposition temperatures (T_D) on the structures,morphologies and field-effect mobilities (μ)of the CuPc films by depositing films (thickness: 20 nm) on bare, octadecyltrichlorosilane (OTS), polystyrene (PS) and polyimide complex (PIC)coated SiO_2/ Si substrates The T_D was varied from 40°C to 120°C. The molecular orientation, structure, and morphology were investigated by X-ray absorption spectroscopy (XAS), X-ray reflectivity (XRR) and AFM techniques respectively whereas the mobilitieswere measured by fabricating thin film transistors.

We find that the polymer modification has a significant effect on the studied structure parameters and mobilities of the CuPc films as well as deposition temperature also plays a crucial role on this parameters depending on the behaviour of the polymeric layers at various temperatures and the diffusion of CuPc molecules . We have achieved the μ as high as ~ 0.1 $cm^2/V.s$ by using OTS/SiO_2 as gate dielectrics and T_D: 80°C. This value is quite high for CuPc TFT; only one tenth of the CuPc single crystal FET. The PS modification is very effective for enhancing μ below T_g of PS (100°C) and comparable to effectiveness of OTS modifications. The PIC modification is helpful to achieve better mobility than bare SiO_2 and μ increases linearly with T_D in both cases. The entire variation of μ of CuPc films with gate dielectric surface and T_D can be explained in terms of variation of molecular orientations,structures and morphologies of CuPc films. Detailed result of the study will be discussed in the conference.

References:

[1] Sinha, S; Wang, C.; Mukherjee, M.; Yang, Y. J. of Phys. D: Appl. Phys. **2014**,47, 245103.
[2] Lee, Y. J.; Park, S. S.; Kim, J.; Kim, H. App. Phys. Lett. **2009**, 94, 223305.
[3] Zeis, R.;Siegrist, T.;Kloc, Ch. Appl. Phys. Lett., **2005**, 86, 022103.

Polyaniline-ZnS Nanotubes for the Fabrication of Dye Sensitized Solar Cell: A Non-destructive Characterization through Impedance Spectroscopy

Arnab Shit, Shreyam Chatterjee and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata- 700032
**psuakn@iacs.res.in*

Polyaniline (PANI)-zinc sulphide (ZnS) nanocomposites (PAZs) are synthesized by polymerizing aniline in the presence of acetic acid with different concentrations of ZnS nanoparticles (NPs). Electron microscopic images indicate the nanotubular morphology of PANI and ZnS NPs remain adhered to the nanotube surface, but at higher ZnS concentration the nanotube morphology is lost. UV-vis spectra indicate PANI is in the doped state and the doping increases with an increase in ZnS concentration. Fluorescence intensity passes through a minimum with ZnS content and the dc-conductivity of the composites gradually increases with an increase in ZnS NP concentration. The current-voltage characteristics of PAZ composites indicates that the photocurrent is higher than that of the dark current at each voltage, and the device exhibits reversible turning ''on'' and ''off'' by switching the white light illumination ''on'' and ''off''. We have optimized the PAZ composites to maximize the photovoltaic performance of the resulting devices, and subsequently, a peak power conversion efficiency of 3.38% was achieved. An attempt is made to shed light on the operating mechanism of the dye sensitized solar cell from the impedance data using a Nyquist plot by drawing an equivalent circuit illustrating the different electronic and ionic transport processes within the cell.

References:

[1] O'regan, B.; Grätzel, M. *Nature*, 1991, 353, 737-740.
[2] Zhang, Q.; Dandeneau, C. S.; Zhou, X.; Cao, G. *Adv. Mater.* 2009, 21, 1-22.
[3] Chatterjee, S.; Shit, A.; Nandi, A. K. *J. Mat. Chem. A.* 2013, 1, 12302-12309.
[4] Shit, A.; Chatterjee, S.; Nandi, A. K. *Phys. Chem. Chem. Phys.* 2014, 16, 20079-20088

High proton conducting fluorinated poly(ether imide) copolymerscontaining flexible alkylsulfonated side chains via post sulfonation approach

Ershad Ali Mistri and Susanta Banerjee*
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
**susanta@matsc.iitkgp.ernet.in*

To produce high proton conductive and durable proton exchange membrane(PEM) for fuel cellapplication, a series of semifluorinated sulfonated co-poly(ether imide)s (co-SPI) containing sulfoalkyl side chains have been synthesized.Firstly, a series of hydroxyl-group containing copolyimides (HQN-XX) were synthesized from 2,2-Bis (3-amino-4-hydroxyphenyl) propane(HAP), a fluorinated quadridiamine(QA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA)by one pot high temperature polycondensation reaction. Thereafter, the copolymers were post-sulfonated using 1,3-propanesultone in presence of NaH and were analysed for their PEM properties.All the copolymers were thoroughly characterized by FT-IR and 1H-NMR spectroscopy. Tough, flexible membranes of the copolymers with good solubility and easy processability were obtained from solution casting in dimethyl sulfoxide(DMSO). The physical properties of all the prepared copolymer membranes before and after post sulfonation were studied. It was observed that eventhe post sulfonated (HQN-XX-PS) membranes exhibited good mechanical properties, high thermaland oxidative stability with low fuel crossover. The proton conductivity of the co-SPI membranes increased with IEC_W value and temperature;maximum upto163.5 mS/cmat 90 °C for HQN-90-PS,which is higher as compare to commercial Nafion®117(150.1 mS/cm)under similar experimental condition.Transmission electron microscopy (TEM) of the co-SPI membranes showedwell-dispersed cluster like hydrophilic domains distributed throughout the hydrophobic matrix, contribute to better proton conducting properties. Furthermore, the oxygen permeability of the co-SPI membranes (for HQN-90-PS, PO_2 = 0.69barrer) were significantly lower thanNafion® 117 (PO_2 = 3.58barrer) indicating excellent gas barrier property.

References:

[1] Asano, N.; Aoki, M.; Suzuki, S.;Miyatake, K.; Uchida, H.; Watanabe, M. J. Am. Chem. Soc. **2006**, 128, 1762-1769.

[2] Krishnan, K.;Iwatsuki, H.; Hara, M.; Nagano, S.; Nagao, Y. J. Mater. Chem. A **2014**,2, 6895-6903.

[3] Sheng, L.;Higashihara, T.; Ueda, M.; Hayakawa, T. J. Polym. Sci. Part A: Polym. Chem.**2014**, 52, 21-29.

[4] Yin, Y.; Du, Q.; Qin, Y.; Zhou, Y.; Okamoto, K. I. J. Memb. Sci.**2011**, 367, 211-219.

[5] Wang, C.; Li, N.; Shin, D. W.; Lee, S. Y.; Kang, N. R.; Lee, Y. M.;Guiver, M. D. Macromol. **2011**, 44, 7296-7306.

BODIPY-based conjugated small molecules and macromolecules for organic electronics

Saumya Singh, Vijay Venugopalan, Sudaresan Chithiraveland
Kothandam Krishnamoorthy*
Polymer Science and Engineering Division, CSIR-National Chemical Laboratory-Pune,
Pune, Maharashtra, India 411008
**k.krishnamoorthy@ncl.res.in*

BODIPY (4, 4-difluoro-4-bora-3a, 4a-diaza-*s*-indacene) dyes are known for remarkable chemical and photochemical stabilities, redox activities and excellent optical properties. Due to tunable optical properties, BODIPY containing conjugated systems have been explored as donor material in organic photovoltaic cells (OPVs) but they have not been very efficient so far.Charge carrier transport propertyis one of the main factors which decidesolar cell performance. Thus an approach that can modulate the charge carrier transport would improve the efficiency of BODIPY based organic solar cells. In order to improve charge carrier mobility we have designed and synthesized both,conjugated small molecules(CSMs)and macromolecules.CSMs consist of BODIPY as acceptor and triphenylamine as donor unit with variation in side chains. We have investigated the impact of side chain on charge carrier mobility and found that CSM with hydrophilic side chain shows higher glass transition temperature than hydrophobic side chain containing CSMsand forms smooth film with ordered packing. Field Effect Transistors fabricated with the same molecule have shownbetter device efficiencies, a very low threshold voltage and two orders of higher hole carrier mobilities compared to all the other derivatives. We have also synthesized low band gap polymers containing BODIPY in conjugation with electron poor co-monomers and have studied their photophysical and electronic properties.

References:

[1] Popere, B. C.; Della Pelle, A. M.; Thayumanavan, S. Macromolecules**2011**, 44, 4767–4776.
[2] Bura, T.; Leclerc, N.; Fall, S.; Léveque, P.; Heiser, T.; Retailleau, P.; Rihn, S.; Mirloup, A.; Ziessel, R. J. Am. Chem. Soc.**2012**, 134, 17404–17407.
[3] Singh, S**.**; Venugopalan, V.;Krishnamoorthy,K. Phys. Chem. Chem. Phys.**2014**, 16**,** 13376-133.

Sulfonated polytriazoles from a new fluorinated diazidemonomer and investigation of the irproton exchange properties

Asheesh Singh[1], Susanta Banerjee[1*],
[1*]Materials Science Centre, IIT, Kharagpur 721302, India
*susanta@matsc.iitkgp.ernet.in

A series of new fluorinated sulfonated polytriazole (PTAQSH-XX) copolymers were synthesized from new bis azide monomer, 4,4-Bis[3-trifluoromethyl-4(4-azidophenoxy) phenyl] biphenyl (QAZ), 4,4′-Diazido-2,2′-stilbenedisulfonic acid disodium salt hydrate (DADSDB) and 4,4′-(propane-2,2-diyl)bis((prop-2-ynyloxy)benzene) (BPEBPA) by click polymerization. The degree of sulfonation (DS) of the polytriazoles was controlled by variation of ratio of DADSDB to QAZ. Thestructuresofthepolytriazoleswereanalyzed byFTIR andNMR(^{1}H, ^{13}C and ^{19}F) spectroscopy.The polytriazoles exhibit high molecular weights and good solubility and film forming capabilities. The copolymer films showed good thermal stabilities, oxidative stabilities and mechanical properties depending upon their chemical compositions. The copolymers showed good dimensional stability and low water uptake values.Transmission electron microscopy (TEM) images of the membranes showed nano-phase separated morphology with ionic cluster sizes from 5 to 65 nm.Ion exchange capacity of the copolymers was calculated ^{1}H NMR spectroscopy and determined by titration. As expected the proton conductivity gradually increases with increasing the IEC_W and temperature also. The proton conductivities of PTAQSH-XX (XX-50, 60, 70, 80, 90) membranes were found in the range of 6-47 mS/cm at 30 °C and 12-76 mS/cm at 80 °C, while the maximum value (51mS/cm at 30°C and 112 mS/cm at°C) of proton conductivity was observed in case of PTASH-100.

References:

[1] Ponomarev, I.I.;Zharinova,M.Y.;Petrovskii,P.V.;Klemenkova,Z.S.;Dokl.Chem. **2009**, 429, 305–310.

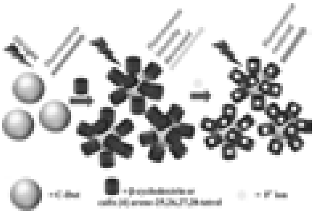
[2] Huang,Y.J.; Ye,Y.S.; Yen,Y.C.; Tsai,L.D.; Hwang,B.J.; Chang,F.C.; Int.J.Hydrog.Energy**2011**,36, 15333–15343.

[3] Singh, A.; Mukherjee, R.; Banerjee, S.;Komber, H.,Voit, B.; J. Mem. Sci.**2014** 469, 225–237.

Chitosan hydrogel derived Carbon dots capped with β-Cyclodextrin and calix[4]arene-25,26,27,28-tetrol for selective and sensitive detection of fluoride ions

Upama Baruah[a], Neelam Gogoi[a], Gitanjali Majumdar[b,**]
Devasish Chowdhury[a,*]
[a] Material Nanochemistry Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Garchuk, Guwahati, Assam, India.
[b] Department of Chemistry, Assam Engineering College, Jalukbari, Guwahati, Assam, India.

In the present work we have designed a novel system based on fluorescent carbon dots prepared from a biopolymeric material i.e. chitosan hydrogel. The prepared carbon dots were then capped with β-cyclodextrin and calix[4]arene-25,26,27,28-tetrol for sensitive and selective detection of fluoride ions in aqueous media. Fluorescent carbon dots showed quenching of its fluorescence intensity upon capping. Introduction of F^- ions to carbon dots capped with β-cyclodextrin and calix[4]arene-25,26,27,28-tetrol system results in enhancement and restoration of fluorescence intensity of the quenched system upto a considerable extent thereby leading to detection of F^- ions. Minimum detection limit was determined to be ~6.6 μM. The detection is found to be selective for F^- ions as with other halide ions i.e. Cl^-, Br^-, I^- and hydroxyl ion (OH^-), there is observed decrease of fluorescence intensity. Therefore the material we have developed can be used as potential fluorescent sensor for F^- ions in aqueous media. A possible mechanism to justify the observation is also discussed herein.



References

[1] Baruah, U.; Gogoi, N.; Majumdar, G. and Chowdhury, D. Carbohydrate Polymers, **2014**, 117, 377-383.

[2] Chowdhury, D.; Gogoi, N. and Majumdar, G. *RSC Advances,* **2012**, 2, 12156–12159.

[3] Wang, C.-I.; Periasamy, A. P. and Chang, H.-T. *Anal. Chem.* **2013**, 85, 3263–3270.

Hofmeister Cations and Anions Effects on Guar Gum Hydration Structure and Viscosity

Sonia Kundu[1], Arup Mukherjee[1]
Department of Chemical Technology, University of Calcutta, 92, A.P.C. Road, Kolkata, India

Guar gum (GG), a very high molecular weight galactomannan available from the endosperm of *Cyamopsis tetragonaloba* (L) is native to the states of Rajasthan, Haryana and Gujarat in India. The biopolymer is traditionally used in food as thickeners and in ice creams for water crystal inhibition and mouth filling quality. GG is in renewed interest recently, due to some successful applications in energy harvesting areas like that in shell gas and petroleum oil drilling.

Franz Hofmeister, presented a classification of series of ions that result in consistent hydration characteristics for salting out of proteins. Ion effects on structure and dynamics of water molecules are also known to determine similar properties of proteins and polysaccharides. *In silico* molecular modeling experiments have proved that the biopolymer GG when hydrated can hold two molecules of water in each galactose interconnection points preventing minimum number of water molecules to close in for ice crystallization. We systematically studied different cations and anions effects on viscous properties of 1% w/v guar gum solution in water and very predictable characteristics can be derived. The ions like K^+, CO_3^{2-} , SO_4^{2-} in the left hand side of the series increased a disorderness leading to decrease in GG solution viscosity and much less formation of aggregates in water. Alternative effects were observed in case of Na^+, Li^+, Cl^-, I^- ions in the right hand side of the series which increased intramolecular interactions of the polymer chains leading to concentration dependent increase in the viscosity of the solutions. In case of energy harvesting, GG in water often present hindrances for the mud and gas outflow due to polymer associated choking of rock pores. Laboratory observations further indicated that the ion composition of drilling mud need first be adjudged based on local ion levels for a predictive high yield optimization in petroleum oil drilling and hydro-cracking operations.

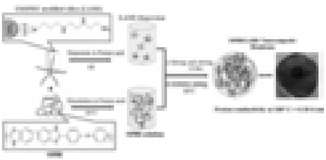
References

1) A Simple Theory for the Hofmeister Series. Wen Jun Xie and Yi Qin Gao. J. Phys. Chem. Lett. 2013, 4, 4247–4252
2) How Hofmeister Ion Interactions Affect Protein Stability. Robert L. Baldwin. Biophysical Journal Vol 71 (1996) 2056-2063.
3) Salt-Assisted and Salt-Suppressed Sol-Gel Transitions of Methylcellulose in Water**.** Y. Xu, C. Wang, K. C. Tam, L. Li. Langmuir (2004) 20, 646-652.

Tailored Organic-Inorganic Interface of Polybenzimidzole/ Silica Nanocomposite PEM with Enhanced Properties for Use in Fuel Cell

Shuvra Singha and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad - 500046, India
**Email: tusharjana@uohyd.ac.in*

Despite significant studies on polybenzimidazole (PBI) nanocomposite based proton exchange membrane (PEM) for fuel cells, the importance of nanocomposite interface, which directly impacts properties like proton conductivity, mechanical and thermal stabilities etc., has been inadequately addressed in literature. Since interface structure depends on the surface functionalization of the nanoparticles (NPs), we need to explore the surface chemistry in order to develop materials with desired properties. I would like to present our recent findings on the effect of aliphatic chain length of the surface modifier of silica NPs on important properties of PBI nanocomposite membranes for use as PEM and to underline the quantitative links between dispersion pattern of NPs in the polymer matrix with proton conductivity and different kinds of stability. Silica NPs decorated with long chain amine silane coupling agent (LAMS) was used to induce the compatibility with oxy-polybenzimidazole (OPBI) matrix. Structure and morphology analysis of nanocomposites by WAXD and TEM respectively, showed the formation of self-assembled networks of the modified NPs in the (OPBI/LAMS) matrix, whereas a completely dispersed structure was observed for the unmodified NPs (UMS) in the (OPBI/UMS) matrix. The self-assembly of LAMS nanoparticles helped in creating more proton hopping sites by hydrogen bonding interactions with OPBI chains. This resulted in remarkable increment in proton conductivity in LAMS loaded membranes which were not observed in UMS loaded membranes. Large mechanical reinforcements were obtained with OPBI/LAMS membranes. The presence of LAMS' assembly safe-guards the polymer chains from thermal and oxidative degradation thus enhancing the membranes' stability and durability in fuel cell operating conditions. Water uptake and dimensional stability studies of the membranes also showed promising results. The findings in this study demonstrates the potential of tailored OPBI/LAMS nanocomposite membranes for use as PEM in fuel cells.



References:

[1] Schadler, L. S.; Kumar, S. K.; Benicewicz, B. C.; Lewis, S. L.; Harton, S. E. Mater. Res. Soc. Bull. **2007**, 32,335-340.

[2] Akcora, P. et al Nat. Mater., **2009**, 8, 354-359.

[3] Ghosh, S.; Maity, S.; Jana, T. J. Mater. Chem., **2011**, 21, 14897-14906.

[4] Singha, S.; Jana, T. ACS Appl. Mater Interfaces *(Accepted).*

Responsive inverse opal photonic hydrogel for sensing application

V. V. Vipin[1], K. G. K. Warrier and Saju Piliai*
Materials Science and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology,
Thiruvananthapuram, Kerala-695019, India
**pillai_saju@niist.res.in*

Photonic crystals are structurally colored materials with periodic nanostructures which prevent the propagation of certain wavelength of light at its photonic band gap [1]. Here we fabricated a responsive inverse opal photonic hydrogel using large area ordered colloidal crystal template for sensing application. Using highly charged polystyrene (PS) microspheres, a well-ordered colloidal crystal template was prepared through an evaporation induced - capillary force driven self-assembly [2]. These colloidal crystals showed closed packed *fcc* structure which was obvious from the SEM image (Figure1a). Using this colloidal crystal template, an inverse opal photonic hydrogel was prepared by free radical polymerization of acrylamide monomer. As revealed in SEM image, the photonic crystal hydrogel was an exact inverse replica of the PS colloidal crystal (Figure1b). Bragg diffraction in visible light provided structural color to this well-ordered photonic nanostructure. Further, we explored the swelling property of the polyacrylamide hydrogel for responsive photonic hydrogel preparation. Using albumin (HSA) protein as a template molecule, molecular imprinting technology [3] was performed within the prepared photonic hydrogel. The optical response of this photonic hydrogel towards HSA solution was studied using a UV - Visible spectrophotometer. Interestingly, we found a shift in wavelength maxima of reflection corresponds to different concentrations of HSA solution.

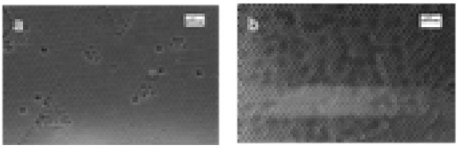


Figure1. (a) PS colloidal crystal and (b) Photonic hydrogel.

References:

[1] Kelsey I. MacConaghy, Christopher I. Geary, Joel L. Kaar, Mark P. Stoykovich, J. Am. Chem. Soc., **2014**, 136, 6896.

[2] Gurvinder Singh, Saju Pillai, Ayyoob Arpanaei, Peter Kingshott, Adv. Mater., **2011**, 23, 1519.

[3] Jennifer E. Loffgreen, Geoffrey A. Ozin, Chem. Soc. Rev., **2014**, 43, 911.

Superior Electrode Material Based on Polyaniline, Zinc Acetate and Graphene Nanoplateletsfor Supercapacitor Application

Amit Kumar Das and B. B. Khatua*
Materials Science Centre, Indian Institute of Technology Kharagpur,
Kharagpur 721302, West Bengal, India

This study discusses a simple and feasible method involving in-situ polymerization of aniline in the presence of zinc acetate dihydrate [$Zn(CH_3COO)_2$. $2H_2O$] and graphene nanoplatelets (GNP) for the preparation of high performance electrode material (PZG composite) for supercapacitor application. The presence of metal salt [$Zn(CH_3COO)_2$. $2H_2O$], enormously enhanced the capacitance value of PANI/GNP (PG) composite. Thus, the proposed method gives specific capacitance value for the PZG composite is ~688 F/g at a 10 mV/s scan rate which is very high compared to the specific capacitance value (~340 F/g) of PG composite at the same scan rate. In the PZG composite, zinc acetate and GNP are successfully coated by PANI, which provides more active sites for nucleation and electron transfer path. In addition, the inter- and intra-molecular interactions among them facilitate the electron transfer path which plays an important role to enhance the capacitance value of the composite. Moreover, the prepared composite is electrically conducting in nature and shows electrical conductivity in the order of $\approx 4.67\times10^{-2}$ $S.cm^{-1}$. In addition, PZG composite shows semi-conducting behavior. Field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM) reveal the interconnected fiber-like/thread-like morphology PZG composite.

Synthesis and characterization of novel polymer complexes having ruthenium polypyridine as a pendent group

J. Gopinath, V. Santosh, A. V. Sesha Sainath*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, Telangana, India
E mail: avss@res.iict.in

Macromolecular architectures and their selective functionality play a fundamental role in solar cell fabrication for tuning various characteristics like band gap, exciton diffusion length and recombination of charge carriers. To control recombination of charge carries in polymeric materials, several researchers aimed and are working on preparation of well defined copolymers in which through well ordered self-assembled nano-segregations, carrier transportation paths are properly channelled. We herewith report novel monomer, 10-(1,10-phenanthrolin-3-yloxy)decyl acrylate and its polymer complexes having ruthenium polypyridine as a pendent group and its di- and tri-block copolymers with poly(*N*-vinylcarbazole) and polystyrene segments (Figure 1), respectively, by reversible addition-fragmentation chain transfer polymerization method. The described model complexes in Figure 1 serve as references. The obtained model complexes and polymer complexes are characterized by UV-visible, infrared, nuclear magnetic resonance spectroscopic techniques, cyclic voltammetry and thermal characteristics by thermogravimetric analysis and differential scanning calorimetry. The detailed synthetic approaches and resulted materials characterization and their applications will be presented in poster.

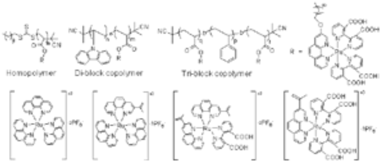


Figure 1. Structures of the polymers and model complexes.

References:

[1] Topham, P.D.; Parnell, A. J.; Hiorns, R. C. J Polym. Sci. Part B: Polym. Phys. **2011**, 49, 1131–1156.

[2] Lindner, S. M.; Huttner, S.; Chiche, A.; Thelakkat, M.; Krausch, G. Angew. Chem. Int. Ed. **2006**, 45, 3364 –3368.

PVDF/ P(VDF-HFP) - PZT composites for large area underwater acoustic sensors

Rahna K. Shamsudeen, Harikrishnan, V. G. Jayakumari,
R. Rajeswari, P. Jayesh & T. Mukundan
Naval Physical and Oceanographic Laboratory (NPOL), Kochi - 682 021, Kerala, India

Study of piezopolymers and composites as transduction materials for specific applications has gathered momentum. The increasing interest in Polyvinylidene fluoride (PVDF) and its copolymers as transduction materials in many fields is mainly due to their unique features such as flexibility, matching characteristic acoustic impedance to that of water (3.94 MRayl), ruggedness, low mass and very broad band (millihertz to gigahertz) applicability. Their availability in large area sheets, and viability of vapour deposition of electrodes on their surface make them suitable for inexpensive transducer arrays. The major objective of the present work is to improve the piezoproperties of polyvinylidene fluoride polymers and poly(vinylidene fluoride-hexafluoropropylene) P(VDF-HFP) copolymers by developing 0-3 composites with the incorporation of PZT-5H. Thick polymer films and composite films (0.5 mm) were made using melt mixing and hot press method. The effect of loading of PZT on the crystalline properties, dielectric properties and mechanical properties is studied in detail. Microstructure and crystalline structure analysis are investigated using scanning electron microscopy (SEM) and XRD, thermo mechanical studies were conducted by TGA, DSC and DMA analysis, dielectric properties are measured using LCR meter. These films were poled using corona poling and the piezoproperties were evaluated for their applicability towards large area sensors such as flank arrays and conformal arrays for curved structures for underwater acoustic applications.

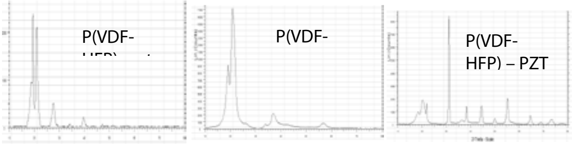


Figure: XRD of different polymer and composite films

References:

[1] XunlinQiu J. Appl. Phys. 108, 011101 2010

[2] H. L. W. Chan, Z. Zhao, K. W. Kwok, and C. L. Choy, J. Appl. Phys. 80 (7), 1, 1996, 3982

[3] E Venkatragavaraj, B Satish, P R Vinod and M S Vijaya, J. Phys. D: Appl. Phys. 34 (2001) 487–492

[4] D.K. Kharat, SandhyaMitra, Sania Akhtar and Vijai Kumar, Defence Science Journal, Vol. 57, No. 1, 2007, 7

Nucleation of gamma poly(vinylidene fluoride) in presence of reduced graphene oxide for energy density storage and piezoelectric application

Sumanta Kumar Karan and Bhanu Bhusan Khatua
Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302

In this work we report the simplest way to formation of polar γ-phase (α to γ-phase) of poly(vinylidene fluoride) (PVDF) using only conducting reduced graphene oxide (RGO) using solution casting method. It was found that RGO can achieved ~99% γ-phase conversion by simply controlling the filler precursor amount. Fourier transformed infrared spectroscopy (FTIR) and Raman spectroscopy confirmed stabilizing the polar γ-phase with molecular interaction of PVDF with the filler RGO. The PVDF film doped with RGO exhibit various functionalities, i.e., human touch response, enhanced ferroelectric remnant polarization with high energy density. Besides conventional piezoelectric sensor and actuators, it naturally lends to futuristic applications as vibration based energy harvester, ferroelectric non-volatile memory element and lightweight foldable optoelectronic device. Compared with pure PVDF film, a significantly increased dielectric constant (ε ~41) and a low dielectric loss (~0.14) were observed in PVDF-RGO nanocomposites at 1 kHz. In addition, PVDF-RGO nanocomposites exhibit a higher electrical released energy density up to 0.74 J/cm3 with a breakdown electric field only at 600 kv/cm with high electrical DC conductivity 3.30 □10^{-3} S.cm^{-1}.

Keywords: PVDF, Reduced graphene oxide, Polar γ-phase, Energy harvesting, Piezoelectric, Sensor, High Dielectric Constant, Low dielectric loss, DC electrical conductivity.

Advanced asymmetric supercapacitor constructed with Mn_3O_4@carbon nanotube - polyanilinenanocomposite and reduced graphene oxide electrodes

Manas Mandal, Debasis Ghosh, Chapal Kumar Das*
Materials Science Centre,
Indian Institute of Technology Kharagpur, Kharagpur 721302, India.
**chapal12@yahoo.co.in*

Supercapacitor also known as electrochemical capacitor is the alternative source of energy, which is unique because of its high power density, moderated energy density and very high cycle life. The superiority of supercapacior solely depends on its active material and the used electrolyte. There are several approaches to prepare active material for supercapacitor by combining the high surface area carbon materials and pseudocapacitive materials in a single composite. However, although these materials exhibit high specific capacitance, the low working potential still cannot avoid the problem of low energy density. The objective of the work is to prepare an electrode material and fabricate a device, which can exhibit high energy density at a high power delivery rate. In order to achieve this goal we have prepared ternary nanocomposites by combining the EDLC active material (CNT) with pseudocapacitive metal oxide (Mn_3O_4) and conducting polymer (PANI) by following a hydrothermal process followed by *in situ* oxidative polymerization of aniline monomer. The high electrochemical utility of the pseudocapacitive Mn_3O_4 was achieved in its graphene based hybrid composite. The combination of PANI with the binary composite resulted in a better synergistic interaction amongst the three and an improved specific capacitance was achieved. PANI formed a conductive network throughout the composite and also induced a porous architecture. However, the ternary nanocomposite was unable to show the cell voltage beyond 1V in aqueous electrolyte. In order to achieve higher energy density we employed an asymmetric electrode configuration by using the as prepared ternary nanocomposites as anode material and reduced graphene oxide as cathode material. The asymmetric supercapacitor was able to give a high operating voltage of 1.8 V, which resulted in very high energy density without any significant loss of power density.

References:

[1] Wu, Z.-S.; Ren, W.; Wang, D.-W.; Li, F.; Liu, B.; Cheng, H.-M. **ACS Nano**, 2010, 4, 5835-5842.

[2] Xiao, Y.; Cao, Y.; Gong, Y.; Zhang, A.; Zhao, J.; Fang, S.; Jia, D.; Li, F.**J. Power Sources** 2014, 246, 926-933.

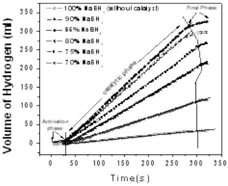
[3] Mandal, M.; Ghosh, D.;Giri, S.;Shakir, I.; Das, C. K. RSC Advances, **2014**, 4, 30832-30839.

[4] Ghosh, D.;Giri, S.; Mandal, M.; Das, C. K. RSC Advances, **2014**, 4, 26094-26101.

Ru-Co incorporated PEDOT-PSS nanocomposites catalyst: Rapid Hydrogen liberation from the hydrolysis of Sodium borohydride

Ankan Dutta Chowdhury, Nidhi Agnihotri, Amitabha De*
Chemical Sciences Division, Saha Institute of Nuclear Physics,
1/AF, Bidhannagar, Kolkata-700064, India
**amitabha.de@saha.ac.in*

We have reported a Ruthenium(0) Cobalt based nanoclusters which is incorporated into conducting polyaniline nanowires via in situ polymerization. Initially the Ru-Co nanocomposites are synthesized by reduction of a mixture of Ru(III) and Co(II) chlorides by $NaBH_4$ solution. After its incorporation into the conducting polymeric (PEDOT) surface, it is used as a reproducible catalyst for hydrolysis of $NaBH_4$ in alkaline medium. The obtained catalyst is characterized by TEM with EDS. The hydrolysis kinetics measurements show that the 85wt% $NaBH_4$ + 15wt% Ru-Co PEDOT nanocomposites in 1M NaOH exert best result of the catalyst among all combination. PEDOT gets soluble in alkaline water during hydrolysis of $NaBH_4$ and the nanocrystalline Ru-Co gets free to act as nano-catalyst to obtain best performance. A hydrogen generation rate of 40.1 $Lmin^{-1}g^{-1}$ at 30°C has been achieved, which shows better performance with respect to other catalysts reported earlier.



References:
[1] Akdim, O.; Demirci, U.; Miele, P. Int. J. Hydrogen Energy 34 **(2009)** 9444-9449.
[2] Jeong, S.; Kim, R.; Cho, E.; Kim, H.J. ; Nam, S.W. J. Power Sources 144 **(2005)** 129-134.
[3] Pozio, A.; De Francesco, M.; Marrucci, M. Int. J. Hydrogen Energy 33 **(2008)** 51-56.
[4] Liu, B.H.; Li, Q. Int. J. Hydrogen Energy 33 **(2008)** 7385-7391.
[5] Krishnan, P.; Advani, S.G.; Prasad, A.K. Int. J. Hydrogen Energy 33 **(2008)** 7095-7102.

Nitrogen and sulfur doped porous carbon from conjugated microporous polymer and its use as electrocatalyst and storage electrode

Manik E. Bhosale and Kothandam Krishnamoorthy*
Polymer science and engineering division, CSIR-National Chemical Laboratory, Pune
*k.krishnamoorthy@ncl.res.in

Conjugated microporous polymer having high surface area was synthesized using well-defined building blocks comprising triazine as a source of nitrogen and thiophene as a source of sulfur by Sonogashira-Hagihara coupling reaction. This porous polymer was used as precursor to prepare nitrogen and sulfur doped porous carbon with exactly controlled locations of nitrogen and sulfur atoms by thermal carbonization. This material was then used as metal free electrocatalyst for oxygen reduction reaction. The material also acts as active material supercapacitor. We studied the effect of carbonization temperature on electrocatalytic performance and supercapacitive behavior of the material.

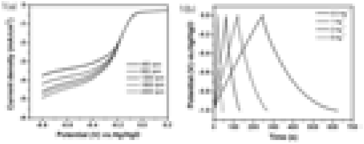


Figure 1: 1(a) ORR and 1(b) Supercapacitor performance of material

Development of Dip-stick Kit for Naked Eye Detection of Fluoride in Water Using Polymeric Hydrogel

Dr. Kakoli Dutta,*[1] and Dr. Priyabrata Sarkar [1]
1 Department of Polymer Science and Technology,
University of Calcutta, 92, A.P.C Road, Kolkata-700009
*E-mail: kakoli_mukherjee@yahoo.com

High levels of fluoride concentration in water cause serious health problems to human being. Fluorosis, caused by intake of fluoride has attained an alarming dimension. In India alone about 30 million people are suffering from fluorosis. According to WHO guideline, the permissible limit of fluoride in drinking water is 1.5 mg/L. So, there is tremendous need for the simpler and easier methods of detection of fluoride in drinking water. Yellow color of PCV (Pyrocatechol Violet) changes to blue or blueish violet depending on the pH by binding to a metal ion. When fluoride is added, the colour changes from blue to yellow and can be detected by naked eye at pH 4.2. This colour change is due to the replacement of water molecule from Zr-EDTA network and formation of the Zr-F complex.The coloring agent i.e. mixture of Zr, EDTA and PCV in a definite amount was entrapped in a hydrogel using PVA, gelatin and glutaraldehyde prepared in the form of a membrane by solution casting method. The membrane was characterized by FTIR and SEM.The water containing known amount of fluoride was tested by this hydrogel and a definite color gradient from blue to yellow was visible through naked eye.

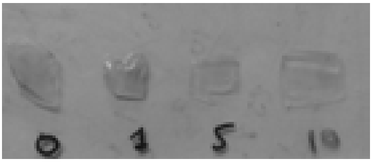


Fig- Change in color with the change in fluoride concentration in ppm

References:
[1] Balaji T and Matsunaga H, Analytical Sciences, 2005, 21, 973-978
[2] Mingcheng Xua, Zuoqing Shia , Lili Fenga, Juxiang Liua, Rongfu Shia, Mancai Xu , Yanlin Lu , Binglin He, Reactive & Functional Polymers, 2001, 46, 273–282
[3] Sathish R. Sai , Sujith U. , Nageswara Rao G. And Janardhana C. , Spectrochimica Acta Part A 2006 ,65, 565–570

Copolymerization of Linseed oil-styrene-Divinylbenzene and its application for the Detection of Aromatic Hydrocarbons

Rashmita Das*[1], Rajib Bandyopadhyay[1], Panchanan Pramanik[2]
[1]Department of Instrumentation and Electronics Engineering, Jadavpur University,
Salt Lake Campus, Kolkata- 700 098, India
[2]Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302, India
kunurashmita@gmail.com

Copolymerization of linseed oil with styrene and divinyl benzene is carried out by thermal free radical polymerization at 120^0 C. Linseed oils are obtained naturally from seeds, which is basically a triglyceride consisting of a mixture of saturated and unsaturated (oleic, linoleic and linolenic) fatty acids. This oil can also be modified via hydro peroxide, peroxide, epoxide and perepoxide formation [1, 2]. In this work, we have attempted to copolymerize linseed oil with styrene and divinyl benzene and the resulting polymer is used as a sensing film on quartz crystal microbalance (QCM) for the detection of aromatic hydrocarbon such as benzene, toluene, p-xylene, dichlorobenzene. QCM is very simple, highly sensitive, easy to use, low cost and can work at room temperature. The sensor is fabricated by using the synthesized linseed oil-styrene-divinylbenzene copolymer by simple solution dip coating method [3]. Linear sensitivity plot is obtained in the concentration range of 10-250 ppm of the aromatic hydrocarbon vapours. The sensitivity values are found to be approx 0.92Hz/ppm. The sensor is found to be more sensitive towards p-xylene vapour than other hydrocarbon compounds. The structure of the polymer film is characterized by FTIR spectroscopy and the morphological study of the film is carried out by FESEM. The sensors are reusable and can be reactivated by releasing the adsorbed vapor. Hence the sensors may find potential application in the monitoring and controlling the concentration of aromatic hydrocarbon vapour in coating industry.

References:

[1] Wick, Z.W.; Jones, F.N.; Pappas, P.S.SPE Monograph Series, New York **1992.**
[2] Singleton, D.A.; Hang, C.; Szymanski, M. J.; Meyer, M.P.; Leach, A.G.; Kuwata, J.S.; Greer, A.; Foote, C. S.; Houk, K. N. J. Am. Chem. Soc. **2003**, 125, 1319-1328.
[3] Das, R.; Pradhan, S.; Biswas, S.; Sharma, P.; Ghosh, A.; Bandyopadhyay, R.; Pramanik, P. Sens. and Acute. B: Chem. **2014**, 198, 94-101.

Ternary nanocomposite based on graphene-single walled carbon nanotubes-poly(3-methylthiophene) for supercapacitor application

Saptarshi Dhibar* and Chapal Kumar Das
Materials Science Centre, Indian Institute of Technology Kharagpur,
Kharagpur – 721302, India
*saptaiit2009@yahoo.com

In this present study we report a cost effective and easy synthetic procedure for the fabrication of graphene-single walled carbon nanotubes-poly(3-methylthiophene) ternary nanocomposite for high performance supercapacitor electrodes. The possible interaction between both graphene (Gr) and single-walled carbon nanotubes (SWCNTs) with poly(3-methylthiiphene) (PMT) was characterized by Fourier transform infrared, UV-visible, and Raman spectroscopies. Morphological confirmed the formation of bridge in between PMT coated SWCNTs with Gr layers. The ternary nanocomposite showed superior electrical conductivity of 4.68 S/cm at room temperature and also reached nonlinear current-voltage characteristics. The ternary nanocomposite achieved highest specific capacitance of 561 F/g at 5 mV/s scan rate. High energy density as well as power density was obtained for the ternary nanocomposite. Here both Gr and SWCNTs takes parts for the increment of electrochemical properties. Higher thermal stability also observed for the ternary nanocomposite. Based on the outstanding properties the ternary nanocomposite can be used as potential candidate for the high performance supercapacitor electrode.

Solid polymer electrolytes for Li-ion conductivity from phosphorus containing polyethers

Krishnamurthi Muralidharan* and H. Vignesh Babu
School of Chemistry, University of Hyderabad, Hyderabad
**murali@uohyd.ac.in*

The designing molecules for diverse uses are the most challenging one. The challenge can be attained by designing the macromolecules with a appropriate chemical structure. Because of the flexible reactivity of P – centres, organophosphorus compounds represent a pool of building blocks for variety of materials with novel properties. Hence, we have synthesized a variety of polyethers having phosphorus in the chain using bis(hydroxymethyl)phosphine sulfides as monomers, polyethers with phosphate pendent groups using catalysts designed in our lab and hyper-structured molecules using cyclophosphazene cores. Further, solid polymer electrolytes (SPE) were prepared using these molecules and studied their Li-ion conductivity. Some of the SPEs showed conductivity in the range of 10^{-4} S cm^{-1} which showed a potential use as polymer electrolytes for Li-ion battery.

References:

[1] VigneshBabu, H.; Muralidharan, K. Polymer, **2014**, 55, 83 – 94.
[2] VigneshBabu, H.; Muralidharan, K. Dalton Trans., **2013**, 42, 1238-1248.

Electrically conducting *Bombyxmori* nanoporous 3D scaffolds: A green sensor for highly efficient Picric acid explosives vapour detection

Sudesna Chakravarty[1], Nandana Bhardwaj[2] and Neelotpal Sen Sarma[3*]
[1, 3]Polymer Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, PaschimBoragaon, Guwahati-781035, Assam, India
[2]Seri-Biotechnology Laboratory, Life Sciences Division, Institute of Advanced Study in Science and Technology, PaschimBoragaon, Guwahati-781035, Assam, India
Email id: sudesnaiasst@gmail.com

"Green materials" and "green technologies" are emerging avenues for achieving ambitious goals in the field of electronics. An interesting area of interdisciplinary research field encompassing Chemistry, Material Science and Biotechnology is "Organic electronics". Herein, we have reported the development of cost effective and highly responsive hybrid material based on carbon coated natural polymer (*Bombyx Mori* silk) as a explosive vapour sensor. The 3D nanoporous scaffolds of *Bombyxmori* silk provides a large surface area while carbon nanopowder impart electrical conductivity to the scaffolds. Such scaffolds as an explosive vapour sensor is highly desirable as it is environmentally benign and its disposal after use is not a problem. The deposition of carbon nanopowder on 3D nanoporous scaffolds has been done by Chemical Bath Deposition. The characterization and morphological studies has been done by TGA, Impedence analyzer and FESEM. Electrical vapour sensing of explosives has been done by I-V measurements. Two fold increase in sensitivity was observed in presence of Picric acid vapour. Such work will help to develop green and miniaturized sensing system for explosive detection.

References:

[1] Q. Zhang, S. Yan and M. Li, Silk fibraoin based Porous Materials, Materials, 2009,2,2276-2295
[2] S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, Polyaniline Nanofibre Gas Sensors: Examination of response mechanism, Nano Letters, 2004, 4 (3), 491-496
[3] M. Irimia-Vladu, "Green" Electronics: Biodegradable and biocompatible materials and devices for sustainable future, Chem Soc Rev, 2014, 43, 588-610
[4] V. Vij, V. Bhalla and M. Kumar,Attogram Detection of Picric Acid by Hexa-peri-Hexabenzocoronene-Based Chemosensors by Controlled Aggregation induced Emission Enhancement, ACS Appl. Mater. Interfaces, 2013, 5, 5373-5380

Liquid crystalline template assisted synthesis of electrically conducting poly (3,4- ethylenedioxythiophene) nanospindles

Neethu Kalloor Sadanandhan and Sudha Janardhanan Devaki*
Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala-695019.
**sudhajd2001@yahoo.co.in*

Owing to the fascinating properties such as good electrical conductivity, reversible doping and dedoping capability, and tunable electrochemical behaviour, nanostructured intrinsically conducting polymers receive a great deal of attention in the field of organic lightweight batteries, flexible photovoltaics, efficient sensors and memory devices.[1] However, the development of nanoscopic conducting polymers with pointed ends such as nanospindles are receiving importance as it can facilitate the smooth transfer of charge carriers from end to end. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most attractive conducting polymers because of its optical transparency, low band gap, flexibility, ease of preparation, good stability, versatility for side chain functionalization and bioconjugation.[2-3] Here we present a unique liquid crystalline template strategy for the preparation of electrically conducting PEDOT nanospindles. Water dispersible PEDOTSs with controlled size, shape and microstructure were prepared using polymerization of the liquid crystalline template EDOT–PDPSA. PEDOTSs were formed by polymerizing this liquid crystalline EDOT-PDPSA. The formation of nanospindles was confirmed by SEM and TEM. Solid state ordering in the template monomer and polymer was confirmed by XRD and SAED patterns. Furthermore, electrochemical studies of PEDOTS modified glassy carbon electrodes were done for studying the electro-catalytic oxidation of ascorbic acid. The electrical conductivity of PEDOTS observed as 2.79 Scm^{-1} and its high thermal stability of 300 °C suggests these water dispersible nanomaterials can be used as a hole transport layer in photovoltaics.

References

[1] K. C. See, J. P. Feser, C. E. Chen, A. Majumdar, J. J. Urban and R. A. Segalman, Nano Lett., 2010, 10, 4664–4667.
[2] J. F. Hulvat and S. I. Stupp, Angew. Chem., Int. Ed., 2003, 42, 778–781.
[3] H. Mao, X. Lu, D. Chao, L. Cui, Y. Li and W. Zhang, J. Phys. Chem. C, 2008, 112, 20469–20480.

Effect of dihedral angle on charge carrier mobility of i-indigo-DPP copolymers

Satej S. Dharmapurikar, S. chithiravel, and K. Krishnamoorthy*
Polymers and Advanced Materials Laboratory, National Chemical Laboratory, Pune 411008.
k.krishnamoorthy@ncl.res.in

Charge transport properties are strongly affected by structural disorder in organic semiconductors. Planar structures increases the packing and improves the charge transport where as distorted structures diminishes the charge transport. Structure of monomers has pronounced effect on distortion in the organic semiconductors, where repulsive forces between two aromatic core leads to distortion in the main chain ex. biphenyl. Effect of distortion can be easily quantified by change in dihedral angle. To study the effect of dihedral angle, we have synthesized Isoindigo (Iso) and Diketopyrrolopyrrole copolymers with variation in structure of DPP unit i.e. P(Iso-TDPP), P(Iso-FDPP) and P(Iso- BDPP). It is noticed that structure of DPP monomer is only accountable for distortion in polymer chain. Distortion in the polymer structures has significant impact on its optical properties. Effect of distortion was observed in charge transport properties of polymers in organic field effect transistors. P(Iso-FDPP) which is less distorted has shown highest mobility compared to P(Iso-TDPP) and the most distorted structure of P(Iso-BDPP) has no field effect mobility

Amphiphilic Co-network Based Ion Exchange Membranes for Water Desalination via Electrodialysis

Suparna Guha[2],Vaibhavee Bhadja[1], Uma Chatterjee[1],and
Suresh K. Jewrajka[1]
[1]Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar, Gujarat
[2] Bhairab Ganguly College, Belghoria, Kolkata

Cross-linked anion exchange membranes (AEM) have been prepared from (i) poly(acrylonitrile)-co-poly(2-dimethylamino)ethyl methacrylate(PAN-co-PDMA) and (ii) polyn-butyl acrylate-co-poly(acrylonitrile)-co- poly(2-dimethylamino)ethyl methacrylate (PnBA-co-PAN-co-PDMA) terpolymer by quaternizing the DMA moieties followed by cross-linking of –CN groups with hydrazine hydrate.[1,2] This process avoids the use of carcinogenic chloromethyl ether (CME) which is widely employed for chloromethylation reaction for the preparation of AEMs.[3] It turned out that the terpolymer-based AEM exhibited superior electrochemical properties and faster desalination of water when tested in electrodialysis (ED) unit. Terpolymer-based AEM (AEM-2) containing 26 wt% PDMA and 17wt% hydrophobic PnBA exhibited low water uptake (12%), high ion-exchange capacity (IEC = 1.30 meq/g), high ionic conductivity (K^m = 4.57 mS/cm) and high transport number (t^-=0.93). The AEM-2 also exhibited low power consumption (0.66-0.95 KWhkg^{-1}) and high current efficiency (94-96%) at applied potential 1.5-2 V/cell pair. On the other hand, AEM prepared from bicomponent copolymer (AEM-1) exhibited higher power consumption (0.94-1.15 KWhkg^{-1}) and lower current efficiency(74-80%) than that of AEM-2 under similar experimental conditions. Similarly, a new cation exchange membrane (CEM) was also prepared from PAN-co-PnBA-co-polystyrene sulfonic acid sodium salt (PAN-co-PnBA-co-$PStSO_3Na$) terpolymer containing 14 wt% $PStSO_3Na$ and 10 wt% PnBA. This membrane also exhibited good electrochemical properties and rapid water desalination via ED. Fig. 1 shows the amount of salt removal (concentration of salt in diluted compartment in ED unit) with time.The remarkable effect of hydrophobic PnBA on the AEM-2 and CEM performance is attributed to the enhanced hydrophobicity, nano phase separation of PAN-co-PDMA or PAN-co-$PStSO_3Na$ domains in the membrane matrix, low degree of water uptake and absence and/or lowering of freezing bound water content in the membrane.

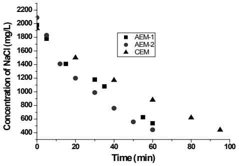


Fig.1 Concentration of NaCl vs time plots for AEM-1, AEM-2 and CEM

Reference

[1] Chatterjee, U.; Jewrajka, S.K. J. Mater. Chem.A**2014**, 2, 8396-8406.

[2] Chatterjee, U.; Bhadja, V.; Jewrajka, S.K. J. Mater. Chem.A **2014**, 2, 16124-16134.

[3] Laskin, S.; Kusschner, M.; Drew, R. T.; Capiello, V. P.; Nelson, N. Arch. Environ. Health, **1971**, 23, 135-136.

Facile Synthesis of Graphene Oxide from Tattered Graphite for Device Applications

Gaurav Kumar[1], Saba Khan[1], Samya Naqvi[1], Neha Gupta[1], Niharika Saxena[1], Pramod Kumar[2], Rachana Kumar[1]* and Suresh Chand[1]
[1]Physics of Energy Harvesting Division, Organic and Hybrid Solar Cells Group,
National Physical Laboratory, New Delhi, India
[2]Department of Applied Sciences, Indian Institute of Information Technology,
Allahabad, Uttar Pradesh, India
*rachanak@nplindia.org

Facile synthesis of graphene oxide (GO) is of high importance for the preparation of graphene sheets. Graphene oxide is prepared from graphite by several methods. In the present work, we introduce a milder method of GO synthesis from tattered graphite. For the preparation of tattered graphite, micron sized graphite is refluxed in conc. Nitric acid for 24 hours.[1] The resultant material is filtered and washed several times with deionized water to remove all acid impurities and dried in oven at 80 °C. Further, potassium permanganate and tattered graphite (3:1 ratio) are milled together until homogeneous. Then transferred to a beaker (in ice-bath) and conc. sulfuric acid (98 %,) is added drop-wise with continuously stirring. The stirring is continued till a large volumetric expansion is observed. Deionized water is added, with rapid stirring followed by heating at 90 °C for ~ 1 hour and black colored suspension is formed. The suspension is centrifuged to remove the acid supernatant followed by washing with water : methanol mixture till neutral pH to remove the impurities of acid and salt. Black GO is dried and collected and characterized by FTIR, UV-vis absorption spectroscopy, Raman spectroscopy, and XRD. $I_{(D)}/I_{(G)}$ ratio from Raman spectra suggests 47.3 Å cluster diameter and from XRD the crystallite size is calculated to be 46.1 Å, corroborating the Raman results. Finally GO is used as hole transport layer in organic photovoltaic device and compared with conventional PEDOT:PSS, which will be included in full paper.

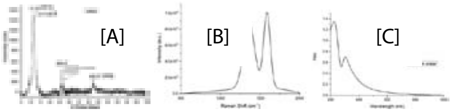


Figure 1. [A] XRD [B] Raman spectra and [C] UV-vis spectra (in water) of GO.

References:

[1] W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, **80**, 1339–1340.

[2] B. C. Brodie, Ann. Chim. Phys., 1860, **59**, 466–472.

[3] R. Kumar, P. Kumar, S. Naqvi, N. Gupta, N. Saxena, J. Gaur, J. K. Maurya, S. Chand, New J Chem. 2014, **38**, 4922.

Modified Zeolite-13X through silane condensation: Its impact in sPEEK to form a composite electrolyte for direct methanol fuel cells

S. Sasikala, S. D. Bhat*, Akhila Kumar Sahu
CSIR-Central Electrochemical Research Institute-Madras Unit,
CSIR Madras Complex, Chennai-600 113

Impact of hydrophilic zeolite namely 13 X modified by introducing organo-sulfonic acid groups through silane condensation; dispersed in sPEEK is studied for direct methanol fuel cells. Crosslinking of sPEEK with SSA is proven to be beneficial to provide the additional stability to the matrix that also helps in enhancing the ionic conductivity. Organo-sulfonic acid groups present in 13X zeolite will restrict the methanol cross-over and also provides the additional ionic conducting groups for the overall improvement in the performance. Ion exchange capacity, water and water-methanol mixture sorption and proton conductivity for the composite membranes have been extensively investigated. DMFCs comprising sPEEK-SSA-organo-modifed zeolite 13X (60:20:20 ratio) composite membrane delivered peak power densities of 92 mWcm^{-2} ,while peak power density of 73 mWcm^{-2} is obtained for the DMFC comprising pristine sPEEK membrane at 70 ^{o}C as shown in the Figure. The results highlight that these sPEEK based composite membranes exhibit higher DMFC performance and lower methanol permeability in comparison to pristine sPEEK membrane.

Use of Fly ash as novel filler for Silicone rubber

Moumita Naskar, Prasenjit Biswas, S. Ganga
Central Power Research Institute
Prof.SirC.V.Raman Road, Sadasiva Nagar (P.O.), Bangalore – 560080

Coal burning power plants that consume pulverized solid fuels produce huge amounts of fly ash (FA), which is the largest industrial waste in the world. Utilization of the waste FA is attempted for electrical application in the present investigation by converting FA to Nano-fly ash (NFA). NFA was prepared from FA by high energy ball milling process. After 60 h ball milling FA became amorphous. The effects of loading level of NFA on the electrical, mechanical, and surface properties of silicone rubber (SIR)nano-composite were investigated. Filler concentration range was varried between 0 to 30 phr (parts of NFA per hundred parts of SIR). SIR/NFA nano-composites showed excellent electrical properties due to the presence of SiO_2 (64%) in NFA. To measure the effect of addition of NFA on the flammability of SIR nano-composite, their limiting oxygen index (LOI) was evaluated. The greater the LOI of a given material the lower is its flammability. It is seen that addition of NFA moderately increases the LOI of SIR nano-composites i.e. the presence of the AL_2O_3 in NFA reduced the flammability of the SIR nano-composites. Transmission electron microscopy (TEM) studies revealed that the NFA nanoparticles were well dispersed throughout the SIR matrix at lower NFA loadings, whereas agglomerated structures were found for higher NFA addition (30phr). The strain dependence rheological study concluded that the elasticity generated in the SIR/NFA nano-composites provides better relaxation mechanism due to the significant dispersion of NFA up to 20phr into the SIR matrix during melt processing. The hydrophobic nature of the nanocomposites increased up to 20phr due to NFA addition as at this concentration dispersed homogeneously and showing better SIR–NFA interactions. The study indicates that NFA can be effectively used as a reinforcing modifier for the SIR for High voltage electrical applications.

Keywords: Nano-Fly Ash, Silicone rubber, Transmission electron microscopy, Limiting oxygen index, Hydrophobicity

Porous Polymers: Preparation, Characterization and Applications

Vikas Kumar and C. V. Avadhani*
Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.
Email: cv.avadhani@ncl.res.in

Porous polymers have been utilized in numerous applications. Porous polymers are polymeric materials containing one or more pores and can be designed to possess high surface area and well-defined porosity. Some interesting examples are hollow bamboo, honeycomb with hexagonal cells, and alveoli in the lungs. Porous polymers can be classified into microporous (pore size smaller than 2 nm), mesoporous (pore size in the range of 2-50 nm) and macroporous (pore size larger than 50 nm) polymers. Porous polymers find applications in gas storage and separation materials, in sensors, in filtration / separation membranes, in proton exchange membranes, etc.

Several techniques are employed for preparing porous polymers, for e.g, phase inversion, direct templating and direct synthesis, among the others.

In this poster, we report the preparation and characterization of porous polymers based on polyetherimide (PEI). The resulting polymers exhibited macroporosity in the range 300-800 nm as seen in SEM. These porous polymers were subjected to Li-ion transport/ conductivity by making a coin cell using $LiPF_6$ in EC / DEC (1:1, V / V) as an electrolyte. The Li-ion transport number was obtained in the range 0. 6-0.7 and is comparable to Celgard the standard Li-ion battery separator material.

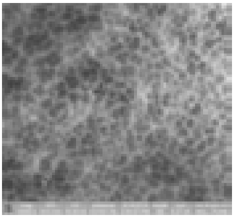


Figure 1. SEM images of polyetherimide (PEI)

References:
1. Xiaosong Huang, *J. Power Sources* **2012,** 216, 216-221.

Preparation and characterisation of partially sulphonated LDPE as a polymer electrolyte membrane in fuel cell application

Ruchira Rudra[1], Vikash Kumar[2], Arpita Nandy[2], Patit P. Kundu*
Advanced Polymer Laboratory, Department of Polymer Science and Technology,
University of Calcutta, 92, A.P.C Road, Kolkata – 700009, India.
**ppk923@yahoo.com*

Need for a proper replacement of high cost per fluorinated membranes has been focused much more attention in order to serve as a polymer electrolyte membrane (PEM) in fuel cell technology. It is well known that any ion permeable material can function as a barrier and serve as PEM in fuel cell operations. In our current research, we have dealt with polyolefin - low density polyethylene (LDPE) membrane, one of the well known commodity thermoplastic materials for daily uses and its surface has been modified through sulphonation at room temperature. The sulphonation of LDPE was carried out by using chlorosulphonic acid (Cl-SO_3H) at different time interval. The maximum degree of sulphonation was found to be 15% which was confirmed by FT-IR spectroscopy and with the increase of degree of sulphonation a reduction in the degree of crystallinity (from XRD and SEM data) was achieved indicating that the crystalline LDPE was transformed gradually into its amorphous equivalent. The enhanced property of the surface sulphonated LDPE membrane was also characterized by its water uptake, swelling thickness, ion-exchange capacity and proton conductivity values. In overall, the study depicts that the sulphonated LDPE can be useful as a low cost PEM for fuel cell application.

References:

[1] Kaneko M, Kumagai S, Nakamura T, Sato H. Study of sulfonation mechanism of low-density polyethylene films with fuming sulfuric acid, Journal of Applied Polymer Science (2004), Vol. 91, 2435–2442

[2] Fischer D., Eysel H. Analysis of polyethylene surface sulphonation. Journal of Applied Polymer Science (1994) Vol. 52, 545-548

[3] Rasmussen J. R., Stedronsky E. R., Whitesides G. M. Introduction, modification,and characterization of functional groups on the surface of low-density polyethylene film. Journal of the American Chemical Society (1977) vol no.99.14

Study of PVA/ PSSA/ Chitosan/ Closite-30B clay based polyelectrolyte composite membrane for direct methanol fuel cell application

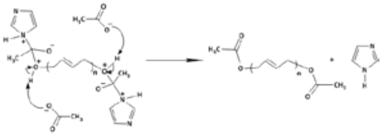
Surendra Singh Gaur, Prodyut Dhar, Amit Kumar, and Vimal Katiyar*
Department of Chemical Engineering, IIT Guwahati
*vkatiyar@iitg.ernet.in

A polymer electrolyte nanocomposites membrane, comprised of poly (vinyl alcohol) (PVA), chitosan and poly (styrene sulfonic acid) (PSSA) polymers and montmorillonite (MMT) Cloisite®30B clay has been fabricated and characterized for the direct methanol fuel cell application. Thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), X-ray diffraction (XRD), methanol permeability and proton conductivity measurements have been carried out to study the electrolyte membrane. A comparative study has been also carried out to compare the properties of PVA/PSSA/Chitosan/Cloisite®30B clay composite membrane with PVA/PSSA, PVA/PSSA/Chitosan and Nafion®117 membranes. Properties such as methanol permeability and water uptake have been found superior than that of Nafion®117. The proton conductivity of the membrane has been found in the range of 10^{-2} S cm^{-1}.

Hydroxyl Value of Hydroxyl Terminated Polybutadiene; An Attempt to Develop a Methodology Free of Pyridine

Ancy Smitha Alex, Vijendra Kumar*, G. G. Bandyopadhyay
Analytical Division, Chemical Systems Group, Propellants,
Polymers, Chemicals and Materials Entity,
Vikram Sarabhai Space Centre, Indian Space Research Organization,
Thiruvananthapuram, Kerala, India
vkvssc@gmail.com

Hydroxyl terminated polybutadiene (HTPB) acts as work horse binder in the formulation of solid propellant. Hydroxyl value is one of the important parameter for the characterization of HTPB. Acetylation using pyridine as catalyst as well as solvent is generally employed for hydroxyl value determination. Pyridine method has certain limitations due to its high toxicity. This paper presents a methodology, free of pyridine for determination of hydroxyl value of HTPB by using catalyst and solvent system comparatively less toxic than pyridine. We have explored the catalytic potential of imidazole and its derivative in the acetylation of HTPB. Effect of various parameters such as amount of sample, reaction (reflux) time, ratio of reagent and solvent, concentration of catalyst etc. on the hydroxyl value of HTPB were investigated. Moreover titration parameters were also optimized with the aqueous NaOH and alcoholic KOH as titrant. The present methodology is comparatively safer alternative than well-established pyridine method to determine the hydroxyl value of HTPB.



Scheme: Proposed mechanism of acetylation of HTPB using imidazole as catalyst

References:

[1] Fernandes, E.; Vicente, J.; Cruz, R.; Nele, M.; Nunes, E.; Costa-Félix, R. Polymer Testing. **2014**, 33, 16–20.

[2] Padilha de Paula, J; Farago, P.V.; Binhara, P.B.; Silva, S.A.; Zawadzki, S.F. Polymer Testing. **2008**, 27, 675–678.

[3] Chalasani, S.R.K.; Hablot, S.D.E.; Shi, X.; Graiver, D.; Narayan, R. J. Am. Oil Chem. Soc. **2013**, 90, 1787–1793.

[4] Tiwari, P.; Kumar,R.; Maulik,P.R.; Misra, A.K. Eur. J. Org. Chem. **2005**, 4265–4270.

High Energy Density Hybrid Supercapacitor Electrode Material Based on 3D Graphene/Lithium Cobalt Oxide/PANI

Anirban Maitra[1], Debasis Ghosh[1], Chapal Kumar Das[1*],
[1.] Materials Science Centre, IIT Kharagpur, West Bengal-721302, India
*chapal12@yahoo.co.in

In recent days, Supercap battery added a new sparkling dimension in energy storage related research. The objective of the present work is to fabricate hybrid supercapacitor by combining the battery like electrode and supercapacitor like electrode in a single system which will be able to deliver high energy density with no compromise with power density. To achieve the goal we choose the polymeric nanocomposites of graphene incorporated Polyaniline wrapped lithium Cobalt Oxide nanoglobules as the battery active material and 3D graphene nanosheet network as the supercapacitor electrode material. The main function of the ternary composite is to provide high specific capacitance, owing to the significant synergistic interaction ammongst the three. Whereas the 3D graphene which is covalently bonded single layer graphene sheets, influence the rate of charging and discharging. It has got a very high specific surface area (~ 3000 m^2g^{-1}) and lithium ion adsorption property. This LiCoO2/graphene/Polyaniline composite shows an improved specific capacitance value as well as very high cycle stability. Formation of lithium cobalt oxide can be confirmed by x-ray diffraction analysis. Spinal structure can be detected by using Rietveld refinement.Spectroscopic analysis reveals the formation of graphene, 3D Graphene and LiCoO2/Graphene/Polyaniline composite. Microscopic analysis shows a porous nature of the 3D graphene and the LiCoO2 are in the form of nanoglobules. Interaction between graphene with LiCoO2/Polyaniline influences its attractive and promising performance along with a very high dimension stability, environmental stability and reproducibility.

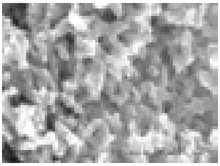
References:

[1] Zhang, F.; Zhang, T.; Yang, X.; Zhang, L.; Leng, K.; Huang, Y.; Chen, Y.; Energy Environ. Sci., **2013**, 6, 1623-1632.
[2] Kim, H.; Park, K, Y, Hong, J.; & Kang, K.; Scientific Reports, 2014, DOI: 10.1038/srep05278.
[3] Zhang, Y.; Ma, M.; Yang, J.; Su, H.; Huang, W.; Dong, X., Nanoscale, 2014, 6, 4303–4308.
[4] Ghosh, D.; Giri, S.; Moniruzzaman, M.; Basu, T.; Mandal, M.; Das, C.K.; Dalton Trans., 2014, 43, 11067–11076.
[5] Chen, H.; Qiu, X.; Zhu, W.; Hagenmuller, P.; Electrochemistry Communications 4 (2002) 488–491.

$(CH_3)(C_6H_5)_3P^+$ MnO_4^-as novel oxidant for aniline polymerization : Formation of nano composite of PANI-Mn_5O_8 and the use of this composite inpseudocapacitor

S. Palaniappan, *,[a]U. Susmitha and B. Rajender
Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology,
Tarnaka, Hyderabad 500 007, India
[a]CSIR – Network Institutes for Solar Energy (NISE), India
susmitha.uppugalla@gmail.com

Nano composites of polyaniline salt with manganese oxide are prepared by aqueous, emulsion and interfacial polymerization pathways of aniline using methyltriphenylphosphonium permanganate as novel organic oxidant. Polyaniline composites are characterized by FT - IR, FE - SEM, EDAX, XRD, TGA and conductivity measurements. XRD spectrum supports the formation of PANI-Mn_5O_8. PANI - Mn_5O_8 sample prepared by emulsion polymerization pathway shows nano fiber morphology with high conductivity (9.4 S/cm). Composites prepared via three different polymerization pathways are used as electrode materials in pseudocapacitor in symmetric configuration. Pseudocapacitor systems are characterized by cyclic voltammogram, galvanostaticcharging/ discharging, and electro-chemical impedance spectroscopy. The results of this study will be discussed.



SEM image of PANI-Mn_5O_8

Acknowledgements:
The authors thank CSIR, New Delhi under the TAPSUN program (NWP-0056) for funding.We are thankful to Dr. M. Lakshmi Kantam, Director and Dr. K.V.S.N. Raju, CSIR-IICT for their support and encouragement. We also thank Dr.Vijayamohanan K Pillai, Director and Dr. S. Gopukumar, Scientist, CSIR-CECRI for their valuable discussion. USis thankful to UGC, India for financial assistance.

References:
[1] Huo, Y.Q.; Zhang, S.B.; Zhang, H.Y. J. Appl. Polym. Sci. 2014, DOI: 10.1002/app.40575.
[2] Sen, PT.; De, A.; Chowdhury, AD.; Bandyopadhyay, SK.; Agnihotri, N.; Mukherjee, M. Electrochim.Acta 2013, 108, 265-273.
[3] Jaidev; Jafri, RI.; Mishra, AK.; Ramaprabhu, S. J. Mat. Chem. 2011, 44, 17601-17605.

Precise detection, discrimination andseparation of anionic surfactants at full pH range *via*cationic conjugatedpolyelectrolyte: An approach to facilitate illicit drug analysis

Sameer Hussain[1], Akhtar H. Malik[1], Parameswar K. Iyer[1,2*]
[1]Department of Chemistry, IIT Guwahati, Guwahati
[2]Centre for Nanotechnology, IIT Guwahati, Guwahati
sameer.icm12@gmail.com,pki@iitg.ernet.in

The use of conjugated polymers (CPs) as a highly sensitive material signifies novel and promising future in the cross-disciplinary areas of chemistry, material sciences, and biological sciences[1]. In recent years, immense research has been focused on the selective detection of chemical and biological species using CPs[2]. A novel water soluble cationic conjugated polymer PMI was synthesized by cheap and economical method of oxidative polymerization. PMI displays extraordinary stability in full range of pH, sea water, brine, urine, etc. and performs efficient detection, discrimination as well as separation of "moderately dissimilar" anionic surfactants *viz.* sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulfate (SDS) in very low parts per billion (ppb) levels respectively. PMI formed stable hydrogels in presence of SDS whereas, SDBS formed precipitates with PMI as a result of different inter polymer co-facial arrangement *via* Columbic attraction. A critical problem associated with anionic surfactants (SDBS and SDS) is their extensive misuse as an adulterant and masking agents along with abusive and performance enhancing drugs to evade detection such as doping tests[3]. The complex forming ability of PMI with SDS and SDBS facilitated their separation and removal from water or drug-doped urine samples without the use of any organic solvent, chromatographic technique or solid support. The surfactant free sample solutions could be precisely analyzed for the presence of illicit drugs by any standard methods. Using this protocol, a rapid and practical method to efficiently detect, distinguish and separate SDS and SDBS in water, urine, harsh conditions and natural chemical environments at ppb levels is demonstrated.

References:

[1] Zhu, C.;Liu, L.;Yang, Q.;Lv,F.; Wang S. **2012**, Chem. Rev. 112, 4687-4735.
[2] Rochat, S.;Swager, T. M. ACS Appl. Mater. Interfaces **2013**, 5, 4488-4502.
[3] Warner, A.Clin. Chem. **1989**, 35, 648–651

Water vapor barrier material by covalent self-assembly for organic device encapsulation

Gayathri N Kopanati,[a] Sindhu Seethamraju,[b] Praveen C Ramamurthy[b, c], Giridhar Madras[1a]

[a]Department of Chemical Engineering, [b]Centre for Nanoscience and Engineering,
[c]Department of Materials Engineering, Indian Institute of Science, Bangalore, 560012, India
[1] *Email id: giridhar@chemeng.iisc.ernet.in*

Development of barrier materials for organic device encapsulation is of key interest for the commercialization of organic electronics. In this work, we have fabricated barrier films with ultra-low water vapor permeabilities by reactive layer-by-layer approach. Using this technique, alternative layers of polyethylene imine and stearic acid were covalently bonded on a Surlyn film. The roughness, transparency and thickness of the films were determined by atomic force microscopy, UV-visible spectroscopy and scanning electron microscopy, respectively. Water vapor transmission rates through these films and the ability of these films to protect the organic photovoltaic devices was investigated. The film with covalently assembled bilayers exhibited lower water vapor transmission rates and maintained higher organic photovoltaic device efficiencies compared to the neat Surlyn film.

References

(1) Groner, M. D.; George, S. M.; McLean, R. S.; Carcia, P. F. Gas diffusion barriers on polymers using Al_2O_3 atomic layer deposition. *Appl. Phys. Lett.* **2006**, *88*, 051907-09.

(2) Hanika, M.; Langowski, H.-C.; Moosheimer, U.; Peukert, W. Inorganic Layers on Polymeric Films – Influence of Defects and Morphology on Barrier Properties. *Chem. Eng. Technol.* **2003**, *26*, 605–614.

(3) Mohanta, V.; Madras, G.; Patil, S. Layer-by-Layer Assembled Thin Film of Albumin Nanoparticles for Delivery of Doxorubicin. *J. Phys. Chem. C* **2012**, *116*, 5333–5341.

(4) Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Performance of an ionomer blend-nanocomposite as an effective gas barrier material for organic devices. *RSC Adv*. **2014**, *4*, 11176–11187.

(5) Gupta, S.; Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Polyvinylbutyral Based Hybrid Organic/Inorganic Films as a Moisture Barrier Material. *Ind. Eng. Chem. Res.* **2013**, *52*, 4383–4394.

Layer-by-Layer Assembly of Nafion on Surlyn with Ultra-high Water Vapor Barrier

Sindhu Seethamraju,[a] Arun D Rao,[b] Praveen C Ramamurthy [a, b] ,
Giridhar Madras*[a]
[a]Centre for Nanoscience and Engineering, Indian Institute of Science,
Bangalore, 560012, India
[b]Department of Materials Engineering, Indian Institute of Science,
Bangalore, 560012, India

A layer-by-layer approach was used for the fabrication of multilayer films for ultra-high gas barrier applications. The ultra-high gas barrier material was designed by incorporating Nafion layer in between bilayers of poly (ethylene imine) and poly (acrylic acid) on a Surlyn substrate. When the barrier film with self-assembled Nafion is exposed to the moist environment, Nafion absorbs and desorbs water molecules simultaneously, thereby reducing the ingress of moisture in to the film. In order to study the effect of Nafion, the fabricated barrier materials with and without the presence of Nafion were tested for water vapor barrier properties. The barrier films were further used for encapsulating organic photovoltaic devices and were evaluated for their potential use in barrier applications. The devices encapsulated with the films containing Nafion exhibited better performance when subjected to accelerated aging conditions. Therefore, this study demonstrates the effectiveness of self-assembled Nafion in reducing the water vapor permeability by nearly five orders of magnitude and in increasing the lifetimes of organic devices by ~ 22 times under accelerated weathering conditions.

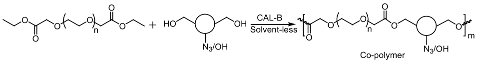
References

(1) Chou, C. T.; Yu, P. W.; Tseng, M. H.; Hsu, C. C.; Shyue, J. J.; Wang, C. C.; Tsai, F.Y. Transparent Conductive Gas-Permeation Barriers on Plastics by Atomic Layer DepositionAdv. Mater. 2013, 25, 1750-1754.
(2) Multilayer Thin Films (Eds: G. Decher, J. B. Schlenoff, Wiley-VCH, Weinheim,Germany 2003.
(3) Stevens, B. E.; Odenborg, P. K.; Priolo, M. A.; Grunlan, J. C. HydrophobicallyModified Polyelectrolyte for Improved Oxygen Barrier in Nanobrick Wall Multilayer ThinFilms. J. Polym. Sci. B: Polym. Phys. 2014, 52, 1153.
(4) Ramamurthy, P. C.; Gupta, S.; Madras, G. Development of "Ultra Low MoisturePermeability Measurement Technique" using Cavity Ring Down Spectroscopy. IPEC137/2012 1651/CHE/2012.

Non-ionic Dendronized Multiamphiphilic Polymers as Multivalent Nanocarriers for Drug Delivery Applications

Sunil K. Sharma
Department of Chemistry, University of Delhi, Delhi-110007
sksharma@chemistry.du.ac.in

Nanotechnology is one of the most rapidly growing fields because of its ability to control the materials on the nanoscale. The amphiphilic polymers and dendritic scaffolds have been explored enormously for the transport of various bio-active components like genes, drugs, growth factors, antibodies and various others.[1] Over the past few years, significant progress has been made in the direction of synthesizing dendritic and multiarm polymeric scaffolds which act as unimolecular transport systems. Our group has also worked on the synthesis of multiamphiphilic dendronized[2] and non-dendronized[3] polymers and explored their transport potential. The dendronized polymers have an extra advantage of the multivalency provided by the surface functional groups of dendrons which provides amphiphilicity along with additional binding sites for various targeting groups and other imaging probes.[1] We have used poly(ethylene glycol) diethyl esters, azido glycerol and modified sugars as synthons for immobilized *Candida antarctica* lipase (Novozym 435) catalyzed polymerization reactions. All the synthons used are biocompatible, non-toxic, and readily available. The resulting co-polymers were then functionalized with alkyl moieties and regular and hyper-branched polyglycerol (PG) dendrons. The multiamphiphilic dendronized /non-dendronized polymers aggregate in aqueous medium to form well defined nanospheres which have been explored for their encapsulation potential using model dyes and drugs. The cyto-toxicity profile of all the resulting multiamphiphilic polymers was also studied and these polymeric systems were found to be non-toxic over a wide concentration range. The synthetic methodology, characterization and transport study results will be discussed during the poster presentation.



Acknowledgements:

We gratefully acknowledge the financial assistance by Indo-German Science & Technology Centre (IGSTC) supported by the Bundesministerium für Bildung und Forschung (**BMBF**), Bonn and Departments of Science & Technology (DST), Delhi and University of Delhi, Delhi.

References:

1. (a) Calderon, M.; Quadir, M. A.; Sharma, S. K.; Haag, R. Dendritic Polyglycerols for Biomedical Applications. *Adv. Mater*. **2010**, *22*, 190-218; (b) Gupta, S.; Tyagi, R.; Parmar, V. S.; Sharma, S. K.; Haag, R. *Polymer* **2012**, *53*, 3053-3078.
2. Gupta, S.; Schade, B.; Kumar, S.; Böttcher, C.; Sharma, S. K.; Haag, R. *Small* **2013,** *9*, 894-904; Kumari, M.; Singh, A. K.; Kumar, S.; Achazi, K.; Gupta, S.; Haag, R.; Sharma, S. K. *Polym. Adv. Technol.* 2014, DOI: 10.1002/pat.3293.
3. Kumar, S.; Mohr, A.; Kumar, A.; Sharma, S. K.; Haag, R. *Int. J. Art. Organ* **2011**, *34*, 84-92; Gupta, S.; Pandey, M. K.; Levon, K.; Haag, R.; Watterson, A. C.; Parmar, V. S.; Sharma, S. K. *Macromol. Chem. Phys.* **2010**, *211*, 239-244; Bhatia, S.; Mohr, A.; Mathur, D.; Parmar, V. S.; Haag, R.; Prasad, A. K. *Biomacromolecules* **2011**, *12*, 3487-3498.

Bio-based hyperbranched poly(ester amide) nanocomposites: Advanced multifaceted materials

Sujata Pramanik and Niranjan Karak*
Advanced Polymer and Nanomaterial Laboratory, Chemical Sciences Department
(Center for Polymer Science and Technology), Tezpur University, Napaam-784028, India
**Email: karakniranjan@gmail.com*

Bio-based hyperbranched poly(ester amide) (HBPEA) nanocomposites awarded the advantages of combination of ester and amide linkages in the same polymer chain and enjoys the properties of both polyesters and polyamides along with renewable natural feed stock together with unique attributes of nanomaterial and thereby bringing revolutionary in the realm of advanced multifaceted materials. Thus the present work highlights the synthesis of bio-based HBPEA from diethanol fatty amide (DEFA) of castor oil with10 wt% branch generating component, diethanol amine along with phthalic anhydride, maleic anhydride and isophthalic acid. The research focused on bio-based HBPEA nanocomposites using different nanomaterials like polyaniline (PAni) nanofiber, PAninanofiber modified montmorillonite (MMT), functionalized multi-walled carbon nanotubes (MWCNT) and silver nanoparticles decorated MWCNT for their possible advanced applications. HBPEA/PAninanofiber nanocomposites exhibited significant improvement in mechanical, thermal and antistatic properties of the pristine system. Whereas PAninanofiber modified MMT based such nanocomposites showed their potentiality as advanced antimicrobial coating materials. Further microwave irradiation and ultrasonication assisted covalent functionalized MWCNT/HBPEA nanocomposites are found to be biocompatible, biodegradable and possessing antibacterial efficacy against Gram positive and acid fast bacterial strains and thus promising antibacterial dressing materials for infected burn wounds. On the other hand non-covalent functionalized MWCNT/HBPEA nanocomposites exhibited pronounced thermostability, antistatic property and selective antibacterial efficacy against Gram positive bacterial strains. At the end, silver nanoparticles decorated non-covalently functionalized MWCNT/HBPEA nanocomposites were fabricated to achieve unique polymeric materials with widened antibacterial activity against both Gram positive and Gram negative bacterial strains, pronounced sheet resistance, strong mechanical performance and thermal stability attributes and to use as potent antibacterial, thermostable and antistatic sustainable materials for different advanced applications including coatings, textiles, biomedical electronics and so on. Thus this presentation will provide an overview of bio-based hyperbranched poly(ester amide) nanocomposites as advanced multifaceted materials.

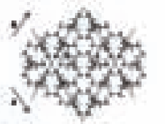
References:

[1] Pramanik, S.; Konwarh, R.;Sagar, K.;Konwar, B.K.;Karak, N. Prog. Org. Coat. **2013**, 76 (4), 689--697.
[2] Pramanik, S.;Hazarika, J.; Kumar, A.;Karak, N. *Ind. Eng. Chem. Res.***2013,** 52(16), 5700--5707.
[3] Pramanik, S.;Barua, N.;Buragohain, A.K.;Hazarika, J.; Kumar, A.;Karak, N. J. Phys. Chem. C **2013**, 117 (47), 25097--25107.
[4] Pramanik, S.;Konwarh, R.;Barua, N.;Buragohain, A.K.;Karak, N. *Biomaterials Science***2014,** 2 (2), 192--202.

Microscopically-Viewed Structural Formation Mechanisms of the Various Crystalline forms of Ply(lactic Acid) and its Stereocomplex

Kohji Tashiro
Department of Future Industry-oriented Basic Science and Materials,
Toyota Technological Institute, Tempaku, Nagoya 468-8511, Japan
ktashiro@toyota-ti.ac.jp

Poly(lactic acid) (-[CH(CH_3)COO]$_n$-, PLA) is one of the most representative biodegradable polymers. PLA exhibits a variety of crystal modificati□ons, □(□, and □ forms) and a stereocomplex between optical enantiomers PLLA and PDLA. The crystal structures of these forms should be a basic information necessary for the structure-property relation of PLA. In these several decades, the structures of these crystalline forms had been proposed on the basis of X-ray and/or electron diffraction data analyses. But, most of them were semi-quantitative and not yet established enough satisfactorily, making the discussion on the formation mechanism of these crystalline forms ambiguous. We reinvestigated these crystal structures by performing the quantitative analysis of X-ray and neutron diffraction data measured using the modernist equipments including the high-energy synchrotron radiation system. The thus-established crystal structures have allowed us to describe the microscopically-viewed structural formation processes of these crystalline forms or the phase transition and crystallization phenomena in a concrete manner. (i) The crystall□ne form consists of relatively large domains in which the (10/3) helixes of regular conformation are packed in a triclinic (pseudo-orthorhombic) unit cell. These domains are disordered in relative height [1]. (ii) In the crystalli□e form (or □form), these domains of more highly disordered structure are packed together. By heating above 120°C the □ form transforms to the □ form, in which the small domains of the □form gather together to form more regular and larger domains [2-4]. (iii) The stereocomplex (SC) between PLLA and PDLA is formed in a relatively wide range of L/D ratio of 7/3 – 3/7. This experimental fact is not consistent with the crystal structure proposed so far ([5, 6], Figure 1). We proposed a new model in which the PDLA and PLLA chains are coexistent in the crystal lattice in a statistically disordered manner (Figure 2 (b) [7]). This model can interpret the various phenomena of SC reasonably.



[illegible]

[illegible]

References

[1] K. Wasanasuk, K. Tashiro, *Macromolecules,* 45, 7019 (2012).
[2] *Macromolecules*, 44, 9650 (2011).
[3] *Polymer,* 52, 6097 (2011).
[4] *Macromolecules*, 44, 6441 (2011).
[5] T.Okihara *et al.*, *J. Macromol Sci.,* **30**,119 (1991).
[6] L.Cartier *et al.*, *Macromolecules*, **30**, 6313 (1997).
[7] K. Tashiro et al., *Polym. Prepr. Jpn.,* 63, 3Z10 (2014).

Synthetic Polymer Therapeutics: Designer Polymer Scaffolds for Modulating Blood Coagulation

Jayachandran N. Kizhakkedathu
Centre for Blood Research, Department of Pathology and Laboratory Medicine,
Department of Chemistry, The University of British Columbia, Vancouver, BC, Canada
Email: jay@pathology.ubc.ca

Heparin-based anticoagulant drugs (blood thinners) have been widely used for the prevention of blood clotting during surgical procedures and for the treatment of thromboembolic diseases. However, bleeding risks associated with these anticoagulants demand continuous monitoring and neutralization with suitable antidotes: the use of approved antidotes like protamine to neutralize heparin is limited. Also there are no approved antidotes available for low molecular weight heparins and fondaparinux; the two most widely used classes of heparins.

Polyphosphate (polyP) is a naturally occurring highly anionic linear inorganic macromolecule released upon platelet activation and has shown to contribute to thrombosis. Thus polyP is good target for developing novel antithrombotics which are not targeting the enzymes unlike current anticoagulants.

In this presentation, I will discuss the design, synthesis and evaluation of dendritic polymer based universal heparin reversal agents (Shenoi *et alScience Translational Medicine*2014) and Polyphosphate inhibitors (Travers *et alBlood*2014). We will discuss the design of new heparin binding groups (HBGs), the presentation of HBGs of polymer scaffold and the selection of optimized antidote based on isothermal titration calorimetry. These studies complemented with a battery of blood compatibility analyses and *in vivo* efficacy, and toxicity studies which demonstrate importance of polymer design, multivalent presentation of heparin binding groups towards the development of first synthetic universal heparin antidotes and non-toxic polyphosphate inhibitors. This polymeric drug will be of potential use in major surgical proceduresand in treating bleeding complications. A subclass of these molecules will have potential in the development of an antithrombotic agent.

Stimuli Responsive Polymeric Micelle for Drug Delivery

Sudipta Panja[1] and Santanu Chattopadhyay[1]*
[1]Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India
*santauchat71@yahoo.com

In the present decades controlled delivery of drug through nanocarriers to the pathological site gained much attention. This present effort introduces the preparation of two different kinds of biodegradable polymeric micelles (PMs). The PMs are prepared by self-assembling the four armed pentaerythretol polycaprolactone (PE-PCL) grafted magnetic nanoparticle (MNP) and folic acid conjugated pentaerythretol-polycaprolactone-block-polyethylenecarbonate (PE-PCL-b-PEC-FA), separately. The four armed polymer was synthesized by ROP of caprolactone and grafted onto the surface of aminosilane modified MNPs. The block copolymer PE-PCL-b-PEC was synthesized by ROP of ethylene carbonate using four armed PE-PCL as a macro initiator. The size and morphology of these nearly spherical PMs are characterized by DLS and HRTEM analysis. The PMs prepared form PE-PCL@MNP can be potentially used for magnetically targeted drug delivery. The PMs prepared from PE-PCL-b-PEC-FA gives rise to cancer cell specific uptake. The cell viability of both kinds of PMs is checked by MTT assay. The prepared PMs displays remarkably high biocompatibility against both the cancer and normal cell line. The cellular uptake study of these PM exhibits a cancer cell specific cellular uptake. The stimuli responsive, *in-vitro* release of DOX from loaded PMs gives rise to a cancer cell environmental specific release of DOX molecule.

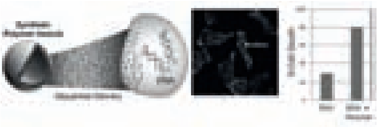
Reference

1. Panja S.; Saha, B; Ghosh, S. K. and Chattopadhyay, S. Langmuir **2013**, 29, 12530–12540
2. Panja, S. Nayak, S. Ghosh, S. K. Selvakumara, M. and Chattopadhyay. S. RSC Adv., **2014**, 4, 51766–51775

Synthetic Polymer Vesicles as Dual Drug Delivery Platforms

Manickam Jayakannan
Department of Chemistry, Indian Institute of Science Education and Research (IISER)
Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India
E-mail: jayakannan@iiserpune.ac.in

Design and development of polymer based controlled drug delivery systems has been emerging as an important area of research to target specific organ or host location. Among the various challenges, delivering multiple anticancer drugs based on single polymer nano-carrier is particularly emerging as challenging task to enhance the tumor resistance to the individual drug molecules and their therapeutic efficacies against cancer cells. Polymer vesicles (or polymersomes) are important classes of nano-carriers for delivering multiple drug loads such as hydrophilic and hydrophobic drugs. Very recently, we have initiated research in this area to develop synthetic polymer vesicles that are stable for encapsulation and preservation of drugs and also cleavable under enzyme and pH stimuli.[1,2] New polysaccharide dextran based nano-vesicular scaffolds and functional poly(caprolactone) vesicles were developed for the above purpose. These polymer vesicles were capable of loading and delivering wide range of anticancer drugs like camptothecin (CPT), doxorubicin (DOX), cisplatin as well as anti-inflammatory drugs like Ibuprofen (IBU) and so on. CPT and DOX loaded polysaccharide vesicles were found to be two to three folds more effective in killing cancer cells compared to drugs alone under physiological conditions similar to that of intravenous delivery.[3] The pH responsive poly(caprolactone) vesicles were stable in the strong acidic conditions (pH < 2.0, stomach) and ruptured to release the loaded cargoes under neutral or basic pH ($7.0 \leq$ pH, similar to that of small intestine).[4] Further efforts were also taken to develop shape transformable thermo-responsive scaffolds[5] and cisplatin drug nano-conjugates[6] for anticancer drug delivery. The presentation will be focused on the design principle, drug loading and delving efficiency and cellular up take mechanism of the above tailor-made vesicular-scaffolds in detail.



References:

(1) Pramod, P. S.; Katamura, C.; Chapaker, S.; Balasubramaniam, N.; Jayakannan, M. *Biomacromolecules*, **2012**, *13, 3627-3640.*

(2) Uma Sridhar; Pramod, P. S.; Jayakannan, M. *RSC Advances*, **2013**, *3*, 21237 – 21241.

(3) Pramod, P. S.; Shah, R.; Sonali, C.; Balasubramanian, N.; Jayakannan, M. *Nanoscale*, **2014**, *6*, 11841- 11855.

(4) Surnar. B.; Jayakannan, M. *Biomacromolecules*, **2013**, *14,* 4377-4387.

(5) Smita, K.; Jayakannan, M. *J. Mater. Chem. B.* **2014**, *2*, 4142 – 4152.

(6) Surnar, B.; Pramod, P. S.; Jayakannan, M. *Z. Anorg. Allg. Chem*., *(ZAAC) (Dedicated issue to Prof. CNR Rao's 80th Birthday)* **2014**, *640* (6), 1119-1126.

Biomimetic Elastomers and Hydrogels for Biomedical Applications

J. Whittaker[1], F. Ahmed[1], N. K. Dutta,[1] C. M. Elvin[2],
A. J. Hill[3], N. Roy Choudhury[1]*
[1]Ian Wark Research Institute, ARC Special Research Centre, Mawson Lakes Campus,
University of South Australia, Mawson Lakes, SA 5095, Australia
[2] CSIRO Livestock Industries, Queensland Bioscience Precinct,
St Lucia 4067, Queensland, Australia
[3] CSIRO Materials Science and Engineering, Clayton, Victoria, Australia

Recently significant research has been focused on mimicking biology with the aim to reproduce superior functional materials. Design of responsive nanostructures, whose characteristics can be modulated on demand, is an important challenge in nanoscience. In this presentation, we discuss the elastic gels, hydrogelsand their interfaces derived from biomimetic protein based polymers. Of particular interest to us are the protein-based elastomers, which are biocompatible and vastly superior to synthetic elastomers. Such elastomeric hydrogels have gained increased research interest in biomedical applications for their remarkable self-assembly behaviour, tunable 3D porous structure, high resilience (elasticity), superior fatigue lifetime (durability), high water uptake, excellent biocompatibility and biological activity. Amongst them, intrinsically disordered proteins, such as elastin, resilin, and flagelliform spider silk have gained much interest in recent years due to their remarkable mechanical properties, particularly their outstanding elasticity and responsiveness. These proteins/polypeptides can be derived naturally (animal or insect sources) or by recombinant (bacterial expression) routes and can be crosslinked via physical or chemical approaches to obtain elastomeric hydrogels. The emergence of genetic engineering of synthetic polypeptides has also recently enabled to synthesize protein-based polymers artificially. These biomimetic elastomers have been of significant interest to understand the molecular basis of their elasticity. They could be used as 3D gels, nanoparticles, electrospunfibres, and injectable gels. The biological properties of these biomaterials can be tuned by proteins engineering or by fusion with other protein and bioactive domains such as cell binding domains to control cell response for wide range of tissue engineering applications e.g. muscles, cardiovascular tissues, and cartilage.Our recent studies have demonstrated that control over biomolecule–surface interactions at interfaces play important role in tissue engineering, In this talk, we discuss elastomeric gels/hydrogels that could be used to control protein adsorption/desorption and cell attachment/detachment for the development of next-generation smart bio-interfaces.

Stimuli-Responsive Intrinsically Disordered Protein Polymers: a new class of biomimetic smart building blocks for materials science and biology.

Rajkamal Balu[1], N. Roy Choudhury[1], C. Elvin[2], A. Hill[3] Naba K. Dutta[1*]
[1]Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095,Australia,[2]CSIRO Manufacturing, Clayton, Victoria 3168, Australia,[3]CSIRO Agriculture, St Lucia, Queensland 4067, Australia.
*naba.dutta@unisa.edu.au

Nature, through evolution over millions of years has perfected native materials with amazing characteristics and awe-inspiring functionalities that exceed the performance of man-made synthetic materials; and bio-mimicry has the potential to yield unprecedented advances.[1]In this presentationI will review the current status, and address thechallenges, opportunities and our recent research in the development of advanced materials based on resilin-mimeticprotein polymers (RMPs).The native resilins are unique extracellular matrix proteins that exhibit outstanding rubber-like elasticity, unparalleled resilience and long fatigue life; and purported to play critical role in the jumping mechanism of fleas, the flight system in the wings of dragonflies and locomotion in many other arthropods.[1]We have reported the presence of unusual multi-stimuli responsiveness of RMPs,[2,3]and tuned their responsiveness to create patterned surfaces[4] and responsive interfaces[5]. We have examined the molecular chain mobility of RMP-based hydrogels that display outstanding resilience (>94%) and creep behaviour.[6] The directed self-assembling of RMPs has been employed as a molecular template to synthesize optically coupled hybrid architectures of gold nanoparticles (1-5 nm)[7], ultra small (2-3nm) platinum(Pt)/Pt-alloy particles of outstanding electrochemical activity[8,9] and noble-metal quantum dots.[10]We will demonstrate thatthe unique chemical composition, molecular flexibility, multi-stimuli responsiveness, conformational dynamics and other physical attributes enable RMPs to be an intelligent biomaterial; and make them versatile building blocks for both industrial and biomedical applications.MoreoverRLPs, being anintrinsically disordered protein (IDP), displaying remarkable functionalities apparently challenges the traditional notion that protein function depends on a unique three-dimensional structure. Once the mechanismand structural origin are appropriately understood it will extendthe opportunity for designing a wide range of smart materialsusing recombinant, combinatorial biosynthesis and even asynthetic methodology.

References:

[1] R. Balu, J. Whittaker, N. K. Dutta, et al. J. Mater. Chem. B, **2014**, 2(36), 5936-5947.
[2] R. Balu, N. K. Dutta, N.R Choudhury, et al. Acta Biomaterialia **2014**, 10 (11), 4768-4777.
[3] N. K. Dutta, M. Y. Truong, S. Mayavan et al. Angew. Chem. Int. Ed.**2011**, 50, 4428-31.
[4] N. K. Dutta, N. R. Choudhury, M. Y. Truong et al. Biomaterials**2009**, 30,4868-4876.
[5] M. Y. Truong , N. K. Dutta , N. R. Choudhury , et al. Biomaterials**2010**, 31,4434-4446.
[6] M. Y. Truong , N. K. Dutta , N. Roy Choudhury, et al. Biomaterials **2011**, 32, 8462-8473.
[7] N. K. Dutta, N. R. Choudhury, S. Mayavan, et al. Biomaterials 2011, 32, 2786-2796.
[8] N.K. Dutta, R. Balu, N. Roy Choudhury, et al. NSTI-Nanotech **2012**, 633-636.
[9] N. K. Dutta et al. Australian Provisional Patent Specification No 2012904970, WO2014/071463A1.
[10] N. K. Dutta et al. Australian Provisional Patent Specification No 2013903210.

Dextrin based chemically cross linked hydrogels: Application in controlled drug delivery

Sagar Pal*
Polymer Chemistry Laboratory, Department of Applied Chemistry,
Indian School of Mines, Dhanbad – 826004, India
Email: pal.s.ac@ismdhanbad.ac.in

Various monomers such as acrylic acid, *N*-isopropyl acrylamide, hydroxyethyl methacrylate have been chemically cross linked on the dextrin backbone via radical polymerization in presence of *N, N'*-methylene bis acrylamide cross linker and potassium persulphate initiator. For each series, various hydrogels have been synthesized and optimized on the basis of higher cross link density and lower % equilibrium swelling ratio. The hydrogels have been characterized in details using various materials characterization techniques. Dextrin/*poly* (acrylic acid) based hydrogel shows excellent behavior as colon targeted drug carrier while dextrin/*poly (*HEMA) hydrogel exhibits great potential as controlled release matrix for ciprofloxacin. Besides, *in-vitro* and *in-vivo* release studies suggest that dextrin/*p*NIPAm hydrogel is a suitable candidate as dual drugs (ciprofloxacin and ornidazole) carrier.

Surface Structurein biomaterials: Studies of protein adsorption and hydration

N. Sanjeeva Murthy
New Jersey Center for Biomaterials, Rutgers University,
The StateUniversity of New Jersey, Piscataway, NJ, USA.
murthy@biology.rutgers.edu

Surface structure plays an important role in facilitating the integration of the implanted biomaterials into the surrounding tissue. Here we focus on the adsorption of proteins on polymer surfaces and how this influences the cellular response [1,2]. The polymers used were based on polylactide, a widely used commercial biomaterial, and poly(desaminotyrosyl-tyrosine carbonate), PDTEC, a tyrosine derived degradable polymer. Hydration leads to phase separation in many polymers used as biomaterials. X-ray reflectivity (XRR) and grazing incidence wide-angle scattering (GIWAXS) were used to study the structure of polymer films, the phase behavior, and the adsorption of proteins onto polymer surfaces in the aqueous media. Structural changes in films that are spread at the vapor/water interface, and the effect of phase separation in poly(ethylene glycol) - containing polymers (PEG-copolymers) on protein adsorption will be discussed. XRR data were used to derive the electron density profiles [3]. These profiles show that a PEG-containing chain orients like an amphiphile at the interface. Fibrinogen (Fg), a blood plasma protein, is adsorbed onto the water-air interface with the long-axis parallel to the interface. The behavior of Fg adsorption in the presence of PEG will be discussed. The results show that PEG in the polymer inhibits the migration of Fg to the DTE-enriched interface. We find that the presence of PEG in the matrix by itself does not make a material protein resistant. Protein-repellency, and by extension cell-non adhesivity, and nonfouling induced by PEG are due to the formation of a continuous hydrophilic layer by the phase separated PEG segments, i.e., PEG needs to bloom to the aqueous interface.

References:

[1] Rabe, M., D. Verdes, and S. Seeger. Advances in colloid and interface science, 2011. 162:87-106.

[2] Felgueiras, H.P., S.D. Sommerfeld, N.S. Murthy, J. Kohn, and V. Migonney. Langmuir, 2014. 30:9477-9483.

[3] Wang, W., N.S. Murthy, I. Kuzmenko, N.A. Anderson, and D. Vaknin. Langmuir, 2013. 29:11420-11430.

Functional Polymers and Block Copolymers. Polymers for Studying Material-Bio Interactions

Jereme Doss[1], Omotunde Olubi[1], Janet Cowins[1], LaDena Bolton[1],
Biswajit Sannigrahi[1], Michael Williams[1], Deepti Gadi[2],
Barbara Baird[2], Ishrat Khan[1*]
[1]Center for Functional Nanoscale Materials and Department of Chemistry, Clark Atlanta University, Atlanta, Georgia 30314, USA
[2]Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY 14853, USA
*ikhan@cau.edu

In the study of nano-bio interactions, polymeric materials functionalized with appropriate ligands have been made, and these have proved to be effective in targeted drug-delivery and bio-sensing applications. Functionalized polymers, α,ω-bi [2,4-dinitrophenyl] [poly(ethylene oxide)-b-poly (2-methoxystyrene)-b-poly (ethylene oxide)] (P2MS-57) of 15 kDa molecular weight was prepared anionically and was sulfonated to render aqueous buffer solubility. Biodegradable polylactide polymers, α,ω-bi [2,4-dinitrophenyl (DNP)] [poly (lactide) -b-poly (ethylene glycol)-b-poly (lactide)] (polylactide 3) of 10.5 kDa molecular weight was synthesized. Incorporation of PEO enhanced their solubility in aqueous buffer. We demonstrate here that they bind specifically to anti-DNP IgE in solution and to IgE-receptor complexes on RBL-2H3 cells. We determined the K_d for polylactide 3 binding to IgE-FcεRI on cells to be 2.8 ± 1.1 nM and to IgE in solution was found to be 4.2 ± 1.8 nM (n = 4). When compared to the dissociation constants for P2MS-57 polymer (54.3nM with IgE on cells and 178.3 nM with IgE in solution), we observe more than tenfold decrease in the K_d of polylactide 3 with IgE in solution as well as with IgE-FcεRI on cells, indicating that polylactide 3 binds much more tightly to IgE. Although these DNP-functionalized ligands do not stimulate the granule exocytosis response, they have the potential to inhibit the robust response stimulated by other multivalent DNP ligands. Additionally, a solution of α,ω-bi[DNP][poly (ethyleneoxide)-b-poly (2-methoxystyrene)-b-poly (ethylene oxide)], polystyrene and single-wall carbon nanotubes (SWCNT) was electrospun onto a silicon substrate at 10kV to prepare fibers with average diameters about 300 nm. Chlorobenzene and dimethylformamide was used as solvents in the electrospinning process. The average diameter of the fibers was about 300nm. Binding specificity of the nanofibers containing 1% single-walled Carbon Nanotubes with anti-DNP IgE (Immunoglobulin E) was studied using fluorescently tagged IgE. It was observed that the DNP groups decorating the nanofibers were capable of specifically binding with anti-DNP IgE. These DNP groups were tethered to the nanofibers via the oligo(oxyethylene) spacers. Electronic activity of the nanofibers was studied by Kelvin sensing. The current-voltage (I-V) plots before stimulation of the fibers with IgE differed from the I-V plots after binding with IgE. The results of the studies strongly indicate the possibility of developing functional nanofibers as the active component in biosensors where DNP can be substituted with some select chemical groups and testing their binding with antibodies having corresponding specificity.

Nanoparticles induced phenomena in polymers for biological applications

Pralay Maiti
School of Materials Science and Technology, Indian Institute of Technology
(Banaras Hindu University), Varanasi 221 005
pmaiti.mst@itbhu.ac.in

Biodegradable nanohybrids offer the possibility of combining biodegradability with the physical and mechanical properties of polymers typically associated with engineering plastics. The challenge remains to design biodegradable alternatives to conventional plastics that combine the mechanical strength and physical properties of the latter, yet they are susceptible to microbial and/or environmental degradation without adverse effect on the environment. Here, we would like to report our efforts on developing nanohybrids of biodegradable polyester with organically modified layered silicates, layered double hydroxide and carbon fillers. Also, the effect of polymer intercalation as well as interactions between polymer and nanoparticles on nanostructure and other properties will be presented. Further, the controlled biodegradation in presence of nanoparticles will be discussed.

Novel bone cement based nanohybrid has been developed which is capable of healing the fractured bone in one-third time (in 30 days) than that of natural healing process. Nanohybrids of bone cement, being used as grouting material in joint replacement surgeries, with organically modified layered silicates/LDH of varying chemical compositions have been prepared by simple mixing. It exhibits considerably low temperature, reduced by 12°C, arising from exothermic polymerization, and thereby, circumvents the reported cell necrosis during implantation using pure bone cement. The biocompatibility and bioactivity have been confirmed using cell adhesion, cell viability and fluorescence image to understand the cell health on different materials and have been compared for their suitability. Osteoconductivity and bone bonding ability have been monitored in vivo on rabbits through radiographic imaging and histopathology of growing bone and muscle near the surgery site. The observed dissimilarity of properties in two different nanoclays as fillers have been visualized through interaction as measured by using spectroscopic techniques and elemental influence on bioactivity exhibiting higher efficiency for greater iron containing nanoclay.

Synthesis of Well-defined Poly(*N*-vinylpyrrolidone)-based Amphiphilic Block Coplymers and Study of Their Aggregation as Nanocarrier for Drug Delivery

Biswajit Ray
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005
E-mail: bray@bhu.ac.in

Poly(*N*-vinylpyrrolidone)(PNVP)-based well-defined and biocompatible amphiphilic block copolymers like poly(ε-caprolactone)-*b*-PNVP [1-2], poly(D,L-Lactide)-*b*-PNVP [3], poly(lactic-co-glycolic acid)-*b*-PNVP, PNVP-*b*-polyketal-*b*-PNVP etc. have been synthesized using RAFT, ROP, step-growth polymerization and click chemistry methods and characterized by ^{1}H NMR, GPC, UV-vis, TGA and DSC studies. Self-aggregation property of such block copolymers has been studied by Fluorescence, DLS and TEM methods. Micelle of these block copolymers has been used as the efficient nanocarrier for the delivery of the FDA approved anticancer drugs like DOX, Methotraxate etc. Drug loading was confirmed from UV-vis, DLS and TEM studies. In-vitro release study showed sustained drug release profile. Drug-loaded diblock copolymer has been found to be significantly effective in controlling the tumor cell growth by retarding the tumor cell proliferation compared to free drug.

References:

[1] Mishra, A. K.; Patel, V. K.; Vishwakarma, N. K.; Biswas, C. S.; Raula, M.; Mishra, A.; Mandal, T. K., Ray, B. Macromolecules **2011**, 44, 2465 – 2473.
[2] Hira, S. K.; Mishra, A. K.; Ray, B.; Manna, P. P. Plos One **2014**, 9(4), e94309.
[3] Ramesh, K.; Mishra, A. K.; Patel, V. K.; Vishwakarma, N. K.; Biswas, C. S.; Paira, T. K.; Mandal, T. K., Maiti, P.; Misra, N.; Ray, B. Polymer **2012**, 53, 5743 – 5753.

Amphiphilic Biosynthetic Hydrogels for Control and Management Reactive Oxygen Species

M. Jayabalan
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Polymer Science Division, BMT Wing, Thiruvananthapuram – 695 012, Kerala State, India
E-Mail. mjayabalan52@gmail.com

The active role of various free radicals in the origin and propagation of several diseases and aging were already revealed before five decades. In biological systems oxygen free radicals or reactive oxygen species (ROS) and reactive nitrogen species (RNS) are significant since these can be formed as a result of normal cellular metabolism. Acute myocardial infarction (AMI) is one of the most important health hazards throughout the world. AMI has devastating consequences in the early phase, such as cardiac rupture, and in the chronic phase, such as chronic heart failure, for which the risk is mainly determined by infarct size. Even though several treatment methods are available for the management of MI, the management of ROS at the infarct site is still a challenge. Materials and methodologies to transform a passive biomaterial hydrogel scaffold into active barrier systems that may promote the survival of encapsulated cell from ROS and proactively protect encapsulated cells from immune-mediated damage are highly essential. It is therefore urgent need to explore substances capable of encountering the ROS and resist the damage caused by ROS. Of several types of biomaterials used for cardiac tissue engineering, hydrogels from both natural and synthetic, origin gained much attention due to its inherent similarity with the native extra cellular matrix (ECM). Moreover the hydrogel biomaterials were proved to offer better cell attachment and response, biocompatibility, unique solute transport properties and so on which are very crucial for the construction of heart tissue in vitro. Biosynthetic hydrogels formed from the combination of both natural and synthetic hydrogels can find advantages from both the partners. Hydrogels with inherent ROS scavenging effects for tissue engineering applications especially to that of heart are sacarce. Biosynthetic hydrogels comprising poly (propylene fumarate)-co-alginate/polyethylene glycol diacrylate were investigated for scavenging of ROS. The effect ROS on the cell growth was studied in H9c2 cells using H_2O_2 as model ROS molecule. The present hydrogel resist the penetration of ROS in the cell which was evident from the live/dead assay, increased intra cellular GSH levels when compared with the H_2O_2 treated positive and curcumin treated negative control cells. The Comet assay reveals genomic integrity of the cells exposed to the present hydrogel. The hydrogel is a promising material for the control and management of ROS in myocardial infarction and ischemia.

Solid-state foam processing and morphology development of PLA based blends & biocomposites

Anup K. Ghosh[*]
[*]Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, New delhi-110016, India
*E-mail: anupkghosh@gmail.com

Producing bio-foams using a supercritical CO_2 is a novel foaming technique finding many applications by competing with the convectional foams. Successful replacement of organic solvent/chemical blowing agentswith sc-CO_2 or sub-critical CO_2induces zero-toxicity in cell morphology which is an added advantage for application ofbiofoam in food packaging and biomedical fields.Foam morphology is an important aspect, which decides the final application of thebiofoam.Plasticization effect of sc-CO_2 increases the foam processability even in the solid-state i.e. viscoelastic state is the scope for developing the different foam morphologies. High pressure solid-state foaming processis an art of fabricating the different foam morphologiesfor variousapplications. However, the control over the foam morphology differs with various material and process parameters. The current study focused on the various material designs like, blending (PLA/PCL), plasticization (PLA/PEG), inclusion of particulate filler (PLA/Lignin) and process approach like ultra-sonication in developing the PLA based foam morphologies. PLA foamability is improved with homogenous inclusions of immiscible domains (PCL), particulate fillers (Lignin) and by internal plasticization (PLA/PEG). The nucleation sites created by these immiscible materials increases the cell density significantly as compared to neat PLA foams.Ultra-sonication assisted batch foaming of plasticized PLA is carried out in hot water bath at 50 °C and open cell morphology is developed. Heterogeneous cell nucleation induced by the sonic energy increases the cell wall coalescences by the cavitation process leads to interconnectivity in the foam structure. Effect of foaming temperature on the mechanism of foam morphology stabilization is discussed.

Keywords: Foamability, cell density, high pressure foaming process, CO_2 induced crystallization, bio-composites.

Development of Polymer Nanocomposite Scaffolds for Tissue Engineering

Sabu Thomas
International and Inter University Centre for Nanoscience and Nanotechnology
Mahatma Gandhi University, Kottayam, Kerala
Email.sabuchathukulam@yahoo.co.uk

Biodegradable polymer scaffolds are useful materials to integrate the femoral part of the implant with the bone, and provide a matrix for cellular growth. Synthetic biodegradable polymers can provide temporary scaffold for cell adhesion and expansion both in vitro and in vivo and guide tissue regeneration with defined sizes and shapes. The fibrillar structure is important for cell attachment, proliferation and differentiated function in tissue engineering. The structure allows for growth and is convenient for transport of nutrients. The synthetic polymers such as Polycaprolactone (PCL), Poly l-lactic acid (PLLA), and their copolymers have attracted wide attention for their biodegradation in the human body and are used for tissue engineering. Several methods have been practiced to create highly porous scaffold including fiber bonding, solvent casting/ salt leaching, gas foaming, phase separation and electrospinning. Out of which electrospinning is the simple and cost effective technique for producing nanofibers from polymer solution. Introduction of organically modified clay in polymers leads to different types of structures which include intercalated or exfoliated morphology. The nano reinforcement increases the mechanical rigidity, mobility, stiffness and biodegradability in biodegradable polymers. Moreover it also increases the porosity of the polymer nanocomposite. Nanoparticle reinforced scaffolds are yet to achieve importance. In fact they have wide range of interest in tissue engineering. Literature reports regarding nanoparticle reinforced scaffolds are very scant. Hence the present investigation will be interesting and will find application in tissue engineering in the foreseeable future. In the present talk the state of the art on the synthesis, morphology, structure, properties and applications of dual porous nanocomposite scaffolds will be presented.

Detection of Dopamine by PPY/PTSA/ AgNP Modified Electrode and Development of Implantable Polymeric Device to Arrest it's Over activity

Suparna Saha and Priyabrata Sarkar
Biosensor Laboratory, Department of Polymer Science and Technology,University of Calcutta, 92 A.P.C. Road, Kolkata-700 009, India
E-mail address: sarkarpriya@gmail.com

In human body, neurotransmitter is present as an endogenous chemical that communicates information throughout brain and body. Dopamine (3, 4-dihydroxyphenyl ethylamine, DA) is one of the most important neurotransmitters regulating mood and behavior in the mammalian central nervous system. This work presents a new approach to detect dopamine using an electrochemical sensor based on a composite made out of chitosan-stabilized silver nanoparticles and p-toluene sulfonic acid (PTSA) doped ultrathin polypyrrole(PPY) film, which exploits the synergy between the conducting polymer matrix and silver nanoparticles. These are characterized by TEM, XRD, UV-vis , FTIR, EDAX and the properties of the modified electrode is investigated by electrochemical impedance spectroscopy (EIS). The linear range is from 1×10^{-9}M to 1.2×10^{-7}M in 0.05M phosphate buffer (pH 7.0) with a correlation coefficient of 0.98 and an estimated detection limit of 0.58 nM is obtained.

It is evident that over activity of dopamine is associated with a serious neurological disorder such as schizophrenia. Risperidone is a widely used antipsychotic drug for the treatment of schizophrenia, bipolar disorder. Thus it is also important to develop a suitable polymeric carrier for risperidone so that it can be used as implantable device to suppress the over activity of dopamine. We have synthesized a conductive hydrogel based on polyacrylamide and polypyrrole in the form of cylindrical devices to confer electro-actuable properties and also controlled release of the drug risperidone. The hydrogel was characterized by various microscopic and spectroscopic analyses, swelling kinetics, and also network parameters. In vitro drug release studies were carried out in 0.1 N HCl and phosphate buffer using dissolution apparatus. Cytotoxic results on HepG2 cell showed hydrogel as highly biocompatible and thus it could have a potential use in implantable drug delivery devices, where the dose could be adjusted by external signaling.

References:

[1] S. Saha, P. Sarkar, A.P.F Turner, Electroanalysis, **2014**, 26, 1
[2] M. Zhang, C. Liao, Y. Yao, Z. Liu, F. Gong, F. Yan, Adv.Funct. Mater. **2014**, 24, 978
[3] L.J Elias, D.M. Saucier, Neuropsychology: Clinical and Experimental Foundations. Boston: Pearson, **2005**
[4] D.S.G Hu, M.T.S. Lin, Polymer, **1994**, 35, 4416.

Crosslinking as a Strategy in the Design of Multi-Functional Polymer Matrices for Soft Tissue Engineering Applications

Bikramjit Basu
Materials Research Centre,
Indian Institute of Science, Bangalore, India
**bikram@mrc.iisc.ernet.in*

For soft tissue engineering, it is essential to design matrices with varying mechanical properties to effectively mimic natural tissue without compromising on the essential aspect of biocompatibility.

By adapting crosslinking to melt condensation polymerization technique, we were able to generate a family of biodegradable, cytocompatible polyesters using mannitol and citric acid as crosslinking agents and ricinoleic acid as the anti-inflammatory and analgesic agent. Tunable physical properties like elastic modulus (22-327 MPa), surface wettability (contact angle 42° - 71°) and degradation properties (surface and bulk erosion) were obtained.The polymer was cytocompatible with C2C12 murine myoblast cells.

We have followed a unique sequence of synthesis of a pre-polymer, which is soluble in solvents and then can be crosslinked (cured) to different degrees. Hence, in spite of forming thermosets, the fabrication requirements are not so rigid. The salt leaching technique was used to produce porous scaffolds for tissue engineering (porosity ~90 % from micro-computed tomography)

In the context of biodegradability, the commonly used biopolymers e.g. poly lactic-co-glycolic acid (PLGA) release chemicals, which can potentially cause inflammation. In another specific example, we discuss the use of crosslinking to incorporate salicylic acid in the polymeric backbone. The *in situ* delivery of non-steroidal anti-inflammatory drugs (NSAIDs) like salicylic acid is gaining importance in the light of adjuvant cancer therapy and biocompatible coatings for slow release of salicylic acid. To the best of our knowledge, this is the first study reporting the sustained release of salicylic acid using a polyester matrix as a pro-drug over a period of 17 months. The *in vitro* cytocompatibility was assessed by MTT assay and flow cytometry while *in vivo* subcutaneous implantation showed a marked reduction in the foreign body response in mouse animal model.

To summarize, the talk will elucidate the proof of concept of using crosslinking as an effective strategy for making multifunctional polymer matrices with mechanical properties/ tunable release rates.

References:

[1] Chandorkar Y, Bhagat RK, Madras G, Basu B. Cross-Linked, Biodegradable, Biomacromol. **2014**,15, 863-75.

Polylactic acid Based Nanocomposites for Food Packaging

Vimal Katiyar
Department of Chemical Engineering,
Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India

Poly (lactic acid) (PLA) has generated great interest as one of the potentially most useful thermoplastic polymers being developed for a wide range of commodity and specialty applications due to its mechanical properties and unique biodegradable characteristics. Poly (L-Lactic Acid) (PLLA) belongs to the family of aliphatic polyesters. It is a thermoplastic, high strength biodegradable polymer, and can be made from annually renewable sources such as corn-starch, sugarcane, etc. Due to increased attention to long product shelf-life for meats and other foodstuffs and to make it environfriendly, there has been an increasing interest towards the use of bioplastics in food packaging. Therefore, bionanocomposites based cast films using bio filler imbedded master batch approach have been successfully implemented in the current strategy. Dispersion of nano/biofillers such as cationic clays (Cloisite®), anionic layer double hydroxide, cellulose nanocrystals, sucrose esters and chitosan microspheres have been made in order to reduce the oxygen permeability (OP) and to improve the mechanical properties. As per the understanding, we have to develop a composite that should be capable to reduce OP by order of magnitude to substitute PET with PLA. We have compared OP values with above filler combination and optimize the OP with filler type, content and the way it disperse in the PLA matrix. We have developed a biocomposite strategy through which we are now capable to reduce the OP values to meet out the above requirements. Subsequently, the migration test has been performed in order to understand the behavior of nanofillers when it comes in contact with food simulent. However, we have found positive trends. In this talk, I would highlight the successful synthesis and processing strategies of bionanocomposites to reduce the OTR and WVTR of PLA with improvement in HDT through incorporation of inorganic as well as bio fillers. However, it will be achieved without compromising the transparencies and mechanical properties of the developed bionanocomposites films. In general, author is going to present comprehensive details of poly (lactic acid) in terms of its developments and properties improvements so far.

Polyaspartamides for Selective and Active Killing of Mycobacterium and Breast Cancer Cells

Aasheesh Srivastava[1]*, Aashish Sharma[1], Munazza Tamkeen Fatima[1],
Abhishek Chanchal[1], Prabhu Srinivas Yavvari[1], Amol A. Pohane[2],
Vikas Jain[2], Sandhya Bansal[3] and Avinash Bajaj[3]
[1]Laboratory of Molecular and Macromolecular Materials,
Department of Chemistry, IISER Bhopal, Bhopal – 462 066.
[2]Microbiology and Molecular Biology Laboratory Department of Biological Sciences,
IISER Bhopal, Bhopal – 462 066
[3]Regional Center for Biotechnology, Gurgaon – 122 016
asri@iiserb.ac.in

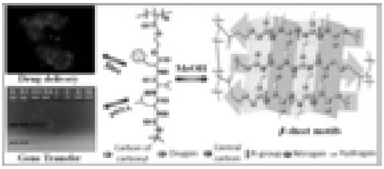
Polyaspartamides were first reported in 1950s,[1] and were employed as plasma expander in early 1970s.[2] Polyaspartamides continue to attract the attention of researchers due to their excellent biocompatibility and biodegradability. These polymers are readily synthesized in gram quantities, and structural variation of these polymers is straight-forward. We realized that polyaspartamides can easily cross the cell membranes and translocate entrapped peptides intracellularly, while maintaining cytocompatibility.[3] We further explored the antibacterial activity of polyaspartamides synthesized in our laboratory and found that these polyaspartamides can selectively kill Mycobacterium smegmatis over E. coli or mammalian cells. The cause of this selectivity and the mode of action of the antibacterial polyaspartamides have been investigated in detail. Further, we have synthesized amphiphilic polyaspartamides to solubilize curcumin through physical entrapment. This results in suspensions in aqueous medium that are stable for months. By exploiting the ready intracellular translocation of polyaspartamides, we delivered curcumin into mammalian cells (cancerous as well as normal). Upon intracellular delivery, curcumin causes selective killing of breast cancer cells over (normal) human embryonic kidney cells. These developments will be discussed in the talk.

References:

[1] Vegotsky, A.; Harada, K.; Fox, S. W. J. Am. Chem. Soc. **1958**, 80, 3361–3366.
[2] Neri, P.; Antoni, G.; Benvenuti, F.; Cocola, F.; Gazzei, G. J. Med. Chem. **1973**, 16, 893–897.
[3] Sharma, A.; Kundu, S.; A Reddy, M.; Bajaj, A.; Srivastava, A. Macromol. Biosci. **2013**, 13, 927–937.

pH Responsive *β*-Sheet Peptide-Polymer Conjugates: A Totally New Synergism

Sonu Kumar and Priyadarsi De*
Department of Chemical Sciences, Indian Institute of Science Education and Research
Kolkata, Mohanpur - 741246, Nadia, West Bengal, India
*p_de@iiserkol.ac.in



Over the past two decades, there has been dramatic advances in the synthetic strategies for the development of multifunctional materials by taking inspiration from nature.[1] Incorporation of peptide residue in the synthetic polymer may create a new class of non-biological hybrid materials with bio-mimetic structure and property.[2-5] In this context, an effective strategy have been developed to synthesize well defined peptidic side-chain macromolecules taking a representative short peptide segment Leu-Val-Phe modified vinyl monomer corresponding to amyloid *β*-peptide $A\beta_{1\text{-}42}$, *via* reversible addition-fragmentation chain transfer (RAFT) polymerization technique.[6] Furthermore, monomethoxy poly(ethylene glycol) (mPEG) macro-chain transfer agent is employed for their RAFT polymerization to prepare peptide based amphiphilic nano-carriers as a promising reservoir for nile red or doxorubicin. These hybrid materials can easily generate primary amino groups in terminal of side-chains providing pH-responsiveness and cationic characteristics having complexation capabilities with DNA to form polyplex. Circular dichroism (CD) spectroscopy demonstrates the formation of *β*-sheet conformation from these peptidic polymers, which was stable against heat within experimental temperature range and solvent polarity. *In vitro* cytotoxicity studies indicates the biocompatible nature of these peptidic materials, and confocal laser scanning microscopy (CLSM) images revealed cellular uptake of their drug/dye loaded micelles, which potentially offers them as a suitable candidate with dual bioapplications for drug delivery as well as gene transfer.

References:
[1] Deming, T. J. Nature **1997**, 390, 386-389.
[2] Kumar, S.; Roy, S. G.; De, P. Polym. Chem. **2012**, 3, 1239-1248.
[3] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. J. Mater. Chem. B **2013**, 1, 946-957.
[4] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. Langmuir **2013**, 29, 15375-15385.
[5] Kumar, S.; De, P. Polymer **2014**, 55, 824-832.
[6] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. Polym. Chem. **2014**, DOI: 10.1039/C4PY00620H.

Switching the Enzymatic Activity: Improvement of Heat-resistance Based on Enzyme/Polymer Complex Formation

Sumon Ganguli[1*], Keitaro Yoshimoto[2], Shunsuke Tomita[3],
Hiroshi Sakuma[3], Tsuneyoshi Matsuoka[3], Kentaro Shiraki[4],
Yukio Nagasaki[5-8]

[1] Department of Applied & Environmental Chemistry, University of Chittagong, Chittagong, Bangladesh, [2]Gdepartment of Life Sciences, The University of Tokyo, Japan, [3]Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Japan. [4]Institute of Applied Physics, University of Tsukuba, Tsukuba, Japan, [5]Graduate School of Comprensive Human, University of Tsukuba, TsukubaJapan; [6]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, TsukubaJapan; [7]Center for Tsukuba Advanced Research Alliance (TARA), University of Tsukuba, Tsukuba, Japan; [8]Satellite Laboratory, International Center for Materials Nanoarchitechtonics (MANA), National Institute of Materials Science. (NIMS), Tsukuba, Japan

Regulation of enzymatic activity has attarcted broad interest in biomedical and biomaterial fields. However, enzymes are generally unstable under extreme conditions such as high temperature, high or low pHs, organic solvents etc and thus they are easily denatured or inactivated leading to the serious problem for biotechnology and pharmaceutical applications. In our study, we show a unique phenomenon for the regulation and preservation of enzymatic activity of lysozyme and ribonuclease A (RNase A) using a cationic smart copolymer, poly (*N,N*-diethylaminoethyl methacrylate)-*graft*-poly (ethylene glycol) (PEAMA-*g*-PEG), even after the severe heat treatment. PEAMA-*g*-PEG suppressed the enzymatic activity of lysozyme owing to capping of the active site of lysozyme, which involved an electrostatic interaction between the negatively charged active site of lysozyme and the positively charged amine moiety of PEAMA-*g*-PEG at neutral pH despite the fact that both are positively charged. The inhibited enzymatic activity was recovered upon the addition of poly(acrylic acid) to the lysozyme/PEAMA-*g*-PEG complex even after the heat treatment[1]. In addition, we found that PEAMA-*g*-PEG prevents heat inactivation of RNase A, which has a positively charged active site opposite to that of lysozyme. Interestingly, after treatment at 98 °C for 10 min, the enzymatic activity of RNase A complexed with PEAMA-*g*-PEG was maintained at up to 75% of the level of the native RNase A whereas PEG was not able to prevent the heat induced irreversible inactivation of RNase A. To note that the heat resistance of RNase A was increased upon the addition of only PEAMA-*g*-PEG . In our another study, we found that the enzymatic activity of RNase A were switched off/on by the external addition of PAAc and PEAMA-*g*-PEG. Moreover, recently the mechanism of interaction between enzyme and polymer was also investigated using other related polymer. Our findings suggested that the hydrophobic interaction coupled with electrostatic interaction may plays the key role for the enzyme/polymer complexation.

Circular dichroism (CD) spectral analysis revealed that heat-induced irreversible inactivation was largely suppressed when enzymes was heated with PEAMA-*g*-PEG. Therefore, we successfully regulated the enzymatic activity and consequently improving the heat resistance of enzymes by means of noncovalent interactions between enzyme and polymer.

Development of Caprolactone Polyol based Biodegradable Polyurethane and Polyurethane-ullerenes Nanocomposites Foams with Antistatic Properties

Senthil Andvan G. T[1*], Moumita Mukherjee[1], Layana Kannan K. V.[1],
B. N. Das[2] S. N. Jaisankar[1*] and A. B. Mandal[1*]
[1]Polymer Division, [2]Shoe Design and Development Centre, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020, India
Email: senthilagt@gmail.com, senthil.clri@res.in, snjsankar@clri.res.in,
abmandal@hotmail.com

Polyurethane (PU) foams are indispensable in the field of footwear in different forms such as sole, insole, memory foam etc. To reduce the adverse impact on environment and disposal cost of foam products based on non-renewable sources, the alternative biodegradable commercial polyester triol, caprolactone polyol (M. W. 2000) has been chosen as monomer. Biodegradable PU foams are formulated from the components, caprolactone polyol, hexamethylene diisocyanate, 1, 4- butane diol, dibutyltin dilaurate, tertiary amine (PMDETA), silicone surfactant/Tegostab B8993 and blowing agent (Tegoamine BDE) at ambient temperature. A series of PU foams were prepared by the variation of components in formulation[1] to improve their physical and morphological properties. Both hard and soft segments of PU foams form less density elastomeric foams with high cross linking network, which are showing the desired properties such as density, hardness, compression set, cushioning energy and cushioning factors to meet the requirement as footwear material.[2] PU foam sample, which can exhibit desired physical properties, potential control sample in insole application has been modified with antistatic properties.[3] Control PU foam formulation loaded with fullerenes (0.1, 0.4 and 1 wt. %) as an additive have formed PU nanocomposites foams. PU control and PU nanocomposites foams were characterized by ATR-IR, UV-*vis* DRS, Optical Microscope, SEM, DSC, TGA, durometer, two-probe method and surface resistivity meter to study structural, morphological, thermal, electrical resistance and antistatic properties.

References:

1. W. Panwiriyarat, V. Tanrattanakul, J. F. Pilard, P. Pasetto, and C. Khaokong. *J. Appl. Polym. Sci.*, 2013, *130*, 453.
2. J. H. Saunders and K. C. Frisch, “Polyurethane-Chemistry and Technology,” Part I, Chemistry, Interscience Publishers, New York, 1961
3. Y.Yang, and P. Westerhoff. *Nanomaterial*. Springer Netherlands, 2014, 1.

Biopharmaceutical evaluation of chemically modified locust bean gum oral controlled release drug delivery system

SantanuKaity and Animesh Ghosh*
Department of Pharmaceutical Sciences and Technology, Birla Institute of Technology,
Mesra, Ranchi – 835215, Jharkhand, India
*aghosh@bitmesra.ac.in

In present investigation locust bean gum (LBG) was selected for exploring its potentiality as a component of IPN microspheres with poly(vinyl alcohol). Highly water soluble, short half lived, buflomedil hydrochloride (BH) was chosen as model drug. The microspheres were prepared by emulsion crosslinking method using glutaraldehyde (GA) as a crosslinker. The microspheres showed poor entrapment and well controlled release property. Moreover, high amount of GA was required to crosslink the polymer combination. The aqueous blend of LBG and PVA showed phase separation on long standing. To overcome these problems, native LBG was replaced by carboxymethylated locust bean gum (CMLBG) to prepare BH entrapped IPN microspheres with PVA. The blend of CMLBG and PVA showed well miscibility and a homogeneous phase was obtained. However, The IPN particles showed less entrapment efficiency than that of LBG-PVA IPN microspheres with faster drug release. Therefore, the native LBG was modified to acrylamide grafted LBG (Am-g-LBG). The modified gum was used in combination with PVA to develop Am-g-LBG-PVA IPN microspheres. The developed microspheres showed better drug entrapment efficiency and well controlled release property than the previous formulations. Particles were moderately pH sensitive in nature. GA requirement for crosslinking the IPN microspheres were much less than the previous formulations. Since the IPN microspheres were composite material, their biocompatibility and real time in-vivo performance should investigate with better understanding. All three IPN microspheres were subjected for comparative stability, toxicity, biodegradability and single dose in vivo pharmacokinetic evaluation. All the three IPN microspheres were observed as stable, nontoxic and biodegradable in nature. From in vivo pharmacokinetic study, it was observed that, the Am-g-LBG-PVA IPN microspheres were having best controlled release property in biological condition. Thus, the modified biopolymer based IPN microspheres can be a better approach for “spatial placement” and “temporal delivery” of highly water soluble drugs.

References:

[1] Kaity, S.; Isaac, J.; Ghosh, A. Carbohyd. Polym.**2013**, 94, 456 – 467.
[2] Kaity, S.; Ghosh, A.Ind. Eng. Chem. Res.**2013**, 52, 10033-10045.
[3] Kaity, S.; Isaac, J.; Kumar, M. P.; Bose, A.; Wong, T. W.; Ghosh, A.Carbohyd. Polym.**2013**, 98, 1083-1094.
[4] Kaity, S.; Ghosh, A.Int. J. Biol. Macromol.**2015**, 72, 883 – 893.

Non-woven nanofibers for tissue regeneration

Rathna VN Gundloori*
Polymer Science and Engineering Division, National Chemical Laboratory, Pune
rv. gundloori@ncl.res.in

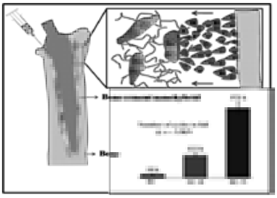
There is growing interest in non-woven nanofibers for biomedical applications because they mimic extracellular matrix and being nano size they enable interactions with cells at molecular level[1]. Electrospinning technique is widely used for developing the nanofibers as it is simple, easy to handle and viable for preparation. We used this technique for developing new nanofiber materials based on natural and synthetic polymers which are environment safe and immobilized bioactive molecules, characterized, and evaluated *in vitro* drug release, antibacterial activity and cytotoxicity. *In vivo* studies were done to find the potential of nanomaterial for wound healing.

1. Rathna et al Polymer Journal, 43, 654 (2011).
2. Rathna et al Materials science and engineering C 2014

Bone cement based nanohybrid as super biomaterial for faster bone healing: Effect of metal ions

Govinda Kapusetti[1], Nira Misra[2] and Pralay Maiti[3]
[1]Department of Medical Device, NIPER-Gandhinagari
[2]School of Biomedical Engineering, IIT (BHU), Varanasi
[3]School of Materials Science and Technology, IIT (BHU), Varanasi
*govindphysics@gmail.com

Novel bone cement formulation has been developed based on nanohybrid technology which is capable of healing the fractured bone in one-third time (in 30 days) than that of natural healing process. Nanohybrids of poly(methyl methacrylate) (PMMA) based bone cement, being used as grouting material in joint replacement surgeries, with organically modified layered silicates of varying chemical compositions have been prepared by manual mixing. It exhibits considerably low temperature, reduced by 12°C, arising from exothermic polymerization, and thereby, circumvents the reported cell necrosis during implantation using pure bone cement. The thermal stability and mechanical superiority have been verified through higher degradation temperature, better stiffness, superior toughness and significantly higher fatigue resistance behavior of nanohybrid vis-à-vis pure bone cement to make it appropriate for implant material. The biocompatibility and bioactivity have been confirmed using cell adhesion, cell viability and fluorescence image to understand the cell health on different materials and have been compared for their suitability. Osteoconductivity and bone bonding ability have been monitored in vivo on rabbits through radiographic imaging and histopathology of growing bone and muscle near the surgery site. The observed dissimilarity of properties in two different nanoclays as fillers have been visualized through interaction as measured by using spectroscopic techniques and elemental influence on bioactivity exhibiting higher efficiency for greater iron containing nanoclay.



References:
[1] Bayston, R.; Milner, R. D. J. Bone Joint Surg Br **1982**, 64, 460–464.
[2] Dunne, N. J.; Orr, J.F. *J. Mater. Sci: Mater. Med.* **2002**, *13*, 17–22.
[3] Wang, J. S.; Franzen, H.; Toksvig-Larsen, S.; Lidgren L. *J. Appl. Biomater.* ***1995***, *6*, 105–108.

Star Telechelic Poly(L-lactide) Ionomers

Amruta Kulkarni[a], Ashish Lele[a], Swaminathan Sivaram[a],
Rajmohanan P. R. [b], Sachin Velankar[c], Apratim Chatterji[d]
[a]Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune, India.
[b]Organic Chemistry Division, CSIR-National Chemical Laboratory, Pune, India
[c]Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania, USA.
[d]Physics Department, Indian Institute of Science Education and Research, Pune, India
E-mail: ak.lele@ncl.res.in

Poly(L-lactide) (PLA), a biodegradable and biorenewable polymer, has many excellent properties that are equivalent to petroleum-derived plastics such as polystyrene, aromatic polyesters etc. However a major disadvantage of PLA which limits its processibility, is its poor melt elasticity. In this work we explore the possibility of improving the viscoelastic properties of PLA melt by incorporating ionic groups on the polymer. Specifically, we demonstrate the synthesis of star telechelic PLA anionomers by a three-step procedure involving synthesis of star PLA, converting the hydroxyl end groups into carboxylic acid end groups, and finally converting these into ionic groups. The ionomers were characterized using NMR, GPC and FTIR to elucidate their molecular structure. Rheology data showed dramatic increase in the elasticity of the star telechelic ionomer melts relative to the star PLA melts. The degree of crystallinity of the star ionomers was found to be lower than that of the precursor star polymers. The star ionomers showed two glass transition temperatures. The viscoelasticity of star telechelic ionomers melts could be modulated by varying the number of ionic groups per molecule.

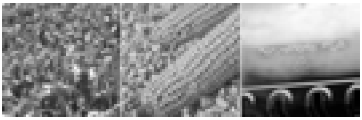
References

[1] Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* 2004, *4*, 835–864.
[2] Eisenberg A.; Kim, J. S., W. *Introduction to Ionomers*; Wiley-Interscience; New York, 1 edition (April 22, 1998), 1998; p.2.
[3] Register, R. A.; Sen, A.; Weiss, R. A.; Cooper, S. L. *Macromolecules* 1989, *22*, 2224–2229.
[4] Ro, A. J.; Huang, S. J.; Weiss, R. A. *Polymer* 2008, *49*, 422–431.
[5] Ro, A. J.; Huang, S. J.; Weiss, R. A. *Polymer* 2009, *50*, 1134–1143.

Role of ligands in the ring opening polymerization of lactones and lactides

Debashis Chakraborty*
Department of Chemistry, IIT Patna, Patna-800013, Bihar

Aliphatic polyesters have attracted attention in the recent years as a result of their permeability, biocompatibility and biodegradability.[1] The classical method in producing them involves the catalytic ring opening polymerization of lactone monomers and lactides.[2] Catalyst research for the ring opening polymerization of lactides and lactones is a topical area of recent developments in homogeneous catalysis. These catalysts are usually metal based although recent endeavors in this direction prove the role of organo catalytic reagents as another alternative. The common methodology of catalyst construction involves the presence of a rigid and polydentate ancillary ligand on the metal center along with the presence of suitable initiating groups. Our main efforts include the judgment of necessary and sufficient conditions required for controlled ring opening polymerization and in understanding the role of ligands[3] present as a catalyst component towards polymerization behavior and stereochemistry. Our investigations have been mainly restricted to the synthesis and ring opening polymerization catalysis of group 4 metal complexes containing imino(phenolate) ligands[4,5] and salen.[6] This presentation would highlight through suitable case studies, the role of the ligand in developing suitable technologies.



References:
[1] Drumright, R. E.; Gruber, P. R.; Henton, D. E. Adv Mater **2000**,12,1841 – 1846.
[2] Dutta, S.; Hung, W.-C.; Huang, B.-H.; Lin, C.-C. Adv Polym Sci. **2012**, 245, 219 – 284.
[3] Gowda, R. R.; Chakraborty, D.; Ramkumar, V. Polymer **2010**, 51, 4750 – 4759.
[4] Saha, T. K.; Rajashekhar, B.; Chakraborty, D. RSC Adv. **2012**, 2, 307 – 318.
[5] Saha, T. K.; Mandal, M.; Thunga, M.; Chakraborty, D.; Ramkumar, V. Dalton Trans. **2013**, 42, 10304 – 10314.
[6] Saha, T. K.; Ramkumar, V.; Chakraborty, D. Inorg. Chem. **2011**, 50, 2720 – 2722.

Application of carboxy methyl tamarind polysaccharide matrix for bone and skin tissue engineering

Luna Goswami [1]*, Satish Kumar[1], Priyanka Choudhury[1],
Sridhar Sanyasi[1], Chandan Goswami[2,]
1Department of Biotechnology, KIIT School of Biotechnology, KIIT University,
Patia, Bhubaneswar, Orissa PIN: 751024
2 National Institute of Science Education and Research,
IOP Campus, PO: Sainik School, Bhubaneswar, Orissa, PIN: 751005
** E-mail: lbh_1975@yahoo.co.in*

Tissue engineering is an approach where reconstruction of the body parts is aimed in order to tackle different degenerative diseases, trauma, chronic debilitating conditions, wounds, burns, scars and other defects. For bone and skin tissue engineering, selection and synthesis of the appropriate materials is governed by their physicochemical properties as well as functional interactions with biological samples. Among all, hydrogels poses several novel properties, such as non-toxicity, easy to use, cytocompatibility, ability to inject within tissues, ability to serve as scaffolds, ability to provide structural integrity as tissue constructs, ability to serve as adhesives or barriers between tissue and material surfaces. Therefore, hydrogels can support cell growth and are suitable material for tissue engineering with huge potential. Remodelling of bone by tissue engineering is a realistic option for treating several bone-related patho-physiological ailments. However, these possibilities are hindered due to lack of proper natural and biodegradable surface on which bone cells can adhere efficiently and grow further. Hydrogel-based skin tissue engineering is desirable as hydrogels have been recognized as “the material of choice” for many applications such as drug delivery and regenerative medicine that has been widely used for studies of skin biology and differentiation.

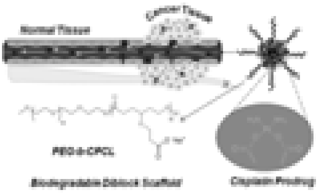
Here, we describe the synthesis and characterization of different new hydrogels as effective surfaces which can act as materials suitable for bone and skin tissue engineering. Carboxy methyl tamarind (CMT) and other polysaccharide-based matrices were selected as semi-synthetic polymers. These hydrogels have been prepared by chemically grafting with different synthetic monomer, namely hydroxyethyl methacrylate (HEMA), Acrylic acid etc. These synthesised hydrogels were characterized for their physico-chemical properties such as UV-Spectroscopy, FT-IR and swelling. We demonstrate that these materials are suitable for effective adhesion, growth and clustering of both osteoclast bone precursor cells (RAW 264.7) as well as immortalized human keratinocyte cells (HaCaT) without any cytotoxicity. We conclude that the drug coated hydrogel made of CMT:HEMA at a ratio of 1:10 is suitable for both bone and skin tissue engineering and thus may have clinical as well as commercial application in near future.

Keywords: Hydrogels, cell adhesion, Raw cells, HaCaT cells.

Functional Poly(Caprolactone) Block copolymer Scaffolds for Cisplatin Delivery

Bapurao Surnar and Manickam Jayakannan*
Department of Chemistry, Indian Institute of Science Education & Research (IISER-Pune)
Dr. Homi Bhabha Road, Pune 411008, Maharashtra, INDIA
E-mail: jayakannan@iiserpune.ac.in

Biodegradable block copolymers are important classes of materials for therapeutics in cancer. Cisplatin is one of the widely used anticancer drugs for treating various types of cancers such as colon, lung, ovarian, testicular and so on. Despite the clinical application of cisplatin; neurotoxicity, non-selective accumulation of drugs in healthy tissues and low circulation time are some of the inherent limitations associated with the administration. Thus, there is a need to design and develop novel biodegradable macromolecular architectures for cisplatin delivery based on biodegradable block copolymers approach. The present work emphasizes the synthesis of γ-carboxylic substituted polycaprolactone and its application in cisplatin drug delivery. Polymers were prepared via Ring opening polymerization, by using $Sn(Oct)_2$ as a catalyst and methoxy triethyleneglycol (mTEG) and methoxypolyethylene glycol ($mPEG_{350}$, $mPEG_{750}$, $mPEG_{2000}$ and $mPEG_{5000}$) as initiators. The synthesized polymers were characterized by NMR, IR and Mass spectroscopic analysis. Carboxylic functionalized polymers were prepared from the aforementioned polymers, in order to chelate cisplatin to polymer back bone and to deliver it to the tumour site. Platinum chelation to the polymer was proved by FTIR, TGA and WXRD. Cisplatin attached polymer scaffolds formed core shell nanoparticles (CSNPs) in water. Self-assemblies were thoroughly studied using DLS, FESEM and TEM. Increasing number of ethylene glycol units from 3 (TEG) to 113 (PEG_{5K}) showed significant influence on CSNP size and cisplatin release profile in PBS. The CSNPs decorated with PEG_{2K} and PEG_{5K} showed similar release of cisplatin and these particles showed slow sustainable cisplatin release compared to the rest CSNPs. Further HeLa cells were treated with CSNPs in order to perceive the cell viability.



References:

1. Surnar, B.; Jayakannan, M. *Biomacromolecules* **2013**, *14*, 4377-4387.
2. Surnar, B.; Pramod, P. S.; Jayakannan, M. ***Z. Anorg. Allg. Chem., (ZAAC) (****Dedicated issue to Prof. CNR Rao's 80th Birthday)* **2014**, ***640*** (6), 1119-1126.

Iodine Complexes of Chemically Modified Natural Gum

Showkat Ali Ganie, Akbar Ali & Nasreen Mazumdar
Department of Chemistry, Jamia Millia Islamia, New Delhi-25
showkat127286@st.jmi.ac.in

Acetylated gum acacia with different degrees of substitution (DS 4.01- 4.21) were synthesized by the reaction of gum acacia with an acetylating agent in the presence of a base under varying reaction temperatures. A similar reaction was carried out by Mazumdar et. al[1] to functionalize gum acacia. In the present work,acetyl derivative of gum acacia was obtained in the form of microspheres and thereafter stable iodine complexes were prepared by doping the microspheres with an iodinating agent. These were characterized by FT-IR, ^{1}H-NMR, SEM, TGA, DSC and UV-VIS Spectroscopy. The iodine molecules were attached to the carbonyl groups incorporated into gum acacia through acetylation.Iodine was released in aqueous medium as iodide ions as determined by UV-VIS spectroscopy. This work suggests that the iodine complex of functionalized gum could be used as a source of iodide ions and this is a necessary precondition for using it as a supplement for iodine delivery.

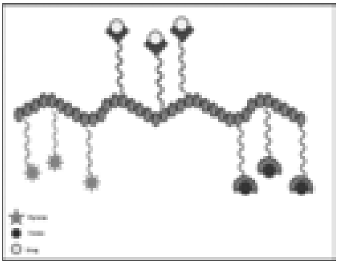
Refrences

1. Nasreen Mazumdar, Syed Ishraque Ahmad and Sunil Kumar (2013).Functionalization of natural gum: An effective method to prepare iodine complex.Carbohydrate Polymers 92, 497– 502.

Norbornene Derived Copolymer for Cis-Pt Delivery as well as Imaging Studies

Saikat Mukherjee, Raja Shunmugam*
Polymer Research Centre, Department of Chemical Science, IISER-Kolkata
E-mail: sraja@iiserkol.ac.in

Norbornene derived copolymers (NOR-PEG-FOL-Py-Pt) having functionalities Cis-Pt, PEG, Folate and pyrene are synthesized by using living ring opening metathesis polymerization(ROMP) technique. ROMP is a powerful technique for preparing highly functional polymeric materials. All the monomers and polymers are characterised by NMR spectroscopy, Mass spectroscopy and GPC technique. Aggregation due to amphiphilicity has been characterised by DLS, TEM, SEM techniques. The highly functional water soluble polymer has been synthesized for cis-pt delivery. This unique amphiphilic copolymer has been functionalized with fluorescence moiety which is expected to be useful in imaging at cellular level.



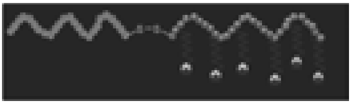
References:

[1] S. Raja, R. Dhamodharan*, "Synthesis and Characterization of a Novel, Water-soluble Polymer with cis-Platinum Chelated Pendant Groups,"J. Macromol.Sci.Pure. and Appl. Chem." 41, 859-871, (2004).
[2] Karim K. J. A., Binauld S., Scarano W., Stenjel M. H.* Polymer Chemistry 2013, 4, 5542-5554.
[3] Rao V. N., Ganivada M. N., Sarkar S., Sarma J. D., Shunmugam R.* Bioconjugate Chem., 2014, 25, 276.

Biodegradable Copolymer for Stimuli Responsive Sustained release of Doxorubicin

Sayantani Bhattacharya, Mutyala Naidu Ganivada,
Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

In this work, we have synthesized a polymeric nanocarrier for the controlled release of anti cancer drug Doxorubicin. Motivated by the hydrolytically labile prospects of acyl hydrazine bonds along with fascinating self-assembly properties of amphiphilic block copolymers; this work investigates design and synthesis of the PEO-SS-PCl-DOXI consisting of acyl hydrazine tethered DOXI and PEG chains in the caprolactone backbone. Targeting optimal properties for controlled drug delivery, we pursued rational structural design of PEO-SS-PCl-DOXI. The incorporation of PEG block makes the system advantageous as it shows no toxicity and can significantly promotes water-solubility and increase plasma clearance half-life of nanostructures. Secondly, acid-sensitive acyl hydrazine-based linkage is chosen to conjugate doxorubicin to trigger the sustained drug release. Pendent functionalization of biodegradable polymers provides unique importance in biological applications. The inclusion of enzymatically cleavable di-thiol linkage in the backbone is adding to the advantage of stimuli-responsiveness of our design.

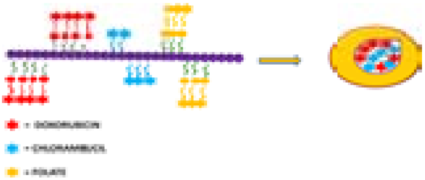


References:
1. Mizutani, M.; Arnold, S. C.; Matsuda, T. *Biomacromolecules* **2002**, *3*, 668-675.
2. Vijayakameswara Rao N,† Shivshankar R. Mane,† Abhinoy Kishore,‡ Jayasri Das Sarma,*,‡ and Raja Shunmugam*,† Biomacromolecules 2012, 13, 221−230

Efficient Synthetic Approach To Make Multi-Cancer Drugs Attached Triblock Co-polymer

Parvathy Venu, Vijayakameswara Rao N and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research, Kolkata.
E-mail: sraja@iiserkol.ac.in

Polymeric carriers are well established as delivery vehicle for a single therapeutic agent, but very recently it has been employed to the delivery of multi-agent therapy. We have synthesized stimuli responsive, multi anticancer drug derived nanocarrier by conjugating doxorubicin (DOX), chlorambucil (CHO) and folate (FOL) to the backbone of norbornene (NOR) polymer. Monomers namely NOR-DOX (mono 1), NOR-CHO (mono 2), norbornene grafted poly (ethylene glycol)-folate NOR-PEG-FOL (mono 3), are connected to norbornene backbone by ester linkers to demonstrate the pH responsive capabilities. Presence of PEG-FOL functionality makes the system water-soluble as well as site-specific. For the preparation of smart nanocarrier, we have utilized living ring-opening metathesis polymerization (ROMP) to synthesize monodisperse polymeric prodrugs due to the exceptional functional group tolerance of the Grubbs' catalyst. Dynamic light scattering, scanning electron and transmission electron microscopies have been used for testing nanocarrier capabilities. Drug release profile shows the importance of having the ester linker which helps to the drug at the mild acidic conditions resembling the pH of the cancerous cells. Confocal microscope studies confirm the cell internalization of the nanocarrier. MTT assay against 4T cells suggests the importance of the nanocarrier in the anticancer efficacy.



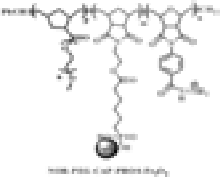
References:

1. V. R. N, H. Dinda, P. Venu, J. Das Sarma and R. Shunmugam, *RSC Adv.*, 2014, DOI: 10.1039/C4RA07549H.
2. V.N. Rao, Naidu, S. Sarkar, J. Das Sarma, R. Shunmugam, *Bioconjugate Chem.*, 2014, **25**, 276.

Magnetic particle attached cationic copolymers as the potential DNA binders

Mutyala Naidu Ganivada and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

Norbornene derived random copolymers (NOR-PEG-PHOS-CAP) are synthesised having cationic, phosphate and PEG functionality using ring opening metathesis polymerisation (ROMP) method. All the monomers and polymers are synthesised and characterised very carefully using NMR, MASS, FTIR spectroscopys and GPC technique. Zeta-potential of NOR-PEG-PHOS-CAP is measured using dynamic light scattering (DSL) instrument. The DNA binding nature of NOR-PEG-PHOS-CAP is conformed through the Circular Dichroism (CD) measurements and UV spectroscopy. Thermo gravimetric analysis (TGA), FT-IR spectroscopy and scanning electron microscope (SEM) techniques are employed to confirm the anchoring of iron particle (Fe_3O_4) to the NOR-PEG-PHOS-CAP. This is the first report, norbornene derived random copolymers conjugated with magnetic nanoparticle, and polyethylene oxide (PEG) motif has been designed (NOR-PEG-PHOS-CAP) to create a magnetic vector under magnetic field. Due to the magnetic properties of NOR-PEG-PHOS-CAP copolymer, it is possible to separate most of the cells that have incorporated a sufficient amount of magnetic material by using a magnetic activated cell sorting system (MACS). These NOR-PEG-PHOS-CAP random copolymers can be used as the potential DNA binders as well as DNA delivery.



References:

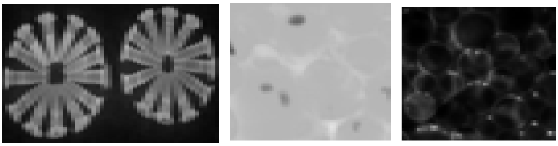
[1] M.N.Ganivada, V.R.Nerella, H.Dinda, P.Kumar, J.D.Sarma,and R.Shunmugam, *Macromolecules*, **47**, 2703 (2014).

[2] K. Fukae, T Terashima,* and M. Sawamoto. *Macromolecules*, **2012**, *45* (8), pp 3377–3386.

Preparation of Acid Responsive Microcapsules for Targeted Drug Delivery System

Nagaraju Pentela, Nikhil Sainath Reddy .V, S. N. Jaisankar,
Debasis Samanta,*Asit Baran Mandal*
Polymer Science Division, CSIR-CLRI, Chennai-20
E-mail: abmandal@hotmail.com

Microcapsules are small capsules of few to several hundred micrometer diameter, are useful as carrier for biological and other important substances. Acid-responsive microcapsules are particularly important for the delivery of a drug to the specific part of the body.[1] Formulation of structural constituents of the microcapsules is an integral part of research for its design in specific application.[2] Recently our group reported the development of acid responsive microcapsules by using functionalized single-walled carbon nanotubes. Now we developed biodegradable acid responsive microcapsules by using vinyl imidazole polymer, functionalized single-walled carbon nanotubes, for better targeted drug delivery system in minimal acidic medium. In this case we used water benign solvents for the making of microcapsules, and also for the releasing study of the drug we used water soluble nutrient such as Riboflavin, cis-platinum is a model drugs. We found that the drug releasing in acidic medium is much faster than compare to neutral medium (almost no releasing), it is confirmed by observing UV visible spectrum. By observing the fluorescent spectroscopy images also determines the releasing of the drug only in acidic medium but not in neutral medium. The MTT assay study also reveals that the formation of microcapsules is biodegradable.
Although we loaded several dyes like Congo red, Bromothymol blue as 'model' compounds for the convenience of spectroscopic and microscopic characterization, the developing method is potentially adaptable to a wide variety of compounds.



Acidic medium Neutral medium Neutral medium Acidic medium

Fig.1. Comparison of Drug releasing in acidic and neutral medium under UV Chamber as well as fluorescent microscopy

Reference

1) Hu, S-H.; Tsai, C-H.; Liao, C-F; Liu, D-M; Chen, S-Y.; *Langmuir,* **2008**, 24, 11811
2) Samanta, D.; Sankar, R. M; Jaisankar, S. N.; Alam, M. S; Mandal, A. B. *Chem. Commun.* **2011**, 47, 11975

Accumulation of Biopolyester Poly(3-hydroxybutyrate) by Bacteria Endophytic to *Helianthus annuus* L.

Rituparna Das[1], Arundhati Pal[2] and A. K. Paul[1]
[1]Microbiology Laboratory, Department of Botany, University of Calcutta, Kolkata
[2]Department of Botany, Serampore College, 9 William Carey Road, Serampore, Hooghly

Polyhydroxyalkanoates (PHAs), the microbially produced linear polyesters have material properties similar to thermoplastics and are completely biodegradable in nature having wide range of applications. Development of low cost production strategies from renewable resources utilizing novel organisms is now a crucial challenge. Plant microenvironment offers a wide range of habitats that support microbial growth and bacteria endophytic to plants can accumulate lipoidal substances including PHAs. In the present study, culturable bacterial diversity from endosphere of *Helianthus annuus* L. were investigated for the production of the biodegradable polyester poly(3-hydroxybutyrate), the most common polyhydroxyalkanoates. A total of 23 bacterial endophytes isolated from surface sterilized plant segments were screened for intracellular P(3HB) accumulation and 44% of the isolates showed accumulation of the polymer. *Bacillus* HAL 03 was found to be the most efficient producer. Mineral salts medium was used for growth and polymer production and the cell mass from the growing culture was harvested by centrifugation, dried in acetone and the polymer was extracted with warm chloroform. The extracted polymer was evaporated to dryness and treated with concentrated H_2SO_4 and the absorbance was recorded at 235 nm. Time course of growth and P(3HB) production by HAL 03 indicated a gradual increase in P(3HB) accumulation till 56 h of growth. The production of P(3HB) by HAL 03 was significantly influenced by the quality and quantity of suitable carbon and nitrogen sources present in the growth medium. At 2% (w/v) sucrose, the P(3HB) content of the HAL 03 cell mass was 50.46 % of CDW whereas using of 0.2% (w/v) yeast extract as nitrogen source P(3HB) production was maximum and accounted for 53.18 % of CDW. Attempt has also been made to enhance the P(3HB) production by using non-conventional carbon sources. Detailed taxonomic consideration of the bacterial isolate and characterization of the polymer are under progress.

Financial support from Department of Science and Technology, New Delhi to R. Das in the form of Inspire Fellowship is duly acknowledged.

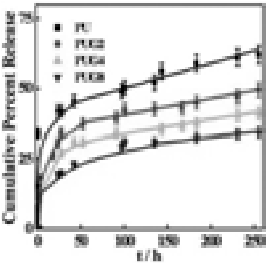
References:

[1] Law J. H. and Slepeckey R. A. (1961) J. Bacteriol. 82: 32-36.
[2] Steinbuchel A. and H.E. Valentin (1995) Lett.128: 219-228.
[3] Strobel G., Daisy B., Castillo U. and Harper J. (2004) Journal of Natural Products, 67: 257–268.

Graphene induced self-assembly in polyurethanes for biomedical applications

Dinesh Kumar Patel and Pralay Maiti*
School of Materials Science and Technology, IIT-BHU, Varanasi 221 005, India
Email:dineshbhud10@gmail.com

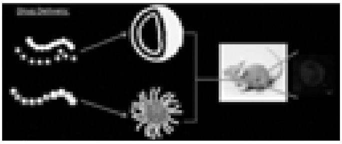
Polyurethanes have been synthesized using diol, diisocyanate and chain extender. Polyurethane/ graphene nanohybrids were synthesized BY in-situ polymerization technique. Nanohybrids of polyurethanes have been prepared using two dimensional graphene by dispersed it in diol followed by prepolymerization and chain extended using di-ol. Nanohybrids are characterized through FTIR, UV-Visible spectroscopy, Mechanical and Thermal properties are measured using UTM and DSC, TGA respectively. FTIR studies indicate that the interaction increases with the graphene content as revealed from the large shifting in the peak position of different functionalities. This interaction has also been verified by through UV-visible spectroscopy in which red shifting occur in nanohybrids containing graphene. Polymer nanohybrids exhibit significant improvement in mechanical properties in presence of graphene. Toughness of nanohybrid increases considerably presumably due to amorphization of polymer in presence of strongly interacted graphane. High temperature stability increases in nanohybrid showing two stages thermal degradation for hard and soft segment separately. Gradual lowering of melting temperature suggest strong interaction between PU and graphene in addition to heat of fusion. Nanohybrids were exhibits the good biocompatible nature in term of cell viability, cell adhesion and fluorescence measurement . Sustained drug release is obtained in nanohybrid leading to the use of the developed hybrid material for biomedical applications. Release profile of drug from nanohybrids are shown in figure.



Evaluation of Best Combination of Multi-chemotherapeutic Polymer Pro-drugs for Cancer Therapy

Himadri Dinda,[1] Jayasri Das Sarma[2] and Raja Shunmugam*[1]
[1]Department of Chemical Sciences, [2]Department of Biological Sciences,
Indian Institute of Science Education and Research, Kolkata.
E-mail: sraja@iiserkol.ac.in

A series of biocompatible chemotherapeutic polymeric nano-carriers have been synthesized namely, COPY-DOX, PHOS-FOL-DOX, PHOS-FOL-DOX-Fe, PVLPEG-PVLDOXI-PCL-PHOS- Fe_3O_4, DOX-CHO-FOL, DTBCP. The biocompatibility as well as the cell viability studies of the newly developed multi-drug nano-carrier system have been thoroughly studied by Confocal laser scanning microscopy (CLSM), flow cytometry (FACS), and MTT assay on 4T mouse mammary gland cancer cell line and HeLa human cervix cancer cell line. Based on FACS analysis, the best anti-cancer activity is observed in the case of PHOS-FOL-DOX-Fe and PVLPEG-PVLDOXI-PCL-PHOS- Fe_3O_4.



References:

1. Vijayakameswara Rao N, Himadri Dinda, Parvathy Venu, Jayasri Das Sarma and Raja Shunmugam*, ***RSC Adv**.,* **2014**, 4, 45625-45634.
2. Mutyala Naidu Ganivada, Vijayakameswara Rao N, Himadri Dinda, Pawan Kumar, Jayasri Das Sarma and Raja Shunmugam*, ***Macromolecules,*** **2014**, *47*(8), pp 2703-2711.
3. Vijayakameswara Rao N, Mutyala Naidu Ganivada, Santu Sarkar, Himadri Dinda, Koushik Chatterjee, Tanmoy Dalui, Jayasri Das Sarma and Raja Shunmugam*, ***Bioconjugate Chem***., **2014**, *25* (2), pp 276–285.
4. Vijayakameswara Rao N, Himadri Dinda, Mutyala Naidu Ganivada, Jayasri Das Sarma and Raja Shunmugam*, ***Chem. Comm**.,* **2014**, 50, 13540-13543.
5. Vijaykameswara Rao N, Shivshankar R Mane, Abhinoy Kishore, Jayasri Das Sarma and Raja Shunmugam*, ***Biomacromolecules,* 2012**, 13 (1), 221-230.

Observation of Enhanced Conductivity and Dielectric Constant in Polyvinyl Alcohol/Polyvinylpyrrolidone Blend-Hydroxyapatite and Graphene Oxide Composites: Biocompatibility Study using Human Mesenchymal Stem Cells

B. Chaudhuri[1], G. Sardar[2], Md. G Masud[3], J.Uddin[4],
B. K. Chaudhuri[5*] and K. Pramanik[1]
1Department of Biotechnology and Medical Engineering,
N.I.T., Rourkela, Odisha-769008, India.
2Zoology Dept., Baruipur College, W.B.,3SSP Dept.,, IACS, Kolkata-700032, 4Govt. School, Kolkata,
5Department of Physics and Astronomy, NIT, Rourkela, Orissa, India
E-Mail: chaudhuribk@nitrkl.ac.in

Polymer blends are often superior materials for technological applications. 80wt% polyvinyl alcohol (PVA)/ 20wt% Polyvinylpyrrolidone (PVP) blend filled with (0-15 wt%) hydroxyapatite (HAP) were used to synthesize composite films by solution-casting technique [1]. Room temperature conductivity (σ) and dielectric constant (ε) measurements of 80wt%PVA/20wt%PVP blend exhibited abrupt increase of ε (~347) and σ (~1.64×10^{-4} S/m) values with the addition of mass fraction of 10wt% HAP and then decreased to lower values which was associated with the onset of percolation. Such flexible high dielectric composite films are suitable for use as electronic material. Addition of small amount of (0.01wt%) grapheme oxide (GO) further enhanced both ε and σ values of the composite films.

The electrospun fibrous mesh prepared with more conducting composites (8.5wt% HAP) showed better biocompatibility compared to the corresponding less conducting composites. GO added composite was also found to be excellent biocompatible. Biocompatibility was studied by using human mesenchymal stem cells (hMSCs) and cells viability on these fibrous scaffolds was determined by MTT [3-(4, 5-di-methylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] assay analysis. Such composites are suitable for both electrical and biomedical applications.

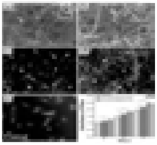


Figure 1. SEM images (a, b) morphology of the scaffolds with hMSCs adhesion on 80PVA/20PVP-5wt%HAP and 80wt%PVA/20wt%PVP-8.5wt%HAP fibrous meshes, Fluorescence images showing hMSCs adhesion on the fibrous mesh surfaces (c: x= 5wt%, d: x= 8.5wt% HAP and e: control glass). (f) Cells viability and proliferation observed by MTT assay. The results are presented as the means ± SD. (* n=5; p<0.05).

Acknowledgement: Authors (BC and KP) are grateful to the DOB for financial assistance to complete the work.

Reference:

[1] Uddin, J.; Middya, T.; Chaudhuri, B.K.; Sakata, H. Polymer, 2014,55, 15-21

Myoblast Differentiation of Human Cord Blood Mesenchymal Stem Cells on Thin Graphene Oxide Sheets and Electrospun Graphene Oxide-PLGA Composite Scaffolds

Biswadeep Chaudhuri[1*], Lorezo Moroni[2], and Krishna Pramanik[1]
[1]Department of Biotechnology and Medical Engineering,
National Institute of Technology, Rourkela, Odisha-769008, India.
[2]University of Twente, Tissue Regeneration Department,
Drienerlolaan 5, 7522NB Enschede, The Netherlands
*Chaudhuri.biswadeep@googlemail.com

One of the current trends in tissue engineering is to discover substrates which can provide favorable cues for the growth and proliferation of specific tissue types. Graphene and graphene oxide (GO)-polymer composite based materials are emerging as the next generation implants for biomedical applications.

In this paper, human umbilical cord blood (UCB) derived mesenchymal stem cells (CB-hMSCs) were cultured directly on spin coated thin GO sheets composed of GO nanoplatelets (GOnPs) and also on electrospun [1] fibrous meshes of GOnPs-PLGA (Poly Lactic-co-Glycolic Acid) composite to explore their potential as functional scaffolds for the differentiation and proliferation into skeletal muscle cells. Our results confirmed that both the scaffold systems could guide excellent myoblast differentiation, proliferation and also promote oriented myotube formation similar to natural orientation when CB-hMSCs are seeded and cultured on the GO film and GO-PLGA fibrous mesh surfaces. It was also elucidated that electrical conductivity (σ), dielectric constant (ε) of GO sheets and surface charge of GO provided important guidance cues for biocompatibility of the scaffolds and the capability of modulating cell behavior. Enhancedε (more than ten times) and σ (two orders of magnitude) of GO-PLGA, due to GOnPs addition in PLGA, improved multinucleated myotubes orientation on GO-PLGA meshes compared to that on thin GO sheets. Both thin GO sheets and GO-polymer scaffolds might be considered as prospective candidates for CB-hMSCs differentiation and proliferation into skeletal myoblasts and other lineages for the next generation tissue engineering and biomedical applications.

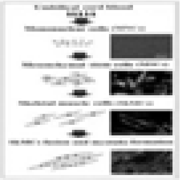


Fig.1. Myoblast differentiation on GO sheet and GO-PLGA electrospun meshes.

Acknowledgement: The authors (BC and KP) are grateful to the Department of Biotechnology, Govt. of India, for financial support.

Reference:

[1] Chaudhuri, B.; Bhadra, D.; Mondal, B.; Pramanik, K. 2014, Mat. Letts. **2014**, 126, 109-112.

Polyurethane-grafted-Chitosan as a smart material for potential antibacterial drug delivery.

Arun Kumar Mahanta and Pralay Maiti*
School of Materials Science and Technology, IIT (BHU), Varanasi- 221005,India.
Email: akmahanta.rs.mst12@itbhu.ac.in

In this work Polyurethane graft chitosan has been synthesized. Prepolymers (polyurethanes) were obtained by condensation reaction between poly (tetra methylene glycol) (PTMG) and Hexamethylene diisocyanate (HMDI). Characterization of graft copolymers was performed by Infrared spectroscopy (IR), ^{13}C Nuclear Magnetic Resonance in the solid state (^{13}C NMR), UV – Visible Spectroscopy, and Spin - lattice Relaxation time (T_1).

Thermal Behavior of the synthesized materials was characterized using TGA and DSC. Mechanical property was determined by UTM. Relaxation behavior of the materials were characterized by DMA and Dielectric measurement

The antibacterial activity and drug releasing strategy of the copolymers were examined by loading antibacterial drug tetracycline hydrochloride and the results showed that the developed copolymer can be effectively act as a drug delivery vehicle.

References:

1. S.S. Silva, S.M.C.Menezes, R.B.Garcia. Eur. Polym. J., 2003, 39, 1515-1519
2. A. Khan, S.Badshah, C.Airoldi, Chem. Eng. J., 2011, 159-166

Arecanuthusk fibre /PLA Composites as cost effective alternatives for commodity plastics

V. S. Prasad, Sumesh Soman, M. Brahmakumar and A. Anandhu
CSIR-National Institute for Interdisciplinary Science and Technology
Thiruvananthapuram 695019

Green composites based on biodegradable polymers reinforced with natural fibres are receiving great attention due to the increased environmental concerns. Arecanut husk fibres are the unutilized fibre resources of our country though India is producing maximum arecanuts in the Asian region. Though PLA is biodegradable the brittleness and the cost limits the wider utlilization of PLA in commodity sector. The use of cost effective fibres in PLA can improve the processability and reduce the brittle fracture. The chopped fibres in the range of 2-4cm showed better elongation with improved modulus compared to long fibre mats based composites. The surface treatment and use of process aids such as saturated long chain acids in injection moulding resulted in composites which can be extruded into flexible films. The results indicated the prospects for application as effective substitute for commodity plastics. SEM morphologies of the fracture surface showed pull out of microfibrils resulting in increased toughness of the composite (Figure 1).

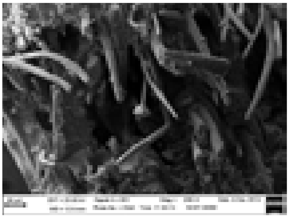


Figure 1 SEM of PLA/Areca Fracture Surface

Reference:

[1] Oksman, K.; Skrifvars, M.; Selin, J.-F.*Comp. Sci. Tech*. **2003**, 63, 1317-1324.

[2] Thakur, V.K.; Thakur, M.K.; Gupta , R.K. *Intl. J. Polym. Anal. Chrn*. **2014**,19,256-271.

Polymeric nanocomposites and nano-biohybrids with CdTe quantum dots as efficient biosensing materials

Sudesna Chakravarty[1] and Neelotpal Sen Sarma[2*]
Polymer Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, PaschimBoragaon, Guwahati-781035, Assam, India
Email id: sudesnaiasst@gmail.com

Nanocomposite and hybrid materials consisting of semiconductor nanocrystals embedded in polymeric gels or electrostatically attached to a macromolecular system find widespread applications in biomedical field particularly as biosensors. Herein we have reported, the synthesis and characterization of four polymeric nanocomposites- PVA-tryptophan (Poly 1), PVA-tryptophan-CdTe QDs (Poly 2), PVA- phenylalanine (Poly 3) and PVA-phenylalanine-CdTe QDs (Poly 4); and a nano-biohybrid cationic curcumin-tryptophan (CT) with FTIR, TGA, DSC, WAXRD, FESEM and TEM. The sensing study of four polymers towards folic acid has been systematically studied and Poly 2 has been found to have excellent sensitivity with LOD 5.77×10^{-9} M for 0.39 pM Folic acid while the nanohybrid synthesized has been found to be excellent DNA sensor with LOD 1.4×10^{-10} M. The nanobio hybrid has also been found to be excellent bacterial DNA sensor. Thus, such systems find wide applicability in biomedical fields.

References:

[1] M. C. Urbina, S. Zinoveva, T. Miller, C. M. SabliovW. T. Monroe, C. S. S. R. Kumar, Investigation of magnetic nanoparticle –polymer composites for multiple-controlled drug delivery, J. Phys. Chem. C 112 (2008) 11102-11108

[2] B. Jeong, A. Gutowska, Lessons from nature: stimuli-responsive polymers and their biomedical applications, Trends in Biotechnology 20 (2002) 305-311

[3] S. Sarma, C. Nirkhe, S. Pethkar, A. A. Athwale, Chloroform vapour sensor based on copper/polyanilinenanocomposite, Sens. Actuat. B 85 (2002) 131-136

[4] S. Chakravarty, D. Saikia, P. Sharma, N. C. Adhikary, D. Thakur and N.S Sarma, Supramolecularnanobiological hybrid as a PET sensor for bacterial DNA isolated from *Streptomyces sanglieri*, Analyst (2014) DOI: 10.1039/C4AN01611D

Branched Polymer-Based pH Responsive Micelle for Delivery of Doxorubicin Selectively on Cancer Cell: Synthesis, Characterization, Cell uptake and Release

S. Panja [1], S. Maji[2], T. K. Maiti [2] and S. Chattopadhyay[1]*
[1] Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India
[b] Department of Biotechnology, Indian Institute of Technology, Kharagpur-721302, India
*santauchat71@yahoo.com

Herein, a series of robust pH responsive, folic acid (FA) conjugated, biocompatible, branched amphiphilic block copolymer were synthesized for sufficient delivery of anti-cancer drug, selectively on cancerous cell. The branched amphiphilic block copolymer, pentaerythretol poly(caprolactone)-b-poly(acrylic acid) (PE-PCL-b-PAA) was synthesized by sequential steps of ring opening polymerization (ROP) and atom transfer radical polymerization (ATRP). The PAA segment of the block copolymer brilliantly performed as hydophilic as well as acid sensitive constituent. To perform cancer cell targeted delivery, bromine (-Br) terminated block copolymer was converted to ammine ($-NH_2$) terminated one and subsequently conjugated with FA by the DCC coupling reaction. The FA conjugated, branched amphiphilic block copolymers give rise to nearly spherical polymeric micelle in water having an average size in the range of 40 to 60 nm. The block copolymers are showing low range of CMC (0.63×10^{-2} to 2.01×10^{-2}mg/mL) which support its beneficial application in drug delivery. These polymeric micelles can carry very high loading (25.1%) of DOX molecules compare to the literature reported micelles prepared from analogous linear amphiphilic block copolymers. The cell viability of DOX loaded and blank polymeric micelles were checked by MTT assay. The selective trafficking of FA provides a fruitful uptake of FA conjugated, DOX loaded polymeric micelles on cancer (HeLa) cell line compare to normal (HaCaT) cell line. Cell cycle analysis by FACS shows inhibition of cell growth by arresting the cell cycle at G2/M. The effective size of the micelles increases about 3 times (monitored by DLS study) after 15h of incubation at a pH of 5.0 but it remains approximately the same at a pH of 7.4. This pH sensitive increase of miceller size affords approximately 67-88% *in vitro* release of DOX molecule at physiological pH (5.0) of cancer cells.

References:

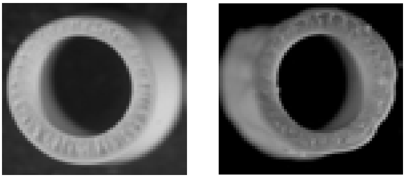
1. You QY.; Ling SZ.; Xin DG.; Yu Q.; and Li JZ. Biomacromolecules **2011**,12,116–122.
2. Qiao ZY.; Zhang R.; Du FS.; Liang DH.; and Li ZC. J Control Release **2011**,152, 57-66.

Effect of treatment conditions on the performance of hollow fiber membranes

Smita D. Kumbhar, Rohit Kulkarni and Ulhas K. Kharul*
Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Pune-411008 (India)
**uk.kharul@ncl.res.in*

Membrane technology for water treatment has attracted wide attention from both, industry and academia, due to worldwide shortageof clean water and demand for better technologies to purify the water for desired application [1].Asymmetric membranes are widely used for water treatment by either ultrafiltration, nanofiltration or reverse osmosis. These membranes are usually prepared by immersion precipitation process using water as the nonsolvent.Hollow fiber membrane modules are usually used for water disinfection(ultrafiltration) as they have higher membrane surface area available per unit volume thanthat of flat sheet membrane based spiral modules. Module preparation after the hollow fiber spinning is a niche technique. The residual water needs to be removed to some extent, during the module making process. Inherent material properties affect membrane performance during such processing.

Objective of the present work was to investigate effects of various parameters used for the removal of water from the membrane surface. Hollow fiber membranes based on polyacrylonitrile (PAN) were prepared using indigenously developed spinning machine. The molecular weight cut off of the membranes was aimed as 68 kD, since membranes with this porosity are known to possess excellent virus rejection capability of 5 log reduction [2]. Conventional solvent exchange [3] as well as drying were employed for the removal of water. The basic membrane performance, viz., water flux and rejection were analyzed to understand effects of these treatment conditions, while morphological changes were observed by stereomicroscopy. Significant effect on membrane morphology and the water flux were observed, endorsing the need of following appropriate treatment protocol after the membrane spinning. Some of the crucial results will be presented.



IPA+PET ether treated Excessive drying

Fig. 1. Cross section of hollow fibre membranes

References:

[1] Journal of Membrane Science 372 (2011) 20–28.
[2] Journal of Applied Polymer Science,101, (2006) 4378–4385.
[3] Journal of Membrane Science 178 (2000) 13–23.

Development of chitosan and chondroitin sulfate based porous scaffold for drug release

Sarada Mallick, *Pradeep Srivastava
School of Biochemical Engineering, IIT (BHU), Varanasi, India - 221005
* *pksrivastava.bce@itbhu.ac.in*

Tissue Engineering Scaffolds are generally highly porous materials with definite three dimensional shapes advantageous for tissue engineering. The Current study deals with the development and characterization of Porous Scaffold formed by varying the Proportion of chitosan and chondroitin sulfate(CS) using novel freeze drying technique. It was studied that chitosan and CS were crosslink to form a biomaterial to support chondrogenesis. The porous structure of the scaffold was studied by light microscopy and it was observed that distribution of these two materials in the scaffold. pH and viscosity was measured prior to the formation of scaffold. pH of the Scaffold lies between 5 to 7. Scaffolds were hemocompatible in nature. Scaffolds were characterized by Contact angle measurement, SEM, FTIR, Porosity and UTM. Compressive strength of the scaffold depend upon the ratio of chitosan and CS. Ofloxacin a model drug was incorporated with composite solution before freeze drying and release kinetics was studied under *in vitro* conditions. Ofloxacin loaded scaffolds were effective against *Escherichia coli*. Based on the preliminary results, it was concluded that the scaffolds are having good potential to be used with cell for *in vivo* study. Further this scaffold being used for the evaluation of the drug release in pathological state of cartilage degeneration.

Keywords: Scaffold, Chondrogenesis, Chondrocyte, freeze drying.

References:

[1] Ma, P. X. (2008). "Biomimetic materials for tissue engineering." Advanced drug delivery reviews **60**(2): 184-198.
[2] Ma, P. X. and J. Elisseeff (2005). Scaffolding in tissue engineering, CRC press.
[3] Vunjak-Novakovic, G., B. Obradovic, et al. (1998). "Dynamic cell seeding of polymer scaffolds for cartilage tissue engineering." Biotechnology progress **14**(2): 193-202.

Silk Sericin based Films and Nanofibers for Biomedical Application

Mangala Joshi
Department of Textile Technology, Indian Institute of Technology,
Delhi Hauz Khas, New Delhi 110016, India
Email: mangala@textile.iitd.ac.in

Sericin is a globular protein which constitutes 25-30% of silk cocoon and envelops the fibroin protein which constitutes the silk fiber. In recent years silk sericin has been investigated for its unique properties in biotechnological field. They include biocompatibility, biodegradability, antibiotic and anticoagulant, antibacterial activity, antioxidant behaviour, anti-tyrosinase activity, anticarcinogenic effects and UV protective properties. Sericin promotes human skin fibroblast attachment in cell culture. It also supports cell adhesion and proliferation and plays a significant role in wound healing process. Recently several studies have been reported on sericin films, membranes, 3D scaffolds, nanoparticles, and composites, conjugated drugs in pure or blended form for cell culture, wound dressings, drug delivery applications.

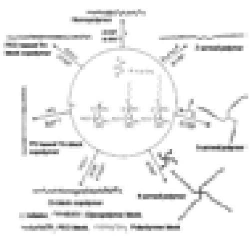
In this paper, our work in the area of sericin based films and nanofibrous webs having potential for biomedical application such as wound dressing etc will be presented. Nanofibres show several advantages in biomedical field especially wound dressing because of its high surface area to volume ratio, high porosity and light weight. Sericin in pure form cannot be converted to nanofibre form because of low molecular weight. Hence blending with polyurethane has been explored to exploit the good properties of both to make a good wound dressing nanofibrous membrane. Sericin film also has lot of potential applications but at the same time it has some drawbacks like poor tensile strength, poor thermal stability and solubility in warm water, which limits many application of sericin especially in film form. In this present paper, a novel eco-friendly approach has been used to enhance the properties of sericin in film form through sericin-metal complex formation using alum salt. It is expected that optimum cross-linking provided by aluminium would enhance the thermal stability and would also make sericin film insoluble in warm water while retaining its other useful properties.

Syntheses and Characterization of Various Well-defined Glycopolymer Architectures by Controlled Radical Polymerization and Their Biocompatibility

M. Trinadh, N. N. Malleswara Rao, A. V. Sesha Sainath*
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, India
E mail: avss@iict.res.in

In recent years, glycopolymers have escalating attention in their use as artificial material for a number of biological and biomedical applications due to their biocompatible and biodegradable nature. From the last decade many researchers have focused on well-defined glycopolymers syntheses by adopting various polymerization methods which include controlled and living polymerization processes. Mainly, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization methods have been employed to produce glycopolymer architectures.

We have synthesized various (meth)acrylate based acetylated glycomonomers and initiators for ATRP and RAFT processes. By adopting controlled radical polymerizations, we prepared different macromolecular architectures such as, homo-glycopolymers, poly(ethylene oxide) (PEO) and polystyrene (PS) based di- and tri-block glycopolymers, and 2-, 3- and 4-armed glycopolymers from synthesized monomers and initiators. Before and after deacetylation of the pendant glucose moieties of the macromolecular chains were characterized by using various analytical techniques. After deacetylation, the macromolecular architectures are soluble in water. These hydrophilic glycopolymers were utilized to understand biocompatibility with osteoblast cells in vitro for the first time based on glycopolymer macromolecular architectures. The biological responses of these macromolecules in terms of cytotoxicity of glucose moieties at various architectures and concentrations were investigated by employing *in vitro* osteoblast cells. Osteoblast cells adhesion, viability and proliferation response with synthesized glycopolymers revealed that the glycopolymer concentration tolerance limit was dependent on the macromolecular architecture and cell proliferation results will be presented in our poster.



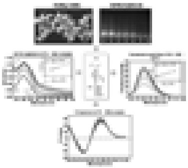
References:

[1] Trinadh, M.; Kannan, G.; Rajasekhar, T.; Sesha Sainath, A. V.; Marshal, D. RSC Adv., **2014**, 4, 37400-37410.

Interaction between Imidazolium based Poly (ionic liquids) and DNA investigated bySpectroscopic Techniques and Molecular Docking Simulations

Kasina Manojkumar[1], K T Prabhu Charan[1], Prakash C. Jha[2], Vijay M. Khedkar[3], Akella Sivaramakrishna[1], Ramamoorthy Siva[4], Gurunathan Jayaraman[5], Kari Vijayakrishna[1*]
[1] Organic Chemistry Division, School of Advanced Sciences, VIT University,
Vellore-632014, TamilNadu, India
[2] School of chemical Sciences, Central University of Gujarat,
Sector-30, Gandhinagar-38200, Gujarat, India
[3] Combi-Chem Resource Centre, CSIR-National Chemical Laboratory, Pune, 411008, India
[4] Plant Biotechnology Division, School of Biosciences and Technology,
VIT University, Vellore-632014, TamilNadu, India
[5] Bioinformatics Division, School of Biosciences and Technology,
VIT University, Vellore-632014, TamilNadu, India
kari@vit.ac.in

Imidazolium based poly(ionic liquids) (PILs) with different alkyl side chains were synthesized using radical polymerization[1] and employed to study their interactions with DNA[2]. The experiments were performed in physiological conditions with constant DNA concentration and varying PIL concentrations. Different experiments such as UV-Visible absorption, fluorescence, FTIR and circular dichroism (CD) revealed the binding mode and binding constants of PILs.[3, 4] The effect of varying ionic strength on the binding between PILs and DNA confirmed their interactions as mainly electrostatic[5]. UV-Vis and fluorescence results showed an increase in PILs binding constants with increase in their alkyl side chain length which is in good agreement with the results from molecular docking simulations[6]. Furthermore, the CD and FTIR results illustrated that the DNA has well retained the secondary structure (B-form) after binding with PILs[7].



References:

[1] Prabhu Charan, K. T.; Pothanagandhi, N.; Vijayakrishna, K.; Sivaramakrishna, A.; Mecerreyes, D.; Sreedhar, B. Eur. Polym. J.**2014**, 60, 114-122.

[2] Manojkumar, K.; Prabhu Charan, K. T.; Jha, P. C.; Khedkar, V. M; Sivaramakrishna, A.; Siva, R.; Jayaraman, G.;Vijayakrishna, K.CommunicatedManuscript,**2014**.

[3] Dey, D.; Kumar, S.; Banerjee, R.; Maiti, S.; Dhara, D. J. Phys. Chem. B **2014**, 118, 7012-7025.

[4] Sirajuddin, M.; Ali, S.; Badshah, A. J. Photochem. Photobiol. B**2013**, 124, 1-19.

[5] Ottaviani, M. F.; Furini, F.; Casini, A.; Turro, N. J.; Jockusch, S.; Tomalia, D. A.; Messori, L. Macromolecules **2000**, 33, 7842-7851.

[6] Elder, R. M.; Emrick, T.; Jayaraman, A. Biomacromolecules **2011**, 12, 3870-3879.

[7] Ding, Y.; Zhang, L.; Xie, J.; Guo, R. J. Phys. Chem. B **2010**, 114, 2033-2043.

Effect of Sepiolite clay content on the properties of poly(lactic acid) nanocomposites

Anil Kumar[1], P. Santhana Gopala Krishnan[1*] and S. K. Nayak[1,2]
[1]Department of Plastics Engineering, Central Institute of Plastics Engineering and Technology, Patia, Bhubaneswar-751024 (India)
[2] Laboratory for Advanced Research in Polymeric Materials, Central Institute of Plastics Engineering and Technology, Patia, Bhubaneswar-751024 (India)
Email: psgkrishnan@hotmail.com

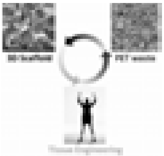
Poly(lactic acid) is one of the most promising biodegradable polymer, which can replace non-degradable polymers in numerous applications such as agricultural mulch films, food containers, water bottles, carry bags. Because of its bioresorbable characteristics, it is now clinically used in surgery as sutures and devices for osteosynthesis and in pharmacology as drug delivery systems. One of the drawbacks is low impact strength, which restricts its applications.

Literature search indicated that poly(lactic acid) could be toughened through blending of various polymers namely poly(butylene succinate), poly(ε-caprolactone), linear low density polyethylene and poly(vinyl alcohol). Another way of improving toughness is by the addition of plasticizers or inorganic fillers into polymer matrix. Plasticizers such as poly(ethylene glycol), poly(propylene glycol), oligomeric lactic acid, glycerol, citrate ester, diethyl bishydroxymethyl malonate oligomers, triacetine, tributyl citrate, partial fatty acid ester were also studied to improve the impact strength of PLA. Nanofillers such as montmorillonite clay, calcium carbonate were also studied. In the current study, sepiolite clay was undertaken to overcome the limitation. Poly(lactic acid)-sepiolite nanocomposites were prepared by melt blending using 0.25, 0.5, 1.0, 2.0 and 4.0 wt. % of sepiolite clay. Incorporation of sepiolite clay into poly(lactic acid) matrix was confirmed by Fourier transform infrared spectroscopy and wide-angle X-ray diffraction studies. Water absorption remained same irrespective of sepiolite clay content in nanocomposites. Tensile stress-strain curve indicated that pristine PLA had brittle failure whereas nanocomposite samples failed after reaching yield state. Tensile strength, % elongation at break and impact strength were found to be higher than that of pristine polymer. Density and impact strength increased with increase in sepiolite clay content. Thermal studies indicated that both pristine PLA and nanocomposite samples were stable up to 300 °C and show single step degradation under nitrogen atmosphere.

From Trash to Tissue: Novel Polyester Derived from Poly(ethylene terephthalate) Waste for Tissue Regeneration

Kishor Sarkar,[1, 2] Sai Meka,[2] Amrit Bagchi,[2] N. S. Krishna,[3] S.G. Ramachandra,[3] Giridhar Madras,[1] Kaushik Chatterjee [2*]
1Department of Chemical Engineering, 2Department of Materials Engineering, 3Central Animal Facility, Indian Institute of Science, C.V. Raman Avenue, Bangalore 560012, India
*kchatterjee@materials.iisc.ernet.in

Engineered tissues are thought to be revolutionizing medicine and may offer promising new treatments for many debilitating diseases [1-3]. Scaffold with non-toxicity, biodegradability and highly porous interconnected structure is ideal for tissue engineering [4]. Despite significant advances in regenerative medicine, the cost of such therapies is likely to remain beyond the reach of many patients globally. The choice of synthetic polymers that are suited for such applications is rather limited and expensive adding to the cost of the treatment. Another global challenge is the efficient management of large volumes of municipal solid waste [5]. Poly(ethylene terephthalate) (PET) products form a significant component of such wastes [6] and its non-biodegradable character poses an environmental hazard [7] but potentially offers an inexpensive source of biomedical polymers. Towards developing biomaterials for affordable healthcare solutions, herein a novel class of polyester was synthesized using a monomer, bis(hydroxyethylene) terephthalate (BHET) derived from recycling PET waste. The polyester was synthesized by catalyst-free, melt polycondensation reaction of BHET with other multi-functional monomers from renewable sources such as citric acid, sebacic acid and D-mannitol. The synthesis of polyester was consisted of two steps processes, pre-polymerization followed by post-polymerization. The mechanical properties and degradation rate of the polyester can be tuned by varying the composition and the post-polymerization time. The mechanical property of the polyester was comparable with many soft tissues such as articular cartilage, aorta, and smooth muscle. The polyester was found to be elastomeric. The elastomer showed excellent cytocompatibility *in vitro* and elicited minimal immune response *in vivo*. Three-dimensional porous scaffolds facilitated osteogenic differentiation and mineralization. This class of polyester derived from low cost, recycled waste and renewable sources may be a promising candidate for soft tissue engineering application and it may be also used in bone tissue engineering application after further improvement of its mechanical properties.



References

[1] Nerem, R. M. Tissue Eng. **2006**, 12, 1143-1150.
[2] Ingber, D. E.; Van C. M.; David, B.; Laura, N.; Johnny, H.; Jeremy, M.; Ioannis, Y.; David, K.; Gordana, V. N. Tissue Eng. **2006**, 12, 3265-3283.
[3] Shastri, V. P.; Andreas L. Adv. Mater. **2009**, 21, 3231-3234.
[4] Chatterjee, K.; Sun, L.; Chow, L. C.; Young, M. F.; Simon, C. G. Jr. Biomaterials, **2011**, 32, 1361-1369.
[5] McDougall, F. R.; White, P. R.; Franke, M.; Hindle, P. John Wiley & Sons. **2008**.
[6] Nikles, D. E.; Medhat, S. F. Macromol. Mater. Eng. **2005**, 290, 13-30.
[7] Panda, A. K.; Singh, R. K.; Mishra, D. K. Renew. Sust. Energ. Rev. **2010**, 14, 233-248.

Rheology and transport properties of thermosensitive pluronic-hyaluronic acid hydrogels

Setti Mahesh*, K. Jagadeeshwar and Abhijit P Deshpande
Department of Chemical engineering, IIT Madras, Chennai
*settimahesh@gmail.com

Thermoresponsive polymer gels are of interest due to applications as sensors, separation systems, drug delivery systems and in tissue engineering. Sol-gel transition, a solution at lower temperature to a gel at physiological body temperature is important. The transport of drug molecules in these gels has specific applications in pharmacology and medicine.

In a well known thermoresponsive gelling system of PEO-PPO-PEO triblock copolymers (pluronic), the process of gelation occurs due to the PPO-block of the pluronic chain, as it exhibits an increased hydrophobicity at elevated temperatures. With critical concentrations of pluronic and at physiological temperature, a close packed cubic lattice leading to the formation of a gel was reported[1]. The gelation temperature of pluronic depends on the length of the PEO and PPO blocks, the pluronic concentration, and the addition of salts or other additives. The addition of polysaccharides to pluronic, has been shown to affect the gelation temperature[2].

In this work, the gelation behavior and gel properties of pluronic in the presence of hyaluronic acid are being investigated. For pure pluronic at 17.5 weight % solution in water, at room temperature in the condition of a gel, the storage modulus is a function of frequency. For the same sample, a temperature sweep with 2 ^{0}C/min of heating rate, these material system showed a sudden transition from solution to gel at 24 ^{0}C. The effect of the addition of hyaluronic acid to pluronic for changes in the phase transition will be elucidated using small and large amplitude oscillatory rheology.

References:

[1] Prud'homme, R. K.; Wu, G.; Schneider, D. K. *Langmuir* **1996,** 12, (20), 4651-4659.

[2] Kjøniksen, A. L.; Calejo, M. T.; Zhu, K.; Nyström, B.; Sande, S. A. *J. Appl. Polym. Sci.* **2014,** 131, (13).

Fluorescent Galactomannan Nanoparticles for Individual Microorganism Sensing in Water Environment

Sumanta Kumar Ghosh*, Md. Farooque Abdullah, Arup Mukherjee$

92 A.P. C Road; Department of Chemical Technology; University of Calcutta

$*arupm1234@gmail.com*

Natural galactomannans for their inherent chemical constitution expresses unique engineering and biomedicinal properties. Cellular surfaces contain recognition receptors which senses and get attached to functional ligands and signal molecules like some amino acids and mannose. Pathogenic bacterium expresses more of mannose specific sites for enhanced pathogenicity. Nanoparticles in tunable size ranges can act more specifically in cellular attachments. We have developed guar galactomannan nanostructures and further functionalized with fluorescent rhodamine dye for low concentration bacterial detection in water environment.

Nanoparticles were extracted from purified native guar gum by a facile acid hydrolysis technique. The new galactomannan particles were characterized extensively in DLS, electron microscopy and FT-IR. Streaker reaction was followed to decorate the nanoparticles surface with amine spacers and subsequently fluorescent labeling was performed. Rhodamine isothiocyanate was covalently conjugated and the nanoparticles were evaluated for individual optical properties. Fluorescently labelled nanoparticles when incubated with very low number of viable bacterium in culture (E.Coli ATCC 8739), demonstrated altered optical characteristics. This was typically due to mannose receptor interactions. Intensity of particle absorbance in visible regions was observed as directly proportional with the microbial load. The remarkable alteration in optical properties is likely due to the molecular attachment and biochemical interaction of the cell with the functionalized galactomannan nanoparticles. The new nanoparticles are demonstrably efficient and facile tools in microbial contamination labeling and estimation in water environment.

Polyacrylamide grafted Barley (BAR-g-PAM): A novel flocculant

Kartick Prasad Dey and Sumit Mishra
Department of Chemistry, Birla Institute of Technolog,
Mesra, Ranchi 835215, Jharkhand, India.
E-mail: chem.kartick@gmail.com

Water treatment is an integral part of any industrial treatment before final discharge of effluents or for recycling purposes also. Flocculants are very effective for the separation of the colloidal particles even in minute dosage and are environmentally benign. They may be natural (e.g.,polysaccharides) or synthetic (e.g., polyacrylamide). Natural flocculants need high dosage and have shorter shelf life. Synthetic flocculants require less dosage owing to their relatively high molecular weight and large surface area. However, synthetic flocculants result in fragile flocs with the colloidal particles.

A novel flocculant, Polyacrylamide grafted barley (BAR-g-PAM) was successfully synthesized by conventional method using ceric ammonium nitrate(CAN) initiator. The grafting of PAM chains on the polysaccharide backbone was confirmed through various physicochemical techniques like intrinsic viscosity measurement, ^{13}C NMR spectra, FTIR spectroscopy, elemental analysis, SEM morphology, TGA study, number average molecular weight and aqueous solubility. Further, flocculation efficacy of the graft copolymers was studied in coal fine suspension through 'jar test' procedure, towards its possible application as a novel flocculant for treatment of coal washery effluent. BAR-g-PAM is reported as a novel flocculant which can be used for bulk treatment of coal washery effluents.

References:

[1] Bharti, S.; Mishra, S.; Sen, G. Carbohydrate Polymers.**2013**, 93(2), 528-536.
[2] Rani, G.U.; Mishra, S.; Sen,G.; Jha. U. Carbohydrate Polymers. **2012**, 90,784– 791.
[3] Sen, G.; Mishra, S.; Dey ,K.P.; Bharti, S. Journal of Applied Polymer Science. 2014, 131(22), 41046.

Hollow nanogel derived from dextrin and pAA for doxorubicin hydrochloride delivery

Dipankar Das and Sagar Pal*
Polymer Chemistry Laboratory, Department of Applied Chemistry,
Indian School of Mines, Dhanbad – 826004, India
E-mail: godisgood.das@gmail.com

Nanogels have attracted much interest because of their many potential applications, including as nanocarriers for drug and gene delivery. Herein we report a surfactant-free method for the preparation of biodegradable, biocompatible, and stimuli-responsive crosslinked hollow nanogels for anticancer drug, doxorubicin hydrochloride delivery. The nanogels were synthesized using dextrin, acrylic acid and MBA as crosslinker and Fe_3O_4 nanoparticle as template followed by removal of Fe_3O_4 from the generated cl-Dxt-pAA nanogel in a hydrochloric acid medium. Magnetite nanoparticles were prepared by coprecipitation from an Fe^{3+} and Fe^{2+} solution. Then folic acid and fluorescein isothiocyanate (FITC) were conjugated with carboxylic acid functionalized magnetite nanoparticles using 2,2-(ethylenedioxy)-bisethylamine. These folate-conjugated nanoparticles were characterized in terms of their size by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Surface functional groups and composition were analyzed by Fourier transform infrared (FTIR) spectroscopy, ^1H NMR, ^{13}C NMR analyses. Biodegradable nature of the nanogel has been confirmed using Aspergillus Niger fungus. The synthesized nanogel also demonstrates that it is non-cytotoxic in nature against human mesenchymal stem cells (hMSCs). Specific transports of doxorubicin by the nanogels into cancer cells and its biological activity as well as *in vitro* release are demonstrated. It is shown that under acidic condition more drug is released. The nanogels can thus not only specifically deliver doxorubicin to its target, but also release the drug depending on the pH.

Keywords: nanogels, hollow, crosslinker, biodegradable, biocompatible.

Reference

1. S. Mohapatra, S. K. Mallick, T. K. Maiti, S. K. Ghosh and P. Pramanik, Nanotechnology, 18, 2007, 385102 (9pp) , doi:10.1088/0957-4484/18/38/385102.
2. S. K. Sahu, S. Maiti, T. K. Maiti, S. K. Ghosh, P. Pramanik, Macromol. Biosci., 2010, 10, 000–000, DOI: 10.1002/mabi.201000353.

Grafting of Acrylamide onto Low Density Polyethylene (LDPE) Films Surface for Biomedical Applications

AkhtarJahan Siddiqa[1], Koel Chaudhury[2] and Basudam Adhikari[1*]
[1]Materials Science Centre, Indian Institute of Technology, Kharagpur, WB-721302, India
[2]School of Medical Science and Technology,
Indian Institute of Technology, Kharagpur, WB-721302, India
akhtariitkgp@gmail.com

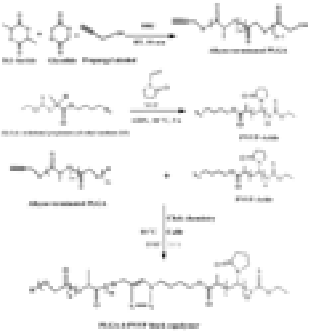
In the present investigation we have functionalized the surface of low density polyethylene (LDPE) film using acrylamide (AAm) via solution grafting technique. The surface chemistry, structure, roughness and wettability of modified LDPE film have been studied using ATR–FTIR spectrophotometry, scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurement, respectively. Subsequently, the films were screened on their fouling behaviour by cell adhesion and proliferation of HaCaT cells with different grafting times. Studies on biocompatibility of LDPE were also carried out. The degree of grafting of AAm was assessed by means of FTIR using a calibration curve. The functionalized film was found to be hydrophilic in nature as seen from its water contact angle (45°±2°). The degree of grafting was above 12.9, indicating that the functionalization procedure followed by us is effective. Scanning electron microscopy and AFM analysis revealed that remarkable surface structure was changed during grafting of LDPE. The grafted film was found to be non-toxic and biocompatible with Hacat cells as confirmed by the Alamar blue assay. Thus, it is understood that the AAm grafted LDPE film is a potential candidate for biomedical applications and also useful for other polar polymer surface coatings.

Keywords: Low density polyethylene (LDPE), Contact angle, Cell adhesion, Biocompatible.

Synthesis and Self-assembly of PLGA-*b*-PNVP AmphiphilicDiblock Copolymers for Targeted Drug Delivery of Doxorubicin in Cancer

K. Ramesh[1,2] , Sumit Kumar Hira[3], Partha Pratim Manna[3],
Nira Misra[1], Biswajit Ray[2*]
[1]School of Biomedical Engineering, Indian Institute of Technology
(Banaras Hindu University), Varanasi - 221005, India
[2] Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi - 221005, India
[3] Immunobiology Laboratory, Department of Zoology, Faculty of Science,
Banaras Hindu University, Varanasi - 221005, India
biswajitray2003@yahoo.co.in

Amphiphilic diblock copolymers poly (lactic-co-glycolic acid) -*b*-poly (*N*-Vinylpyrrolidone) (PLGA-*b*-PNVP) have been synthesized through click reaction of alkyne-terminated PLGA and azide-terminated PNVP (scheme). Polymers have been characterized by ^{1}H NMR and gel permeation chromatography. The critical miceller concentration (cmc)s of these block copolymers have been determined by fluorescence spectroscopy. To study the potential application of this diblock copolymer as micellernano-carrier in controlled drug delivery, an anticancer hydrophobic drugdoxorubicin (DOX) has been chosen as a model drug. UV-Vis, DLS and TEM studies support the successful loading of the drug. P^H-dependent in-vitro drug release study shows faster release at lower pH.DOX loaded diblock copolymer has been found to be significantly effective in controlling the tumor cell growth by retarding the tumor cell proliferation and caused lysis of the tumor cells compared to free DOX.



Strontium- Graphene Hybrid Nanoparticles in 3D Polymeric Scaffold for Bone Tissue Engineering

Sachin Kumar and Kaushik Chatterjee*
Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India
*kchatterjee@materials.iisc.ernet.in

Hybrid nanoparticles of graphene sheets decorated with metallic nanoparticles have been used to prepare polymeric composites or hybrid materials to synergistically leverage the properties of the individual components. However the potential advantage of using such graphene decorated hybrid particles for biomedical applications remains largely unexplored. Thus, the objective of this work was to prepare hybrid polymeric scaffold having graphene sheets decorated with bioactive strontium metallic nanoparticles and demonstrate its application in bone tissue engineering.

Strontium-decorated reduced graphene oxide (RGO_Sr) hybrid nanoparticles were synthesized by a facile reduction of graphene oxide and strontium nitrate. Synthesized RGO_Sr were characterized by X-ray diffraction, transmission electron microscopy (TEM), and atomic force. TEM showed RGO surface with well dispersed strontium (200-300 nm) nano metallic particles Thermal gravimetric analysis (TGA) was used analyse the composition of the RGO_Sr hybrid nanoparticles. TGA profile of RGO_Sr showed presence of 22 wt% of strontium on RGO surface. Also contact angle analysis of RGO_Sr flakes showed increased in hydrophilicity of RGO due to presence of metallic strontium on RGO surface. Poly (ε-caprolactone) (PCL) macroporous scaffolds reinforced with hybrid RGO_Sr nanoparticles were prepared by gas foaming technique. PCL/RGO_Sr scaffolds were used to evaluate osteoinductive properties using mouse osteoblasts (MC3T3). It was found PCL/RGO_Sr scaffold showed better osteoblast proliferation and mineralization than neat PCL and PCL/RGO scaffold. The release of strontium ion from PCL/RGO_Sr scaffold resulted in the increase biological activity. This study demonstrates that using graphene decorated metallic hybrid nanoparticles that elute bioactive strontium ions can be used to prepare next generation bioactive macroporous scaffolds with better biocompatibility and osteoinductive properties.

Terpolymer metal complexes: Synthesis, characterization, thermal degradation kinetics and antibacterial screening

M. Riswan Ahamed
Department of Chemistry, Oxford Engineering College,
Tiruchirappalli – 620 009, Tamil Nadu, India
polyrizwan@gmail.com

A new terpolymer ligand involving 2-amino-6-nitro-benzothiazole, melamine and formaldehyde (BMF) has been synthesized in the presence of DMF medium. The BMF ligand was characterized by elemental analysis and various spectral techniques like FTIR, UV-Visible, ^{1}H & ^{13}C NMR to elucidate the structure and properties of the terpolymer ligand. The BMF metal complexes were prepared using BMF ligand with some transition metal ions such as Cu^{2+}, Ni^{2+} and Zn^{2+} ions in the presence of ethanol medium. The prepared complexes have been characterized by elemental analysis and FTIR, electronic, ESR, ^{1}H & ^{13}C NMR spectral studies. The molecular weight of the BMF ligand and its metal complexes was determined by gel permeation chromatography (GPC). The surface features and crystalline behavior of the ligand and its complexes were analyzed by scanning electron microscope (SEM) and X-ray diffraction (XRD) methods. Thermal stability of the ligand and its metal complexes was studied by thermogravimetric analysis (TGA). Kinetic parameters such as activation energy (E_a) and order of reaction (n) and thermodynamic parameters *viz.* ΔS, ΔF, S^* and Z were calculated using Freeman-Carroll (FC), Sharp-Wentworth (SW) and Phadnis-Deshpande (PD) methods. Thermal degradation model of the terpolymer ligand and its metal complexes was also proposed using PD method. The antibacterial activities of the BMF ligand and its metal complexes were checked against chosen microbes such as *Shigella sonnei, Escherichia coli, Klebsiella* species, *Staphylococcus aureus, Bacillus subtilis*, and *Salmonella typhimurium*.

References:

[1] Riswan Ahamed, M.; Subha, R.; Jeyakumar, D.; Burkanudeen, A.R. Polym. Int. **2014**, doi: 10.1002/pi.4768.

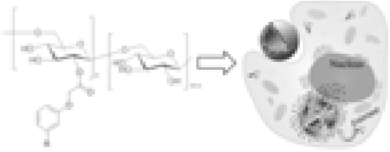
[2] Riswan Ahamed, M.; Burkanudeen, A.R. Adv. Polym. Technol. **2013**, 32, 1-16.

[3] Riswan Ahamed, M.; Burkanudeen, A.R. J. Inorg. Orgnomet. Polym. **2012**, 22, 1046-1061.

Dextran Nano-assemblies for Loading and delivering of Anticancer Drugs

Nilesh Deshpande, Thameez Mohammed, P. S. Pramod,
Manickam Jayakannan
Department of Chemistry, Indian Institute of Science Education & Research (IISER-Pune)
Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India

In the last two decades polymeric vesicles (polymerosome), have attracted rapidly growing interest based on their cell and virus mimicking dimension and potential application in the delivery of hydrophilic as well as hydrophobic anticancer drugs to tumor tissues.[1] The present work is emphasized to design dextran vesicular carriers using naturally available hydrophobic renewable resources for the molecular self-organization of dextran into vesicular assemblies or nanoparticles. These assemblies were anchored with enzyme and pH responsive functionalities to disassembly under the cancer tissue environment to release the loaded cargoes. The self-assemblies of the modified dextran were confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM), and Static Light Scattering (SLS) analysis. Dextran assemblies were found to be a unique dual carrier in which water soluble molecules (like Rhodamine-B, Rh-B) and polyaromatic anticancer drug (camptothecin, CPT) were selectively encapsulated in the hydrophilic interior and hydrophobic layer of the vesicles, respectively.[2,3] Doxorubicin (DOX) and camptothecin (CPT) were loaded in these dextran vesicles and their cytotoxicity was tested in breast and colon cancer cells. Confocal microscopic images confirmed that both DOX and CPT-loaded vesicles was taken up by cancer cells better than normal cells. The custom designed dextran vesicular provides new research opportunities for dual loading and delivering of hydrophilic and hydrophobic dug molecules.



References:

1. Pramod, P.S.; Takamura, K.; Chaphekar, S.; Balasubramanian, N.; Jayakannan, M.; *Biomacromolecules*, **2012,** *13*, 3627–3640.
2. Pramod, P.S.; Takamura, K.; Chaphekar, S.; Balasubramanian, N.; Jayakannan, M.; *Nanoscale*,**2014**, *6*, 11841–11855.
3. Sridhar, U.; Pramod, P. S.; Jayakannan, M. *RSC Adv.*,**2013**,*3*, 21237-21241.

Functional Block Copolymers Based on Poly(caprolactone)s: Synthesis and Self-assembly

Maitreyee Mhatre, Bapurao Surnar and Manickam Jayakannan
Department of Chemistry, Indian Institute of Science Education & Research (IISER-Pune)
Dr.Homi Bhabha Road, Pune 411008, Maharashtra, India

Aliphatic polyesters are important class of polymers for applications inbiomedical and pharmaceutical industry. Ring-opening polymerization (ROP) of cyclic ester is one of the extensively employed synthetic methodologies for aliphatic polyesters.[1] ROP facilitates formation of narrow molecular weight distribution (PDI) as well as block and graft copolymer architectures.[2] The present work highlighted the synthesis and structural analysis of new class of γ -substituted caprolactones. New carboxylic functionalized caprolactone monomer was synthesized through multi-step reactions. The ROP of γ- substituted caprolactoneperformed using $Sn(Oct)_2$ as a catalyst and mono-functional PEG as initiators.[3] The monomer and polymers were characterized by NMR, IR and Mass spectroscopic analysis. The molecular weights of the polymers were tuned based on the ratio of monomer/initiator as well as catalyst concentration.Selective syntheses of random co-polymers and substitutedPCL-PCL block copolymers were also achieved. Further, the roles of hydrophilicity / hydrophobicity on the molecular self-assembly of the newly developed block copolymers were investigated. Thus, the current design provides the new opportunity to tune the structure - property relationships of the new poly (caprolactone) block copolymer self-assemblies.

References:

1. Al-Hilal, T. A.; Alam, F.; Byun, Y. *Adv. Drug Delivery Rev*. **2013**,*65*, 845–864.
2. Rieger, J.;Bernaerts, K. V.; Du Prez, F. E.; Jérôme, R.; Jérôme, C. *Macromolecules***2004**, *37*, 9738–9745.
3. Surnar, B.; Jayakannan, M. *Biomacromolecules***2013**, *14*, 4377-4387.

Inverse Vulcanization of Elemental Sulphur using Cardanolmonomer

Swapnil Shukla,[a] Prasun Kumar Roy,[b*] and Bimlesh Lochab[a**]
[a]Department of Chemistry, School of Natural Sciences, Shiv Nadar University,
Gautam Budh Nagar,Uttar Pradesh 203207, India
[b]Centre for Fire, Explosive and Environment Safety, DRDO, Timarpur, Delhi 110054, India

In the face of depleting petroleum resources, monomers and chemical intermediates generated from petro-industry will become limited and expensive. Therefore, it has become imperative to explore the incorporation of naturally derived building blocks in polymeric frameworks.[1]However, ease of synthesis and commercial viability are important factors to be taken care of while designing such sustainable monomers. In this context, elemental sulphur(S) whichis generated in huge swathes from hydrodesulphurization processes during petroleum refining, makes its consumption challenging as a suitable polymeric building block.[2-3]On other hand, cardanol is derived during processing of cashew nut as an agro-waste. Cardanolwas chemically modified to benzoxazine monomer (Bzc).[4-6]The present work explores the utilization of both theseindustrial wastes, Sand Bzc as a feedstock for the synthesis of poly(S-*ran*-Bzc) via a simplistic, easy scalableand solventlessapproach.Inverse vulcanization of S with a high percentageof its incorporation (>50%)is demonstrated usingbulk polymerizationto form organo-soluble copolymers which were characterized by ^{1}H-NMR, Raman, DSC, TGA and GPC.

References:
[1] Lochab B.; Shukla S.; Varma I. K.; RSC Adv.,**2014**, 4, 21712-21752.
[2] ChungW. -J.;GriebelJ. J.;Kim E.-T.; YoonH.; SimmondsA. G.;JiH.-J.;DirlamP. T.; GlassR. S.;Wie J. -J.; NguyenN.- A.;GuralnickB. W.; ParkJ.;SomogyiÁ.;TheatoP.;Mackay M. E.; SungY.-E.; CharK.;PyunJ.;Nat. Chem., **2013**,5, 518-524.
[3] SimmondsA. G.;GriebelJ. J.; ParkJ.; KimK.-R.; ChungW.- J.;OleshkoV. P.; Kim J.; KimE.-T.; Glass R. S.; Soles C. L.; Sung Y. -E.; CharK.;Pyun J.;ACSMacroLett.*,* **2014,** 3, 229-232.
[4] Lochab B.; Varma I. K.;Bijwe J.; J. Therm. Anal. Calorim.,**2010**, 102, 769-774.
[5] Lochab B.; Varma I. K.;Bijwe J.; J. Therm. Anal. Calorim.,**2012**, 107, 661-668.
[6] Lochab B.; Varma I. K.;Bijwe J.; J. Therm. Anal. Calorim.,**2013**, 111, 1357-1364.

Physical evaluation and Formulation of Donepezil Oral thin films containing Cellulose Derivatives for Alzheimer's Disease

Keshireddy Anji Reddy, S. Karpagam*
Organic Chemistry Division, School of Advanced Sciences,
VIT University, Vellore – 632014, Tamilnadu, India
**skarpagam80@yahoo.com*

Donepezil hydrochloride oral thin films were prepared by solvent evaporation method using different natural polymers such as HPMC, sodium CMC. The various physical characteristics were evaluated for prepared films. The drug-polymer film was structurally analyzed by FT-IR and NMR spectroscopy. The surface morphology was observed by 3D atomic force microscopy (AFM). Influence of polymers and plasticizers on drug release was studied by *in-vitro* dissolutionparameters. Films containing combination of HPMC and sodium CMC were showed 95 % of cumulative drug release. But films containing HPMC alone was shown 80% and marketed formulation released 85% in 90min. From these results, enhanced dissolution rate, better patient compliance and effective therapy was achieved.

References

[1] Cristina, D. N. Carmen, B. Z. Iuliana, S. Valentina, C. Dana, O. D. J. Mol. Struct. **2013**, 1044, 262–267.
[2] Kyoung .A, Kim. Jong Lae. L, Clin**.** Ther. **2011.** 33.7-10.
[3] Sonal, S. Purna, C. Kasha, Int. J. Pharm**.2013**.453. 395– 399

In vitro study on Gelatin nano fiber based Oral drug delivery vehicle for hydrophobic drug

AninditaLaha, Shital Yadav, Saptarshi Majumdar,
Chandra Shekhar Sharma*
Department of Chemical Engineering, IITH, Hyderabad
*cssharma@iith.ac.in

The sole intention of the study is to develop a natural bio-degradable polymer based oral drug delivery vehicle to deliverhydrophobic drug in a sustained and controlled pattern under physiological conditions. Gelatin (type A) was used as an excipient for the same. The motivation behind choosing electrospun gelatin nanofiber mat as an oral drug delivery vehicle is due to their unique porous structure and high surface to volume ratio. Piperine, a bio enhancer is used as a model hydrophobic drug. We entrapped the drug molecules inside the hydrophilic nanofiber to increase the bioavailability of the hydrophobic drug. To increase the water resistive properties and to expand the lifespan of the mat, these were cross-linked with Glutaraldehyde (GTA) saturated vaporwithin few minutes. Varying crosslinking time, the porosity of fiber mat, as well as the degradation is also varied which ultimately provides a controlled and sustained release pattern. From FESEM study we got an idea of the effect of crosslinking on surface morphology.To investigate the interaction between drug and polymer matrix, ATR/FTIR analysis was done. Finally,*in vitro* release study was done maintaining the physiological conditions mimicking GI tract to analyze the effect of crosslinking on the drug release profile.The *in vitro* results showed that the drug release amount decreased with increase in crosslinking degree and with lower pH.Basically, we have designed an oral drug delivery vehicle in such a way so-that varying crosslinking degree and pH of the release medium, it can give the desired drug release profile and also can be used as a potential drug delivery carrier.

References:

[1]. Zhang,Y.Z; Venugopal,J; Huang, Z.M; Lim, C.T; Ramakrishna,S; Polymer.**2006**,47,2911–2917.
[2]. Laha, A.; Yadav, S.; Majumdar, S.; Sharma, C.S.; Coll. Surf. B (Submitted).

A simple approach of soluble Lead (II) removal using chemically modified guar gum

Abhijit Pal and Abhijit Bandyopadhyay*
Department of Polymer Science and Technology,
University of Calcutta, 92, A.P.C. Road, Kolkata – 700 009, India
abhijitpal@ymail.com

Acrylic acid grafted guar gum or GG-g-AA shows sharp polyelectrolytic character and that feature was used for adsorptive separation of soluble Pb (II) from contaminated water. Graft copolymerization of acrylic acid onto guar-gum was accomplished using potassium persulphate as initiator. Synthesis portion of the work was communicated and published independently. Adsorption studies were carried out in a thermostated orbital shaker using batch method at various temperatures, pH, adsorbate concentrations, agitation speeds, adsorbate-adsorbent contact times and adsorbent concentrations for optimization. The results showed on addition of only 10 ml of 0.25 wt% GG-g-AA at 40^{0}C removed nearly 95% of the contaminated Pb(II) from its initial concentration of 350 ppm within 75 min at a pH of 5.5. The adsorbed lead ions were settled at the bottom as precipitate and were removed through filtration. The data were fitted to standard adsorption isotherms which showed compliance with Langmuir isotherm model. Kinetic investigation showed that the adsorption followed pseudo second order kinetics.

Keywords: Adsorptive removal, Lead, Acrylic acid grafted guar gum, Homophase adsorption, Polyelectrolytic character.

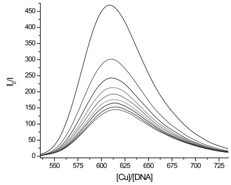
Related Articles:

[1] Pal. A, Nasim. T, Giri. A, Bandyopadhyay. A; Carbohydr. Polym. 110 (**2014**) 224 – 230.
[2] Min. M, Shen. L, Hong. G, Zhu. M, Zhang. Y, Wang. X, Chen. Y, Hsiao S. Benjamin; Chem. Eng. J. 197 (**2012**) 88–100.
[3] Ge. F, Li. M.M, Ye. H, Zhao. B.X; J. Hazard. Mater. 211– 212 (**2012**) 366– 372.
[4] Tofighy. M.A, Mohammadi. T; J. Hazard. Mater. 185 (**2011**) 140–147.
[5] Ghorai. S, Sinhamahpatra. A, Sarkar. A, Panda. A.B, Pal. S; Bioresour. Technol. 119 (**2012**) 181–190.

Spectroscopic characterization and Biological applications of four Copper(II)-Schiff base metal complexes

Chirantan Roy Choudhury*, Niladri Biswas
Department of Chemistry, West Bengal State University,
Berunanpukuria, Barasat, Kolkata – 700 126
E-mail: crchoudhury2000@yahoo.com

Schiff bases derived from aliphatic amine and carbonyl compound are important classes of ligand that coordinate to metal ion via azomethine nitrogen and have been studied extensively[1]. In azomethine derivatives, the C=N linkage is essential for biological activity and several azomethines have been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities[1]. Transition metal complexes that are suitable for binding and cleaving double stranded DNA are of considerable current interest due to their various applications in nucleic acid chemistry[2-3]. Based on these activities of Schiff base ligands, four copper (II) complexes were synthesized using ONO or OON donor Schiff base ligands derived from L-amino acids. All the complexes were characterized by elemental analyses, IR, electronic, EPR, and also by mass spectral studies. Magnetic susceptibility measurements of the complexes show magnetic moment very close to one electron system. DNA binding ability of the synthesized complexes was investigated using absorption and fluorescence spectroscopic studies, as well as by viscosity measurements. The binding constant (K_b) values for all the complexes were calculated from the absorption spectra and from fluorescence spectra the apparent binding constant (K_{app}) values were calculated. From the above K_b and K_{app} values, the binding of the complexes to CT-DNA is revealed to be through classical intercalative mode. The large enhancement in the relative viscosity of DNA on binding to the complexes supports the proposed DNA binding mode.



References:

[1] Vigoto, P.A.; Tamburini, S. Co ord.Chem.Rev. **2004,** 248 , 1717.

[2] Sigman, D. S.; D. R. Graham; D'Aurora V.; Stern A. M., J. Biol. Chem. **1997**, 254 , 12269.

[3] Barboin, C. T. ; Luca, M. ; Pop, C.; Brewster, E.; E. Dineulescu,; M. Eur. J. Med. Chem. , **1996**,31, 597.

Ratiometric Sensing of Serum Albumin Using a Novel Organic Salt

Susmita Das, Amrita Basu and Amitava Patra*
Department of Materials Science, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700032, India

Serum Albumin is the most abundant plasma protein in mammals. Low level of albumin in the blood is referred to as hypoalbuminemia and is indicative of cirrhosis of liver and persistent excretion of albumin in urine indicates kidney disorder normally observed in patients with diabetes and hypertension. Therefore, its accurate detection in blood samples as well as in urine is extremely important for treating pathological conditions. Herein we report a highly sensitive detection (LOD 220 nM) of serum albumin using a novel fluorescein based fluorescent organic salt by use of a ratiometric approach in phosphate buffer at various pH conditions including physiological pH. Ratiometric approach for detection is generally more preferred as it excludes interferences in complicated physiological media. Fluorescence and circular dichroism results indicate insignificant change in secondary structure of serum albumin in presence of the fluorophore suggestive of its non-invasive characteristics. Steady state fluorescence measurements indicate FRET between serum albumin and the fluorophore resulting into a linear correlation between the intensity ratios and protein concentration.

Synthesis of PEG Containing Cationic Block Copolymers with Different Architectures and their Interaction with Biomacromolecules

Debabrata Dey,[a] Rakesh Banerjee,[a] Santosh Kumar,[b]
Souvik Maiti,[b] Dibakar Dhara[a]*
aDepartment of Chemistry, Indian Institute of Technology Kharagpur,
West Bengal 721302 India
bProteomics and Structural Biology Unit, Institute of Genomics and Integrative Biology,
CSIR, Mall Road, Delhi 110007 India
*Email: dibakar@chem.iitkgp.ernet.in

Interactions between cationic polymers with biomacromolecules like DNA and Human serum albumin (HSA) have gained tremendous research interest across the world due to their potential medical and engineering applications.On the other hand, recent advancement in controlled radical polymerization technique providesnovel approach to synthesize block copolymers with different architectures. We have synthesized two sets of PEGylatedcationic copolymers – linear block copolymers (BCPs) andbottle-brush copolymers (BBCPs) - bysequential polymerization of (3-methacrylamidopropyl) - trimethylammonium chloride (MAPTAC) and poly(ethylene glycol) based monomers (PEGs with M_n= 480, 5000 D respectively) employing RAFT polymerization technique.After characterization of the polymers, we have studied the interaction behavior of these copolymers with nucleic acid (DNA) and protein (HSA). Equilibrium studies were done using UV-visible, steady-state fluorescence spectroscopy, circular dichroism (CD), gel electrophoresis and dynamic light scattering (DLS) techniques.Kinetic studies were performed by stopped-flow fluorescence technique. Results showed that at physiological pH, PEG containing cationic blocks interact with negatively charged DNA more strongly compared to PMAPTAC homopolymer where PEG content is nil. Here, hydrophobic interaction between PEG and DNA acts in a synergetic manner in addition to normal electrostatic binding force. Stopped-flow fluorescencetechnique was employed to monitor the fast kinetic pathway of the binding process. All the results of BCP-DNA binding studies suggested a two-step reaction mechanism - a rapid electrostatic binding between the cationic blocks and DNA, followed by a conformational change of the polyplexes in the subsequent step that led to DNA condensation. The relative rate constant (k_1') of the first step was much higher compared to that of the second step (k_2'). The charge ratios as well as the PEG contentwith different architectures in the cationic blocks had marked effect on the kinetics of the DNA-BCP polyplex formation.On contrary, cationic BCPs-HSA interactionresults revealed that at physiological pHmaximum binding affinity is between HSA and PMAPTAC while the binding efficiency decreases with increasing PEG content in the resultant blocks.Here, PEG containing block copolymers efficiently prevents, to some extent, perturbation caused to the polypeptide chain as a result of interactions with the cationic polymers.The details of the results including the effect of polymer architecture will be presented.

Stabilization of Chitosan-*grafted*-polyacrylamide/Silver nanoparticles through PEGylation for Efficient Antimicrobial Activity

SovanLal Banerjee[a,b], Kishor Sarkar[c], Moumita Khamrai[b], PP Kundu[b], Nikhil K. Singha[a]

[a] Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India.
[b]Department of Polymer Science and Technology, 92 A.P. C. Road, University of Calcutta, Kolkata, India
[c]Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India

Present work deals with a one-step rapid synthesis of polymer stabilized silver nano particles (Ag Nps) in a neutral medium by the reduction of aqueous 0.01M $AgNO_3$ solution using aqueous blend of chitosan-graft-polyacrylamide / polyethyleneglycol (CTS-g-PAAm/PEG) as a reducing and stabilizing agent. The UV-vis spectroscopic analysis was used to characterize the formed Ag Nps which showed a maximum absorbance at 420 nm. The CTS-g-PAAm was synthesized by using grafting from technique. Fourier transform infrared (FTIR) and^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy were used to characterize the prepared CTS-g-PAAm. The X-ray diffraction (XRD) analysis exhibited the characteristic Bragg's peaks at a diffraction angles of 38.25°, 46.35°, 64.65° and 76.92° having the Miller indices of 111, 200, 220 and 311 respectively. This indicated the crystallinity of Ag Nps. Again, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were utilized to study the surface morphology and shape of Ag Nps in presence of CTS-g-PAAm/PEG. The results indicated that the synthesized Ag Nps were spherical in shape having the particle size in the range of 5-50 nm. Dynamic light scattering (DLS), FESEM and TEM analysis indicated that the Ag Nps formed by CTS-g-PAAm/PEG were more stable and lower in size than CTS-g-PAAm stabilized Ag Nps. A comparative study of antimicrobial activity of CTS-g-PAAm/PEG and CTS-g-PAAm stabilized Ag Nps were also carried out against six micro-organisms (Alkaliphilus, Bascillussubstillis, Lysinibascillus, Enterobacteraerogenus, Vivbriovulnificus and Escherichia coli) and it was observed that the CTS-g-PAAm/PEG/Ag Npswere more effective than that of CTS-g-PAAm/Ag Nps.

Keywords: Chitosan-graft-polyacrylamide (CTS-g-PAAm), polyethyleneglycol (PEG), chitosan-graft-polyacrylamide/polyethylene glycol solution blend (CTS-g-PAAm/PEG), silver nano particles (Ag Nps) and antimicrobial activity.

References:

1. Rinaudo, M. Chitin and chitosan: Properties and applications. Prog. Polym. Sci. 2006, 31, 603–632.
2. Anna Regiel, Silvia Irusta, AgnieszkaKyzioł, Manuel Arruebo, Jesus Santamaria, Preparation and characterization of chitosan–silver nanocomposite films and their antibacterial activity againstStaphylococcus aureus, Nanotechnology, 2013, 24, 015101 (13pp).
3. Shameli, K.; Ahmad, M.B.; Zargar, M.; Yunus, W.M.; Ibrahim, N.A.; Shabanzadeh, P.; Moghaddam, M.G. Synthesis and characterization of silver/montmorillonite/chitosan bionanocomposites by chemical reduction method and their antibacterial activity. Int. J. Nanomed.2011, 6, 271–284.
4. Kong, M., Chen, X.G., Liu, C.S., Liu, C.G., Meng, X.H., Yu, L.J., Antibacterial mechanism of chitosan microspheres in a solid dispersing system against E. coli. Colloids and Surfaces. B, Biointerfaces, 2008, 65, 197–202.

Synthesis of a novel pH responsive phyllosilicate loaded polymeric hydrogel based on poly (acrylic acid-co-N-vinylpyrrolidone) and polyethylene glycol: Modelling and kinetics study for sustained release of antibiotic drug

Sayan Ganguly, Narayan Ch. Das*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

Hydrogels are one of the forth coming families of polymer-based sustained-release drug delivery systems. Besides displaying swelling-controlled drug release, hydrogels also show stimuli responsive deformational attitude in their morphological network and the drug release.PEG hydrogels have been widely explored as water-soluble biocompatible, non-toxic, non-immunogenic and level of bioadhesive polymer for numerous biomedical and pharmaceutical applications. In this study, we developed the novel pH-sensitive composite semi-interpenetrating polymeric network (IPN) hydrogel based on polyethylene glycol (PEG), poly (acrylic acid-co-N-vinylpyrrolidone) crosslinked with N,N-methylenebisacrylamide (MBA). These composite is used in the controlled release (CR) of cefadroxil, an antibiotic drug. A systematic method via in-situ polymerization in sodium aluminosilicate dispersion media is also performed in order to achieve much higher degree of swelling behaviour followed by sufficient gel strength in the simulated pH atmosphere. The resulting hydrogel imprinted was characterized by Fourier transform infrared spectroscopy (FTIR) to confirm the copolymer formation and cross linking reaction and scanning electron microscopy (SEM) to understand the surface morphology. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were also used for investigating deviations from crystallinity and swelling experiments. In vitro release of the drug loaded hydrogel results performed in acidic and basic media affected the drug release characteristics. Release data have been analyzed using an empirical equation to understand about the transport of drug containing solution through the polymeric matrices. The wt% of PEG, MBA, initiator, total monomer concentration, pH of the medium was found to strongly influence the drug release behaviour of the gels. Impression of drug loading on encapsulation efficiency was also investigated. The release rate of the drug was much faster at pH of 7.8 than at pH 1.7.Modelling and kinetics of sustained release of antibiotic was reported.

Key words: polyethylene glycol, poly (acrylic acid-co-N-vinylpyrrolidone), composite hydrogel, synthesis, characterization, drug release

Synthesis And Characterization Of Polysaccharide Based Ternary Hydrogel As Matrix For Potential Application in Tissue Engineering

Sridhar Sanyasi[1*], Satish Kumar[1], Chandan Goswami[2],
Abhijit Bandyopadhyay[3], Luna Goswami[1]
[1] School of Biotechnology, KIIT University, Patia, Bhubaneswar 751024, India
[2] School of Biological Sciences, NISER, Bhubaneswar 751005, India
[3]Department of Polymer Science and Technology,
University of Calcutta, 92, A.P.C.Road, Calcutta 700009, India
[*] *Email: sridhars2002@gmail.com*

Bone remodelling by tissue engineering is a realistic option relevant in several bone related patho-physiological situations such as osteoporosis, bone tumor, bone cancer or abnormal bone development (1). So far these possibilities are hindered due to lack of proper natural and biodegradable surface on which bone-precursor cells can adhere efficiently and grow further (2). Recent progress in tissue engineering research has revealed tremendous potential and new perspectives for the novel biocompatible materials for making scaffolds and tissue engineering constructs for the treatment of bone related disorders. In this context biomaterials/hydrogels have potential to address the bone disorder related ailments. The hydrogels as biomaterial essentially requires hydrophobic-hydrophilic balance to find application in tissue regeneration and drug delivery. In this work we report the synthesis a new ternary hydrogel from natural polysaccharides which can be used as effective surfaces for bone tissue engineering and controlled drug delivery. In this project we have synthesised a ternary hydrogel by grafting two different synthetic monomer namely 2-HEMA and Acrylic acid (AA) into a semi-synthetic biopolymer Carboxy Methyl Tamarind (CMT) Polysaccharide. The hydrogel was prepared by varying the mole ratios of monomers with respect to CMT by radical polymerization reaction. The synthesized hydrogels were characterized by several physico-chemical analysis such as UV spectroscopy, FT-IR spectroscopy, ^{1}H-NMR, swelling kinetics, DLS, FE-SEM etc. We further demonstrate that this material is suitable for effective adhesion, growth and further clustering of bone precursor cells (RAW 264.7). This material is also compatible for growing other sensitive cells demonstrating non-cytotoxicity. We suggest that the hydrogel matrix can be suitable for bone tissue engineering and thus may have clinical as well as commercial application in future.

Keywords: CMT, ternary hydrogel, tissue engineering, bone-precursor cells.

References:

1. Nauth A., McKee M. D., Einhorn T. A., Watson J. T., Li R., Schemitsch E. H. Managing bone defects. *J Orthop Trauma* (2011), *25*, 462-466.
2. Sanyasi S, Kumar A, Goswami C, Bandyopadhyay A, Goswami L. A carboxy methyl tamarind polysaccharide matrix for adhesion and growth of osteoclast-precursor cells. *Carbohydr Polym*. (2014), 101, 1033-42.

Stress/CO2 induced morphology development during solid-state foaming of Poly (Lactic-acid) with high pressure CO2

Sabapathy Sankar, Anup K. Ghosh *
Centre for Polymer Science & Engineering, Indian Institute of Technology Delhi,
HauzKhas, New Delhi- 110016, India.
** anupkghosh@gmail.com*

Poly (Lactic acid) samples were foamed at their solid-state by high pressure CO2. In-situobservation of tri-axial stresses and their effect on solid-state nucleation in CO2 treated sampleswere investigated by polarized optical microscopy. Isothermal crystallization studies of CO2treated samples were carried out at different temperatures and their corresponding crystallinemorphologies were reported. The CO2 treated samples crystallized at higher temperatures hadinterconnected highly compacted crystalline structures with various degrees of compactness. It is

found that the development of low order primary crystalline structures and their spontaneousransformation into compacted crystalline structures lead to anisotropic crystalline morphology.Results indicate that high pressure foaming process can be used to prepare interconnectedcrystalline morphology by controlling the foaming temperature of CO2 treated samples.

Efficient approach to prepare multiple chemotherapeutic agent conjugated nanocarrier

Vijayakameswara Rao N and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

A pH-responsive, multiple chemotherapeutic agent derived nanocarrier has been synthesized by conjugating doxorubicin, indomethacin, and folate to the backbone of norbornene polymer. Drug molecules are connected to the norbornene backbone by an ester linker to demonstrate the pH-responsive capabilities. The complete chemical and biological properties of the new norbornene-based polymeric nanocarrier, intended for combination cancer chemotherapy, are discussed.

References:

1. Rao, V. N., Mane, S. R., Kishore, A., Das Sarma, J., Shunmugam, R. Biomacromolecules.**2012,** 13, 221-230.
2. Rao, V. N., Kishore, A., Sarkar, S., Das Sarma, J., Shunmugam, R. Biomacromolecule*s*. **2012**, 13, 2933–2944.

Review of Developments in Advanced Medical Biopolymers

Aditi S. Marathe[1*], Dr. Sanjay C. Marathe[2], Dr. Parag P. Raut[3]
[1]Dept. Of Polymer & Surface Engineering, Institute Of Chemical Technology, Mumbai400019
[2]Dept. Of Botany, ICLES' Motilal Jhunjhunwala College, Vashi, Navi Mumbai 400703
[3]Asst. Manager (application development), Connell Bros.Co (india) Pvt.Ltd., Mumbai 400038
*aditi.marathe92@gmail.com

Biopolymers are polymers that are produced by living organisms and constitute a special class of polymers that are biodegradable in nature. Biopolymers that are employed for medical applications are classified as `advanced medical biopolymers'. Cellulose is the most common biopolymer on Earth. Biopolymers can be sustainable, carbon neutral and are always renewable, because they are made from plant materials which can be grown indefinitely. Unlike synthetic polymers which feedstock can be derived from petrochemicals or chemical processes, biopolymers are produced from renewable resources such as plant/living organisms. They can be degraded by natural processes, microorganisms and enzymes down to elemental entities that can be resorbed in the environment. Biopolymers thus offer the possibility to create a sustainable industry and reduce CO_2 emissions. The use of biopolymers in the medical field is a relatively new and emerging area of research. Biopolymers are widely used to develop biopolymer-based biomaterials in fields such as orthopaedics, cardiology, and general surgery. Biopolymers are an alternative to petroleum-based polymers (traditional plastics).The belief is that biodegradable polymer materials will reduce the need for synthetic polymer production (thus reducing pollution) at a low cost, thereby producing a positive effect both environmentally and economically. This paper is intended to provide a brief outline of the work in the area of biopolymers, application of these materials and the future work that awaits.

References:

[1] Analava Mitra and Baishakhi Dey, Indian Journal Pharm Sci, **2011** July-Aug, 73(4):355-366.
[2] Phillip Presley, J. The Use of Biopolymers in the Medical World, October 14, **2013**
[3] Pradip Kumar Dutta et al, J Scientific & Indian Research, Vol:63, January **2004**:20-31

Fabrication and characterization of curcumin loaded carboxymethylated guar gum grafted gelatin film for advanced tissue engineering research

Piyali Jana Manna[1], Tapas Mitra[1], P. P.Kundu[1*]
[1]Department of Polymer Science & Technology, University of Calcutta, University College of Science & Technology, 92, A.P.C road, Kolkata – 700009, West Bengal (India)
piyalijana1985@gmail.com

Guar Gum (GG) is a natural and non-ionic polysaccharide that, due to its physicochemical properties, is extensively investigated for biomedical applications as a matrix for cutting edge drug delivery. The purpose of this work was to develop new additive combinations between carboxymethylated GG (CMGG) grafted gelatin and curcumin as an antimicrobial compound. GG with molecular weights ranging from 74 to 210 kDa was modified to carboxymethylated GG (CMGG) with monochloro acetic acid in presence of sodium hydroxide and isopropanol/water mixture. The prepared CMGG was further grafted with the free $-NH_2$ group of gelatin using carbodiimide chemistry to prepare an antimicrobial film and characterized using FTIR/ATIR, DSC, TGA, SEM and XRD. The ^{1}HNMR and FTIR/ATIR analysis were performed to ensure the modification of GG to CMGG and the maximum 45% of amine group interaction was observed for CMGG conjugated gelatin. CMGG conjugated gelatin film showed three times higher tensile strength than that of native GG. Curcumin drug was isolated for the present study using conventional process and was blended with CMGG conjugated gelatin film for in vitro drug release study. About 50% of curcumin was released from CMGG conjugated gelatin film after 5hrs when incubated in phosphate buffer at physiological pH. In vitro cell line studies using fibroblast cell revealed that there is no cytotoxicity of the prepared CMGG conjugated gelatin film and curcumin loaded CMGG conjugated gelatin film. Finally the antimicrobial study was revealed the appreciable antimicrobial property against gram positive and gram negative bacteria of the prepared curcumin loaded CMGG grafted gelatin film.

Conjugated polyelectrolyte based selective detection of copper and pyrophosphate in physiological conditions:Monitoring alkaline phosphatase activity and multiple cell imaging

Akhtar H. Malik[a],Sameer Hussain[a], Arvin SainTanwar[a] and
Parameswar K. Iyer*[a]
[a]Department of Chemistry, IITGuwahati, Guwahati
*gmmakhtar@gmail.com,pki@iitg.ernet.in

Conjugated polymers with extendedπ -electron system and receptors in the side chain or main chain have been widely used as chemical and biochemical sensors. A novel anionic polyfluorene derivative PFT displays selective "turn-off/turn-on" fluorescence responses towards Cu^{2+} and pyrophosphate (PPi) in aqueous media. High sensitivity of polymer PFT for Cu^{2+} was verified *via* Stern-Volmer plot. The detection limit calculated for PPi using PFT was significantly high at ppb levels. Remarkably, PFT showed high selectivity for PPi over inorganic phosphate (Pi), the most common interfering substrate for PPi; and several other organic phosphates. Since, PPi is a unique substrate for alkaline phosphatase (ALP) enzyme, PFT based fluorescent assay was designed to monitor its activity. Urinary PPi acts as a biomarker in several urinary disorders; detection of PPi by PFT was performed in urine samples to explore the practicability of system in urinary diagnosis. Furthermore, its viability in cellular systems was confirmed by *ex-vivo* imaging studies performed in mouse macrophage and human breast cancer cells.

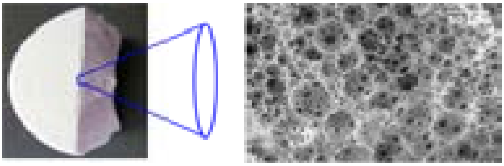
References:

[1] Zhu,C.;Liu, L.; Yang, Q.; Lv, F.; Wang, S.Chem. Rev. **2012**, 112, 4687–4735.
[2] Rao, L. O.;Morghom,G. M. M. Enzyme **1986**, 35, 57-63.
[3] Lorente, J. A.;Valenzuela, H.;Morote,J.;Gelabert, A. Eur. J. Nucl. Med. Mol. Imaging **1999**, 26, 625-632.

Porous hydrogels by inverse-high internal phase emulsion (i-HIPE) polymerization as scaffold\ for tissue engineering

Archana nalawade,[1] Ravindra ghorpade,[2] Mohammad Qureshi,[1*] Surendra Ponrathnam,[2] Nayaku Chavan,[2]
[1] Chemical Engineering and process Development Division, NCL, Pune
[2] Polymer Science Engineering Division, NCL, Pune
*ms.qureshii@ncl.res.in

Emerging field of tissue engineering aims to regenerate damaged tissue with the highly porous scaffold material with the requisite properties which acts as template for tissue regeneration[1]. We have synthesized the porous hydrogels using inverse high internal phase emulsion polymerization for use as scaffold for tissue engineering[2]. The interconnected pore architectures, porosity and surface area of hydrogels were characterized by scanning electron microscopy, mercury intrusion porosimetry and BET nitrogen physisorption method. SEM studies revealed that the porous architecture of hydrogels has pores diameter in 20-35 µm range with interconnecting pore throats of 5-10 µm. Porosities of samples were ranging from 92-97 % The swelling ratio of hydrogels has shown the increasing trend with respect to addition of HEMA. The biocompatibility studies were performed on hydrogels according to ISO-10993-5 criteria and were found compatible materials for soft tissue engineering applications. These porous hydrogels highlight the great potential as scaffold material.



References:

[1] O'Brien, F. Materials Today, **2011**, 14, 88 – 95.
[2] Zhang, H.; Cooper, A. Soft Matter**, 2005**, 1, 107.

Detoxification of Bone Cement by free radical scavenging with Natural Antioxidant

Govinda Kapusetti[1,2], C. K. Balavigneswaran[1], Shilpa Jaiswl[1],
Nira Misra[1] and Pralay Maiti[3]
[1]School of Biomedical Engineering, Indian Institute of Technology (BHU),
Varanasi-221005, Uttar Pradesh, India
[2]National Institute of Pharmaceutical Education & Research,
Ahmadabad-380054, Gujrat, India
[3]School of Materials Science & Technology, Indian Institute of Technology (BHU),
Varanasi-221005, Uttar Pradesh, India
nmishra.bme@iitbhu.ac.in

New formulation of Bone cement based on Natural antioxidant has been developed to avoid adverse affects of free radicals, which are present in the pristine bone cement. Generally, Poly(methyl methacrylate) (PMMA) based bone cement, being used as grouting material in joint replacement surgeries. It contains MMA monomers and toxic free radicals such as benzyl peroxide and *N,N*-Dimethyl-p-toluidine. Mangiferin was extracted from bark of *Mangifera Indica* (mango tree) by solvent extraction technique. Varying percentages of Mangiferin to pristine bone cement exhibited considerably low exothermic temperature, reduced almost by 10°C (1 wt%) arising from polymerization. Enhanced mechanical properties were achieved with mangiferin-bone cement (Mg-BC) compared to pristine Bone Cement due to higher polymerization there by increased molecular weight. Higher free radical scavenging nature of mangiferin was revealed through DPPH assay. Cytotoxicity of Mg-BC was evaluated through *in vitro* cell culture studies and shown superior biocompatibility than pure bone cement.

Controlled release of anti-cancer tamoxifen in human breast cancer cell using regulated poly (lactic-co-glycolic acid) nanoparticles

Sanjeev K. Pandey[1], Dinesh K. Patel[2], Ravi Thakur[3],
Durga P. Mishra[3], Chandana Haldar[1], and Pralay Maiti[2]
[1]Department of Zoology, Faculty of Science, Banaras Hindu University,
Varanasi 221 005, India
[2]School of Materials Science and Technology, Indian Institute of Technology
(Banaras Hindu University), Varanasi 221 005, India
[3]Cell Death Research Laboratory, Division of Endocrinology,
Central Drug Research Institute, Lucknow - 226031, India
Email: pmaiti.mst@itbhu.ac.in

Tamoxifen (Tmx) is an estrogen receptor modulator which is used chronically for the treatment of estrogen receptor positive breast cancer. Chemotherapy is a very complicated and high risk procedure due to its severe side effects. Hence, drug delivery systems may help to overcome adverse side effects by increasing local concentration of the drug at the receptor site.

This study was carried out to synthesize tamoxifen (Tmx) embedded in poly(lactic-co-glycolic acid) (PLGA) nanoparticles to demonstrate anti-cancer efficacy using human breast cancer cells. PLGA-Tmx were synthesized by using novel emulsified nanoprecipitation technique with varying dimension of 20 to 38 nm of drug implanted nanoparticles with 70% entrapment efficiency by changing polymer, emulsifier and drug concentrations. Nanoparticles dimension has been measured through transmission electron microscopy indicating networking of particles along with larger size at higher concentration of PLGA. Particle nature has also been confirmed through scanning electron and atomic force microscopy. The release rate of drug from PLGA-Tmx nanoparticles was found to be greatly sustained for larger particle dimension (38 nm). Interactions between tamoxifen and PLGA have been verified through spectroscopic and calorimetric methods. Delayed diffusion and stronger interaction in large nanoparticles caused the sustained delivery of drug from the polymer matrix. *In-vitro* cytotoxicity study indicate the killing of 50% breast cancer cell in just one day at very low concentration of 5 mg/ml of drug while the similar destruction of cell requires 5 days in smaller particle (20 nm). On contrary, only 20% cells are killed in similar time with larger size (38 nm) of nanoparticles of PLGA-Tmx arising from its sustained release kinetics revealing novel vehicle for the treatment of breast cancer by reducing adverse side effects.

Micellar medium-a tool for identification of transients in laser flash photolysis

Adity Bose*[1], Samita Basu[2]
[1]Department of Chemistry, Presidency University
86/1 College Street, Kolkata 700073, India
[2]Chemical Sciences Division, Saha Institute of Nuclear Physics,
Block - AF, Sector - 1, Bidhannagar, Kolkata, West Bengal 700064, India
*adityc17j@gmail.com

Electron transfer (ET) and H atom transfer/H abstraction (HA) are two very important modes of reactions in biological systems. I have been working with different nucleic acid bases and their nucleosides separately with two quinone molecules 2–methyl 1, 4-naphthoquinone, commonly known as menadione (MQ) and 9,10-anthraquinone (AQ) which can be considered as model anticancer drugs. Nucleic acid bases and their nucleosides generally serve as electron donors and quinone molecules as electron acceptors in an ET reaction. But detection of the exact transients often becomes difficult as they often absorb around similar regions. In this respect application of a magnetic field within micellar medium proves helpful. For proper utilization of electron transfer, the photogenerated ions should be prevented from subsequent rapid recombination, a prevalent event in homogeneous media. Organized assemblies such as micelles can prolong the lifetime of charge-transfer states and thus increase the efficiency of charge separation by partitioning of the reactants and/or products. These microheterogeneous systems provide a fundamental understanding of how electron transfer dynamics is influenced by restricted system geometry. Magnetic field effect (MFE) is basically the interplay between spin dynamics and diffusion dynamics. By diffusion, the radical ion pairs can separate to an optimum distance where the exchange interaction becomes almost zero. In this situation, the electron-nuclear hyperfine coupling induces efficient mixing between the triplet and the singlet states. The application of an external magnetic field removes the degeneracy of the triplet states and reduces intersystem crossing thus resulting in an increase in the population of the initial spin state. Hence application of MF leads to an increase in absorption of the radicals. This helps in the proper identification of the transients and hence the proper reaction channel.

References:

1. Steiner, U. E.; Ulrich, T. Chem. ReV. **1989**, *89*, 51-147.
2. Bhattacharya, K.; Chowdhury, M. Chem. ReV. **1993**, 93, 507-535.
3. Dynamic Spin Chemistry magnetic controls and spin dynamics of chemical reactions; Nagakura, S.; Hayashi, H.; Azumi, T., Eds.; Kodansha Ltd.: Tokyo**, 1998**.
4. Gould, I. R.; Turro, N. J. ; Zimmt, N. B. ; AdV. Phys. Org. Chem.,Vol. 20, Academic Press: London, **1980**
5. A.Bose, S. Basu**,** J of Mol. Liq. **2014**, 191, 92–99

The interaction nature of Hydroxy Propyl Cellulose (HPC) with Cationic and Anionic Surfactants Including Bile Salts

Anupam Das Burman[1] and A. R. Das[2]
[1] Regent College, Gulshan, Dhaka, Bangladesh
[2] Indian Association for the Cultivation of Science, Kolkata- 700032, India
E-mail:adasburman24@yahoo.com

In presence of neutral polymer hydroxy propyl cellulose (HPC), micellar behaviors of cationic surfactants, hexadecyl trimethyl ammonium bromide (CTAB), tetradecyl trimethyl ammonium bromide (TTAB), dodecyl trimethyl ammonium bromide (DTAB), and anionic surfactants, sodium dodecyl sulfate (SDS), sodium cholate (NaC), sodium deoxycholate (NaDC), sodium taurodeoxycholate (NaTDC) have been investigated using microcalorimetric, conductometric, and fluorimetric methods. The critical aggregation concentration (CAC), critical micelle concentration (CMC), saturation concentration (C_2) and extent of binding of the surfactants with polymer and association of the counterions (*g*) are obtained from the calorimetric and conductometric results. The thermodynamic properties of the critical aggregation concentration (ΔG^0_{agg}, ΔH^0_{agg}, ΔS^0_{agg} and $\Delta G^0_{(PS)1}$) and critical micelle formation ($\Delta G^0_{mic.}$, $\Delta G^0_{mic\text{-}pol.}$, $\Delta H^0_{mic\text{-}pol.}$, $\Delta S^0_{mic\text{-}pol.}$, and $\Delta G^0_{(PS)2}$) are evaluated from microcalorimetric and counterion condensation data. The conductometric studies yield the extent of counter-ion condensation of TTAB and DTAB which are considerably higher than that of CTAB as well as SDS and those of the bile salts are extremely low in the polymer domain. The micellization process is influenced by the hydrophobicity of the polymer and surface charge of the surfactant. The extent of binding of the bile salts with polymer is found to be higher than the other synthetic surfactants. The fluorescence results provide an idea of the decreasing micro-polarity with increasing surfactant concentration and the decreasing trend of I_1/I_3 (micro-polarity) in the bile salts is conspicuous compared to the ordinary surfactants studied.

Studies on Poly (3,4-ethylenedioxythiophene) Thin Films as Potential Transparent Conductor and as Electrochormic Material

Anil Kumar
Chemistry Department, National Center for Photovoltaic Research & Education (NCPRE),
Center for Excellence in Nanoelectronics (CEN), IIT Bombay, Mumbai, India
anilkumar@iitb.ac.in

Since the invention of electronic conductivity in otherwise insulating synthetic polymers in last three decades, conjugated polymers have evolved from the academic curiosity to one of the most important commercial material for wide ranging applications in many modern optoelectronic devices such as Displays, Photovoltaics, Field Effect Transistors (RF tags), Chemical and biological sensors etc. Organic electronics is leading this new revolution of so called "pervasive electronics" wherein the electronic devices are becoming more and more personal with each passing year and soon will become an integral part of our life. The total market size for "Organic Electronics and Electrics" has been projected to be of USD 96 Billions by year 2020. This is possible because of the low cost of materials as well as low fabrication cost. In this direction development of transparent conductors based on conjugated polymers to replace ITO has attracted significant attention. In this direction, poly(3,4-ethylenedioxythiophene), PEDOT, has been found to be a potential candidate as transparent conductor. Recently, we have started developing processes to simultaneously improve conductivity and transparency in thin films based on PEDOT. We also explored various parameters to improve electrochromic contrast also in case of thin films based on PEDOT. In this presentation, I will discuss our recent results in these directions and some of the applications of these materials in optoelectronic devices.

Anisotropic Properties of Nanostructured Conducting Polymers Prepared Through Liquid Crystalline Template Approach

Sudha J. Devaki
Chemical science and Technology Division, CSIR-NIIST, Trivandrum.
E- mail: sudhajd2001@yahoo.co.in

Nanostructured conducting polymers are attractive due to their unique opto-electronic properties, short transport path for ions and large surface area which makes them potential applications as building blocks of nanoelectronic devices, biological sensing, drug delivery, energy storage, intelligent switching materials and super capapcitors. Several approaches were reported for the synthesis of nanostructured conducting polymers which include template assisted, interfacial and seeding polymerisation. Among the various strategies, liquid crystalline (LC) template approach is receiving importance since it can be readily applied in the fabrication of electronic devices. Recently, we have reported a novel method to prepare nanospindles of PEDOTS within a self organised LC template formed by the self-assembly of adduct of amphiphic dopant and monomer(1-2). This approach utilises an aqueous lyotropic LC with a hexagonal mesophase to solublise the monomer and direct its chemical polymerisation in presence of an oxidant to form PEDOT nanospindles which replicate the texture and birefringence of the LC template. During the propagation step, polymer form thermodynamically stable spindles of inherent nanoscale dimensions via self-assembly process. This presentation addresses on the chemical and electrochemical LC template mediated approach for the preparation of nanostructured conducting polymers such as polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene) having an unusual morphology and anisotropic properties. This approach could be used for the bulk production of nanostructured conducting polymers in controlled morphology.

References:

1. Liquid crystalline approach for the synthesis of PEDOTS, Sudha J. Devaki, Hans-Juergen P. Adler, Andrij Pich JMC C, 2014, DOI: 10.1039/..
2. Bio based Ionic liquid crystals. Renjith S, T. P. Rao, and Sudha J. D*. ACS Applied Materials and Interfaces 2014, 6 (6), 4126-4133.

Structure of Conjugated Polymer Solutions

M. Habibur Rahman[1*] and Hsin-Lung Chen[2]
[1]Department of Chemistry, University of Rajshahi, Rajshahi6205, Bangladesh
[2]Department of Chemical Engineering,
National Tsing Hua UniVersity, Hsinchu 30013, Taiwan
*psumhr@gmail.com

A class of *pi*-conjugated organic polymers known as 'hairy rod type' polymers having flexible side chains attached to rigid conjugated backbone is known to exhibit true solubility, down to the molecular level, in dilute solutions with common organicsolvents.[1,2]However, the semidilute regime of the polymers, which is more of a practical concentration regime for the fabrication of optoelectronic devices from these materials, are complex fluids that constitute at least two distinct domains: The dynamic bulk matrixof these fluids constitutes a transient network formed by interchain overlap, while small domains of aggregated chain segments are dispersedin this matrix.When the aggregates are formed under the influence of a strong magnetic field, the chain segments in the aggregated domains getaligned andform alyotropicliquid-crystal-like structure in aromatic solvents through polymer-solvent *pi-pi* stacking interaction. This structure of these solutions has been established for three vastly studied polymers of the said class: poly(9,9-dioctylfluorene-2,7-diyl)[2], poly[9,9-bis(2-ethylhexyl)fluorene-2,7diyl][3], and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene][4] using ^{1}H NMR spectroscopy and small-angle neutron scattering as the probing tools.

References:

[1] M. Knaapila, V. M. Garamus, F. B. Dias, L. Alma´sy, F. Galbrecht, A. Charas, J. Morgado, H. D. Burrows, U. Scherf, and A. P. Monkman. *Macromolecules* **2006,** *39,* 6505-6512.

[2] M. Habibur Rahman,Cheng-Si Tsao,Chun-Yu Chen,Jean-Hong Chen,Shao-Ching Liao,Jing-Long Liao,Hsin-Lung Chen,Viktor A. Ivanov,andShow-An Chen. *Macromolecules* **2007,** *40,* 6572-6578.

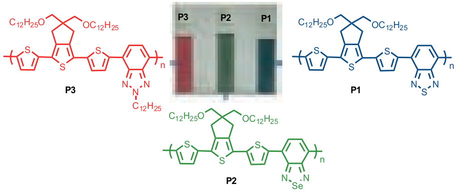
[3] M. Habibur Rahman, Shao-Ching Liao, Hsin-Lung Chen, Jean-Hong Chen, Viktor A. Ivanov, Peter P. J. Chu, and Show-An Chen. *Langmuir*, **2009**, 25 (3), 1667-1674.

[4] M. Habibur Rahman, Hsin-Lung Chen, Show-An Chen and Peter P. J. Chu. *Journal of the Chinese Chemical Society*, **2010**, *57*, 490-495.

Atomistic Approach to Tune the Optoelectronic Properties of Conjugated Systems

Anjan Bedi, Soumyajit Das, Sashi Debnath, Palas Baran Pati,
Sanjio S. Zade*
Department of Chemical Sciences,
Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246
sanjiozade@iiserkol.ac.in

Conjugated polymers have attracted considerable attention for their applications in organic electronics such as organic photovoltaics (OPVs), field effect transistors (OFETs), light emitting diodes (OLEDs) and electrochromic devices (ECDs).[1] Here we present the atomistic approach to tune the optoelectronic properties of two conjugated systems as shown in the figure. Three new donor-acceptor (D-A) type copolymers P1, P2 and P3 have been synthesized by Stille condensation between distannyl derivative of thiophene-capped cyclopenta[*c*]thiophene (CPT) with 4,7-dibromo[2,1,3]benzothiadiazole (P1), 4,7-dibromo[2,1,3]benzoselenadiazole and 4,7-dibromo[2,1,3]benzotriazole, respectively. These new CPT-based D-A copolymers showed an interesting trend of visible color (red, green and blue) in solution as the acceptor was varied keeping the donor constant. The optical band gaps of the polymers, which were estimated by measuring the absorption onset in the UV-vis spectra of the film, were found to be 1.57, 1.44 and 1.86 eV for P1, P2 and P3, respectively. DFT calculations correlated the strength of the acceptors with the interesting trend in the colors of these $(D)_{\text{non-variant}}$-$(A)_{\text{variant}}$ copolymers. Further, we have studied new conjugated system, diselenolodiselelenols (Ar-C_4Se_4-Ar), and compared their optoelectronics properties with sulfur analogue, dithiolodithioles (Ar-C_4S_4-Ar).[2]Both the systems showed two reversible oxidations. Structural and optoelectronic properties of C_4Se_4-derivatives were tuned by varying capped aromatic substitutions.



References:

[1] S. Das, P. B. Pati, S. S. Zade,*Macromolecules*, **2012**, *45*, 5410.

[2] A. Bedi, S. Debnath, S. S. Zade, *Chem.Commun.***2014**, *50*, 13454.

Rational Design of Ambipolar Conjugated Polymers for Optoelectronic Devices

Satish Patil
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore
E-mail: satish@sscu.iisc.ernet.in

A rapid improvement in performance of organic solar cells, light-emitting diodes and field-effect transistors largely originate from the successful development of new conjugated polymers. However, the fundamental question still remains related to the unequal mobility of hole and electron in π -conjugated polymers. A rational design of polymers is necessary to target n-type stable polymers, which can work in ambient processing conditions. Our laboratory employs a molecular engineering approach to develop high charge carrier n-type polymers for enhancing the performance of optoelectronic devices. In this talk, the integrated approach to materials design for enhanced electron mobility will be discussed. Specific emphasis will be placed on the guideline principle of the *donor-acceptor* approach to rationally design the low band-gap polymers with minimum defect, optimum energy levels and high electron mobility.

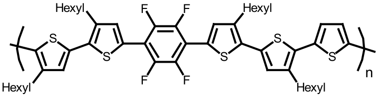
References:

1) Mallari A. Naik, N. Venkatramaiah, Catherine Kanimozhi, and **SatishPatil*, J. Phy. Chem-C, 2012, 116, 26128–26137**
2) Kanimozhi, C.; Yaacobi-Gross, N.; Chou, K. W.; Amassian, A.; Anthopoulos, T. D.; **Satish Patil,J. Am. Chem. Soc.2012**, 134, 16532

The use of heteroatom interactions towards band-gap tuning, planar structures and increased dimensionality

Gary Conboy, Jesuraj Inigo, Filipe Vilela, Greg McEntee,
Alexander Kanibolotsky, Peter Skabara*
WestCHEM, Department of Pure and Applied Chemistry,
University of Strathclyde, Glasgow G1 1XL, UK
**peter.skabara@strath.ac.uk*

The extent to which the optoelectronic properties of molecules are controlled by their conformation and packing is now well appreciated. In particular, the planarity (or nonplanarity) of a molecule has a dramatic influence on its behavior, and hence on its potential application. In the context of light emission, disorder can be beneficial in controlling aggregation, but for photovoltaics and transistors where low energy absorption and effective charge transport are key issues, planar molecules are preferable. Of particular relevance to this talk is the development of planarised conjugated architectures that should support much-enhanced charge transport properties as a result of their ability to self-assemble into tightly packed frameworks. This high level of self-assembly is achieved not only through π-π stacking but also non-covalent interactions between heteroatoms of adjacent monomers. The nature of these interactions is not entirely clear, but one possible source of an attractive potential is a 3c-2e interaction between lone pairs and relatively low-lying antibonding orbitals, although these are likely to be counteracted to some extent by significant lone pair-lone pair repulsions. For example, polymer **1** ($\mu = 10^{-3}$ cm^2 V^{-1} s^{-1}), has a planar repeat unit in the solid state as a result of close intramolecular sulfur/fluorine and hydrogen/fluorine contacts. Interestingly, variations in the absorption spectrum of these molecules suggest that the band gap is very sensitive to the degree of planarity. Whilst the mobility values for **1** are modest, the importance of the work is that it establishes a principle for the rational design of second generation materials with enhanced charge-transport properties.



1

This lecture will discuss several further examples that underline the importance and influence of non-covalent interaction in organic semiconductors.

Dynamics of charge carriers and relaxation in PMMA based polymer electrolytes embedded with ionic liquids

P. Pal and A. Ghosh
Department of Solid State Physics,
Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, india

We have studied dynamics of charge carriers and relaxation in polymer electrolytes based on poly(methylmethacrylate) (PMMA) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), embedded with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI) ionic liquid. We have observed that the incorporation of BMPTFSI into PMMA-LiTFSI electrolyte is an effective way for increasing the amorphous phase to a large extent. The ionic conductivity of these polymer electrolytes also increases with the increase of BMPTFSI concentration. The temperature dependence of the ionic conductivity and the hopping frequency exhibits Vogel-Tamman-Fulcher type behavior, indicating a strong coupling between the ionic and the polymer chain segmental motions. The frequency dependence of the ac conductivity exhibits a power law with an exponent n. The value of n is less than unity in the low frequency region (100 mHz – 10 MHz), while in the high frequency region (10 MHz – 3 GHz) its value is higher than unity, suggesting two relaxation mechanisms in these frequency regions. The scaling of the ac conductivity spectra has been obtained in the low frequency region indicating validity of the time-temperature superposition principle. However, scaling of the conductivity spectra in the high frequency region fails due to contribution of vibrational motion of ions. We have also analyzed the dielectric permittivity in the framework of a Havriliak-Negami equation and the shape parameters obtained from the analysis show slight temperature dependence, but change sharply with BMPTFSI concentration. The stretched exponent β obtained from Kohlrausch-Williams-Watts fit to the modulus data is much lower than unity signifying that the relaxation is highly non-exponential. The decay function obtained from analysis of experimental modulus data is highly asymmetric with time.

Role of Ionic Liquid in Modifying Properties of Polymer Electrolytes

Rajendra Kumar Singh, Shalu, Varun Kumar Singh,Y L Verma and A.L. Saroj
Department of Physics, Banaras Hindu University, Varanasi-221005, India
rksingh_17@rediffmail.com

Ionic Liquids, recently discovered novel class of materials, consisting of dissociated ionic species, possess unique properties such as high thermal stability, high ionic conductivity, low vapor pressure, wide liquidus range, high ionic conductivity etc. and have wide industrial, electrochemical and many other applications. In recent years, ionic liquid based polymer electrolytes / polymeric membranes have been widely studied. This talk discusses the role of ionic liquid in plasticization of polymeric membranes, enhancement of ionic conductivity, changing crystallization kinetics, phase transition and thermal behaviour of polymers/ polymer electrolytes.

Ion-Polymer and ion-ion interactions in PEO-based polymer electrolytes having ionic salt and ionic liquid with same as well as different anions have been explored using Raman spectroscopic technique and AC impedance spectroscopy. In polymer electrolytes having IL and dopant ionic salt with different anions, it has been found that the formation of contact and cross contact ion pairs occurs. Ionic conductivity of ionic liquid based electrolytes with different anions has been found to first decrease with IL content, exhibits a plateau region and then starts increasing at higher IL content while for the same anionic system, ionic conductivity shows a monotonic increase with increasing IL content in polymer matrix.

In PVA based polymer electrolytes containing ionic liquid [EMIM][BF_4], two relaxation peaks have been found to occur corresponding to complexed and uncomplexed polymer.

Polymer gel electrolytes membranes based on co-polymer PVdF-HFP and ionic liquid [EMIM][BF_4] have been studied and it has been found that the cation partly complexes the copolymer PVdF-HFP and partly remains as such in the polymer matrix as evidenced by DTGA. At lower polymer content, ionic liquid conductivity of polymeric gel electrolyte has been found to be large as compared to the bulk IL. In order to explain this anomalous behavior, disordered liquid model coupled with concept of breathing polymer chain has been invoked. At higher polymer content, conductivity has been found to decrease.

Incorporation of IL in Polymers has been to change T_g, T_m as well as thermal stability. Effect of ionic liquid [BMIM][BF_4] on crystallization kinetics of PEO based polymer membranes has been investigated using different techniques viz. isothermal, non-isothermal DSC studies and nucleation / growth of spherulites using polarizing optical microscope. IL has been found to slow down the crystallization kinetics.

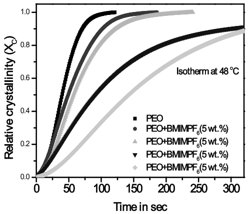


Fig.1 Relative crystallinity obtained from isothermal crystallization DSC curves of PEO+x wt.% $BMIMPF_6$ membranes for x=0-20.

Charge and Radii of Gyration of Polyelectrolytes in Salt Solutions

Bijan Das*
Department of Chemistry, Presidency University, Kolkata 700 073
**bijan.chem@presiuniv.ac.in*

Polyelectrolytes comprise a fascinating area in polymer science owing to the wide variability of their molecular and supramolecular architecture and the strong dependence of their properties in solution or in dispersion upon the surrounding medium. They are intimately related to the processes of life and play an indispensable role in industrial processes as well as in numerous products of our everyday life. In majority of the cases, polyelectrolytes are present along with electrolytes. A preliminary understanding of the influence of electrolytes on the physical properties of polyelectrolytes is, therefore, really only the first step toward understanding their behavior in biological and industrial systems. In this regard, a knowledge on the effective charge and the size of these species in electrolyte solution is, therefore, of utmost importance. We will describe how these key parameters can be obtained from simple experimental measurements coupled with two models (models I and II) for polyelectrolyte-salt solutions recently developed by us. Although the polyelectrolyte conductivities have been well understood in salt-free solutions, the situation was quite unsatisfactory for salt-containing polyelectrolyte solutions for a long time. Model I provides a quantitative description of the electrical conductivities of polyelectrolyte solutions in the presence of an added electrolyte [1,2] using the scaling description of Dobrynin *et al*. [3] and helps obtain information on the charges on polyelectrolytes. Static light scattering measurements are widely used to determine the root-mean-square radii of gyration of polyelectrolytes in solution [4]. Model II, however, shows how the root-mean-square radii of gyration of a polyelectrolyte dissolved in a solution could be obtained using simple viscosity measurements in a convenient manner [5]. Some interesting results on a few selected polyelectrolyte-salt solutions will be discussed.

References:

[1] De, R.; Das, B. J. Chem. Eng. Data 2010, 55, 2108-2115.
[2] Nandi, P.; Das, B. J. Chem. Eng. Data, 2011, 56, 2870–2876.
[3] Dobrynin, A.V.; Colby, R.H.; Rubinstein, M. Macromolecules,1995, 28, 1859 -1871.
[4] Dautzenberg, H.; Jager, W.; Koetz, J.; Philipp, B.; Seidel, C.; Stscherbina, D. In Polyelectrolytes: Formation Characterization and Application, 1994, Munich: Hanser Publishers, Ch. 5.
[5] Das, B.; Ray, D.; De, R. Carbohydrate Polymers, 2014, 113, 208-216.

Electromagnetic Shielding Interference Behavior of Polymer Composites

Veena Choudhary
Centre For Polymer Science and Engineering,Indian Institute of Technology,
Delhi Hauz Khas, New Delhi -110016
Email: veenac@polymers.iitd.ac.in

Electromagnetic interference (EMI) shielding refers to the reflection and/or absorption of electromagnetic radiation by a material, which thereby acts as a shield against the penetration of the radiation through the shield. The rapid increase of the electromagnetic pollution due to the proliferation of electronics and instrumentation demands fabrication of light weight and effective EMI shielding materials. Conventional metals were generally used as strong shielding materials because of high electrical conductivity but suffer from disadvantages in terms of cost, weight, corrosion, poor processing and molding properties. Further, metals mainly reflect the radiation and cannot be used in applications where absorption is prime requisite, e.g., in stealth technology Compared to conventional metal based EMI shielding materials, electrically conducting polymer composites are attractive due to their light weight, corrosion resistance, flexibility, and processing advantages. A variety of fillers such as different forms of carbon, e.g., graphite and its exotic forms such as flexible graphite, expanded graphite, single or multiwalled carbon nanotubes, carbon fibers, carbon black, reduced graphene oxide, graphene, conducting polymers, dielectric and magnetic materials incorporated in various polymer matrices have been widely used as EMI shields. Effective shielding is in critical demand to protect the environment, workplace and devices from EMI. A shielding effectiveness of 30 dB, corresponding to 99.9% attenuation of the EMI radiation, is considered an adequate level of shielding for many applications. Polymer based nanocomposite that add EMI shielding efficacy can provide significant weight savings as well as resistance to corrosion and other environmental degradation.

Conjugated Polymer Based Fluorescent Probes for Biosensors and Therapeutic Agents

Atul K. Dwivedi, B. Muthuraj, Sameer Hussain, Akhtar H. Malik,
Arvin S. Tanwar, Parameswar K. Iyer*
Department of Chemistry, Indian Institute of Technology Guwahati, Assam, India
pki@iitg.ernet.in

The development of new fluorescent probes (oligomers and polymers) that work as highly selective sensors for metals, metalloprotein and in competitive biological and cellular environment will be discussed.[1-5] The application of these probes has been extended to study neurological disorders. It is known that the altered heme metabolism and its increased accumulation in the brain has a significant role in the pathogenesis of Alzheimer's disease (AD) by accelerating amyloid β (Aβ) peptide aggregation in the brain of an AD patient. The Aβ is also found to have high affinity for iron and copper, resulting in the accumulation and localization of these metals in brain plaques, which accounts for the generation of neurotoxic hydrogen peroxide, oxidative stress, and free-radical formation. Hence, mediating the neurotoxicity in the brain involves the regulation of redox-active metals present along with the Aβ. A conceptually new and prospective therapeutic strategy using fluorescent probes is developed, which involves the inhibition and clearance of Aβ peptide fibrils, removal of bound heme and non-heme iron in CSF, structurally modifying the aggregates, and preventing them from aggregating again, to control AD pathogenesis will be discussed. The reported probes have a unique ability to bind metals, metalloproteins selectively in a competitive biological environment and are utilized to interact with bound metals, in the Aβ aggregates and diminish fibril accumulation. The experiments were performed in cerebrospinal fluid (CSF) since it is a very important biomarker of AD-Aβ due to its continuous presence and contact with the brain. Because the CSF samples studied in these experiments had metals, metalloproteins as well as the aggregated Aβ, a common pathogenesis mechanism exists in such amyloidoses. Hence, therapeutic strategies involving the modulation and clearance of Aβ accumulated in the plaques of brain tissues, removal of metals to reduce neurotoxicity, structurally modifying the aggregates, and preventing them from aggregating again into toxic polypeptides which are vital strategies to control AD pathogenesis were applied here using these probes. The application of these probes is further shown for enzyme catalysis also.[6-8]

1. Muthuraj, B.; Deshmukh, R.; Trivedi, V.; **Iyer, P. K.** *ACS Appl. Mater. Interfaces* **(2014)**, *6*, 6562-6569.
2. Muthuraj, B.; Layek, S.; Trivedi, V. **Iyer, P. K. (2014),** *Communicated.*
3. Dwivedi, A. K.; **Iyer, P. K.** *Macromolecular Bioscience* **(2014)** *14*, 508-514.
4. Muthuraj, B.; Hussain, S.; **Iyer, P. K.** *Polymer Chemistry* **(2013)**, *4*, 5096-5107.
5. Dwivedi, A. K.; Prasad, K. M. N.; Trivedi, V.; Iyer, P. K. *ACS Appl. Mater. Interfaces* **(2012)**, *4*, 6371-6377.
6. Dwivedi, A. K.; **Iyer, P. K.** *J. Mater. Chem. B* **(2013)**, *1*, 4005–4010.
7. Dwivedi, A. K.; **Iyer, P. K.** *Anal. Methods*, **(2013)**, *5(9)*, 2374–2378.
8. Malik, A. H. Hussain, S. Tanwar, A. S. Layek, S.; Trivedi, V. **Iyer, P. K. (2014),** *Communicated.*

Safer, Greener, hygienic coatings for healthier living

B P Mallik
Research & Technology Function
Asian Paints Limited, Plot no C-3 B/1, TTC Industrial Area, MIDC Pawane,
Thane-Belapur Road, Navi Mumbai - 400 703.

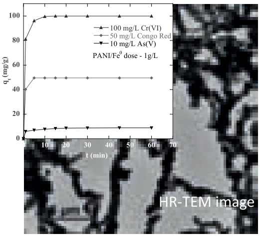
Polyaniline-Fe^{0}composite nanofibers: synthesis, characterization and applications for water treatment

Arjun Maity*[1], Madhumita Bhaumik[2], Suprakas Sinha Ray[1],
[1]National centre for Nanostructured Materials,
Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa
[2]Department of Chemistry, Tshwane University of Technology,
Private Bag X680, Pretoria, South Africa
*amaity@csir.co.za

The world is facing a major challenge regarding water quality issue due to the contamination of natural water resources introduced by industrial pollution. Industrial wastewater containing inorganic, organic and other hazardous contaminants has serious impact on human health as well as on environment. To make the wastewater dischargeable to aquatic environment or reusable in the industries, clean and economic removal of the contaminants must be adopted. This can be achieved by developing advanced separation technologies and new adsorbents [1]. In this context recent advances in nanoscale science and engineering suggest that water pollutionproblem could be resolved or greatly diminished up to allowable limit by using nanoadsorbents[2].

Conducting polymer based nanomaterials are promising for the removal of both inorganic and organic contaminants from water [3,4]. Accordingly, polyaniline-Fe^{0}composite nanofibers (PANI/Fe^0 CNFs) with interconnected structures were synthesized by rapid mixing of the aniline monomer with Fe(III) chloride followed by reductive deposition of Fe^0 nanoparticles, using the polymerization by-products as the Fe precursor. The structures and properties of the composite nanofibers thus obtained were investigated by FE-SEM, HR-TEM,ATR-FTIR, XRD, XPS and VSM.

The effects of various operational parameters including solution pH, contact time, initial concentration and temperature on the removal of arsenic(V), one of the most toxic ground water pollutants, chromium(VI), the most common heavy metal pollutant in industrial wastewater and one organic pollutant, Congo red, a carcinogenic anionic azo dye from water[5,6].The fibers are easily recovered from fluids by exploiting their ferromagnetic properties. The experimental results suggest that the composite nanofibers of PANI/Fe^0 have great potential to decontaminate water containing inorganic heavy metals and organic pollutants. Finally, using this synthesis protocol, a variety of nanostructured conducting polymers supported metals nanoparticles could be prepared for applicationssuch as sensors, nanoelectrocatalysts, nanoelectronics in diverse fields of nanotechnology.

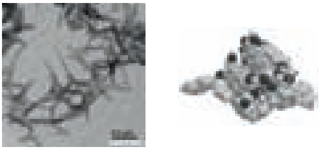


Self Assembled Conducting Polymer Nanostructures: How do they grow ?

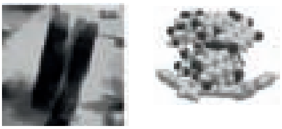
Rupali Gangopadhyay
Centre for Advanced Materials,
Indian Association for the Cultivation of Science, Kolkata 32

Conducting Polymer nanomaterials viz. nanowires, nanofibres, nanotubes, nanoflakes etc are well known in materials science for their unique properties and versatile applications. These structures are grown in two general techniques viz. template guided and template free methods. This article describes the formation of a series of conducting polymer nanomaterials exploiting the self assembly of different molecular templates. Synthesis technique and several characterizations with some quantum mechanical modeling studies are included.

Basic idea of the work is to polymerize the monomers) in presence of (or dope the polymer with) some molecules having self assembly. We have selected a liquid crystal (5CB) and one tetracarboxylic acid (TCA) for this purpose. 5CB was used as the matrix for polymerization of EDOT, a severely intractable polymer that does not form any defined structure during general synthesis. However, in presence of 5CB, the polymer (PEDOT) is grown in very nice rope like structure. Quantum mechanical modeling studies have revealed that 5CB itself is spirally oriented and acts as template to the growing PEDOT chain. TCA on the other was utilized in two different ways; for polypyrrole (PPy) it was used as the matrix within which the polymer was grown from the monomer following a general synthesis technique. Polyaniline (PAni) was however synthesized via standard technique in aqueous medium and was dedoped prior to the exposure to TCA solution. Both for PPy and PAni, the TCA self assembly acts as counterion to the polymer chain in effect of which the polymers attain nanorod and nanoribbon like structures respectively. Modelling studies have exhibited the different orientations of these molecular assemblies that accounts for their ultimate structures observed from electron microscopy.



A. Polyaniline : TEM image and model



B. Polypyrrole : TEM image and model

Enhancing the conductivity of carbon-nanotube filled blends by tuning their phase separated morphology with a copolymer

Avanish Bharati[1], Ruth Cardinaels[1,2], Michael Wübbenhorst[3],
Paula Moldenaers[1]
[1]Soft Matter Rheology and Technology, Department of Chemical Engineering,
KU Leuven, Willem de Croylaan 46, P.B. 2423, B-3001 Leuven, Belgium
[2]Structure and Rheology of Complex Fluids, Department of Mechanical Engineering,
TU Eindhoven, Den Dolech 2, 5612 AZ, P.B. 513, Netherlands
[3]Acoustics and Thermal Physics Section, Department of Physics and Astronomy,
KU Leuven, Celestijnenlaan 200D, P.B. 2416, B-3001 Leuven, Belgium
e-mail: paula.moldenaers@cit.kuleuven.be

We describe an approach to engineer bi-continuous blends of (P□MSAN/PMMA)by formation of a percolating network of MWNTs in the P□MSAN phase of the blend undergoing spinodal decomposition. Its electric properties are further tailored by compatibilization with an interfacially segregated random copolymer(PS-r-PMMA).A systematic study of the effect of copolymer concentration revealed a huge increase in electrical conductivity of bi-phasic blends due to the copolymer, both above the spinodal temperature of 220 °C (Fig. 1) and quenched to room temperature. These findingswere corroborated with the linear viscoelastic properties, optical micrographs and scanning transmission electron micrographsfor blends with 0.5wt% and 2 wt%MWNTs (micrographs 1-5 in Fig. 1).The latter show a substantial morphology refinement and increased degree of cocontinuity after copolymer addition. "Conductivity free" dielectric loss spectra were used to study the dependence of the relaxation timeand dielectric strength of interfacial polarization on temperature and copolymer concentration (Fig. 2). The former allowed to determine the localized motion of interfacial relaxation, and the latter to predict changes in intrinsic length scale, which are linked to refinement (micrographs 1,6-8) and Debye length.

Absolute molecular weight determination using Light Scattering

Manoj D Bhataria
Inventys Research Company Pvt Ltd, Mumbai

Detailed size or molar mass distribution information is useful in many areas such as investigating protein aggregation and understanding (or predicting) polymer properties. Since chromatography fractionates a sample before analysis, it is an ideal tool for characterizing these distributions. Sometimes, calibration curves relating mass or size to elution volume can be obtained by a series of measurements of known standards. However, this column calibration is often impossible due to the unique nature of the analytes; suitable standards, which must match both analyte chemistry and structure, are simply unavailable. Fortunately, with judicious choice of detectors, column calibration is unnecessary for absolute size and absolute molecular weight determination.

We provide detectors for determining analyte size, analyte molecular weight, and analyte mass distribution all without the need for column calibration. Determine size (hydrodynamic radius) of proteins and their aggregates in a chromatography measurement as a function of elution volume with an extremely sensitive dynamic light scattering instrument. Or determine absolute molecular weight with a multi-angle, flow-through light scattering instrument and augment it with a differential refractometer for use as an RI concentration detector. Determine intrinsic viscosity and concentration using the Viscosity or UV dual detector. Ideal when universal calibration is preferred over light scattering or as another method for characterizing difficult polymer samples.

Contact the 'Particle Science' experts at Inventys Research Company Pvt Ltd for details about how our instruments can solve your analysis problems.

Interconnected polyaniline-Fe^{0}composite nanofibers: A superior adsorbent for the removal of arsenic from water

Madhumita Bhaumik[a*], Rob Mc Crindle[a], Arjun Maity[b]
[a]Department of Chemistry, Tshwane University of Technology,
Private Bag X680, Pretoria, South Africa
National centre for Nanostructured Materials,
Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa
E-mail-bhaumikm@tut.ac.za

Occurrence of elevated arsenic (As) levels in groundwater has been reported in many countries and regions throughout the world [1]. Specifically, As contamination of groundwater has led to a massive epidemic of arsenic poisoning in South and South East Asia. It is estimated that 60 million people are drinking groundwater with As concentrations above 10 µg/L [2]. Therefore, it is important to develop simple, highly efficient and cost effective methods for the removal of As from aqueous environments. In this context recent advances in nanoscale science and engineering suggest that Aspollutionproblem could be resolved or greatly diminished up to allowable limit by using nanoadsorbents with large surface area and highly reactive surface sites [3].

Over the past decade zero-valent iron nanoparticles (Fe^0 NPs) have received considerable attention as a promising material for *in situ* remediation of As contaminated groundwater and drinking water because of large reactive surface area and high As adsorption capacity [4]. However, during synthesis rapid aggregation owing to high surface area and magnetic interactions among the particles results in the formation of much larger Fe^0 particles, thus greatly diminishes their chemical reactivity and also results in poor mobility and successful transport to the contaminated site for *in situ* remediation [5]. To overcome the inherent limitations of the Fe^0 nanoparticles, in this work conducting polyanilinenanofibers (PANI) with high surface area were used effectivelyto support Fe^0 nanoparticles for the removalofAs from water. The structures and properties of the composite nanofibers (PANI/Fe^0 CNFs) thus obtained were investigated by FE-SEM, HR-TEM, BET, XRD, ATR-FTIR, and XPS. The effects of various operational parameters including solution pH, contact time, initial concentration and temperature on removal ofAs were investigated in batch adsorption mode. Compared with homo PANI and Fe^0 nanoparticles counter parts the improvedAs removal capacities (227.2 and 232.5 mg/g for As(V) and As(III), at pH 7.0) of PANI/Fe^{0}CNFswere observed due to the increased surface areaand highly reactive surface sites of the PANI/Fe^{0}CNFs.

References:

[1] United States Environmental Protection Agency (US-EPA), Arsenic occurrence in public drinking water supplies, Washington, DC, 2000.

[2] Mandal, B.K.; Suzuki, K.T. Arsenic round the world: a review, Talanta**2002**, 58, 201-235.

[3] Savage, N,;Diallo, M.S. Nanomaterials and water purification: opportunities andChallenges. J. Nanopart. Res. **2005**, 7, 331-342.

[4] Bhaumik, M.; Choi, H.J.;McCrindle, R.I.;Maity, A. J. Colloid Interf. Sci. **2014**, 425, 75-82.

[5] Kanel, S.R.; Manning, B.; Charlet, L.; Choi, H. Env. Sci. Technol.**2005**, 39, 1291-1298.

Effect of salt valency and concentration on structure and thermodynamics of Na^+ - Polyethacrylate in aqueous solution

Praveenkumar Sappidi and Upendra Natarajan
Macromolecular Modeling and Simulation Laboratory, Dept. of Chemical Engineering,
Indian Institute of Technology Madras, Chennai 600036, India.
Email: praveenche@gmail.com

Structure and thermodynamic properties of anionic polyelectrolyte *atactic* Na^+-polyethacrylate (PEA) in aqueous solution, as a function of salt concentration C_s(dilute to concentrated) and valency (NaCl versus $CaCl_2$), were investigated via explicit-ion explicit-solvent molecular dynamics simulations. The simulationsshow the reduction in radius of gyration $<s^2>$ with increase in C_s while stabilizing to a constant value beyond the critical C_s. The change in $<s^2>$ across the entire range of $C_s$is found to be higher for divalent salt in agreement with theory and experimental studies in literature [1, 2]. The chain shrinkage is greater for divalent salt as compared to monovalent salt. A significant decrease in number of H-bonds between PEA and water is observed with increase in C_s for NaCl relative to CaCl2. A slower decay of H-bond autocorrelation function occurs with increase in salt concentration. Ca^{2+} ions bind closer to PEA as compared to Na^+, thusforming bridge between adjacent and nonadjacent monomers, and this behavior is in agreement with observation on PAA-Ca^{2+} system[3].The thermodynamic enthalpy of hydration is more exothermic in case of Ca^{2+} salt. The strength of the intermolecular interaction between PEA and Water increaseswith C_s in conjunction with the results of the hydrogen bonding analysis. The PEA backbone shows existence of *gauche* and *trans* states, and observation of a decrease in*trans* probability and increase in*gauche*probability with increase inC_s, in conjunction with the behaviorobserved for$<s^2>$. To our knowledge this is the first report of an atomistic molecular simulation study on investigation of interactions between PEAchain and salts in aqueous solution. Various details of structure and thermodynamic properties will be presented.

Reference

1. Liu, S.; Ghosh, K.; Muthukumar, M. *J.Chem. Phys.**2003**, 119, 1813-1823.*
2. Kay, P. J.; Treloar, F. E.*Makromol. Chem.* ***1974**, 175,3207-3223.*
3. Molner, F.; Reiger, J. *Langmuir.***2005**, 21, 786-789.

Effect of tacticity on chain dimension of Poly-(methacrylic acid) in dilute aqueous solutions

Abhishek Kumar Gupta and Upendra Natarajan
Macromolecular Modeling and Simulation Laboratory, Dept. of Chemical Engineering,
Indian Institute of Technology Madras, Chennai-36, India. Emails:
abhisheklovesastra@gmail.com

A detailed study elucidating the conformational properties, intermolecular hydrogen bonds and hydrogen bond dynamics was performed to understand the difference between *atactic*-polymethacrylic acid (*a*-PMA), *isotactic*-PMA (*i*-PMA) and *syndiotactic*-PMA (*s*-PMA) using atomistic molecular dynamic (MD) simulations with explicit description of solvent and ion molecules. Radial distribution functions (RDF's) between different pairs was analyzed. The radius of gyration $\langle R_g \rangle$ tends to increase with degree of neutralization (*f*) by Na^+ counterions for *a*-PMA and *i*-PMA chain. The increase in $\langle R_g \rangle$ was higher in the case of *i*-PMA than *a*-PMA. Fully-ionized *i*-PMA exhibits fully extended conformation as compared to slightly bent structure observed for *a*-PMA. The number of intermolecular hydrogen bonds is nearly same for both *i*-PMA and *a*-PMA at all ionizations between 0 and 1 signifying identical hydration behavior. Our results reveal that the total number of H-bonds is independent of the limits posed on the chain tacticity. Simulations were done for two types of *s*-PMA chains differing the % of RR triads. The purely *syndiotactic* chain showed $\langle R_g \rangle$ change 62% ($0<f<1$), while that containing triad fractions as per experimental data showed 30% in agreement with 25% observed in experiments [1]. As expected, increase in R dyads and RR triads results in increase in $\langle R_g \rangle$. Fully ionized *i*-PMA has been found to be more extended as compared to both *s*-PMA's at $f = 1$. The behavior of H-bond relaxation dynamics cannot be utilized to understand the difference in behavior of these chains, and thus being independent of stereochemistry. The details of the behavior of Na^+ counterion distribution will be presented. Backbone dihedral angle distribution of all simulated PMA chains demonstrates increasing *trans* probability with increasing *f*, in conjuction with observed increase in $\langle R_g \rangle$. Also, the results obtained for the intermolecular thermodynamics will be presented.

References:

[1] Sitar, S.; Aseyev, V.; Kogej, K. Polymer **2014**, 55, 848-854.

Intermolecular structure and dimensions of Poly(vinyl amine)PVAm and hydrophobically modified PVAm in dilute aqueous solution investigated by molecular dynamics simulations

Ila Sarkar and Upendra Natarajan
[§]Macromolecular Simulation and Modeling Laboratory, Dept. of Chemical Engineering,
Indian Institute of Technology Madras, Chennai 600036.
[§] *Emails: ch14d007@smail.iitm.ac.in*

Intermolecular Structure and conformational properties of two different substituted modified *atactic* poly(vinyl amine) PVAm in aqueous dilute solution was studied via atomistic molecular dynamics (MD) simulations in explicit solvent. The effect of the degree of neutralization (ionization) was investigated (range $0 < f < 1$). We have analyzed the intermolecular structure via the radial distribution functions for specific atom types between polymer chain, water molecules and as well as the hydration near the polymer chain in the solvated system. The hydrogen bonds have been identified and characterized by studying their distribution. We observe that an increase in f provides an increase in $\langle R_g \rangle$ of the PVAm chain and modified PVAm chains. The number of intermolecular hydrogen bonds also increases with f for PVAm and modified PVAm. The resulting conformation is of the coiled type for PVAm in its un-neutralized form, while the coil opens up as a result of ionization (increase in charge density). Chains having a higher counter-ion charge density show higher values of $\langle R_g \rangle$, which is effected by intermolecular electrostatic interactions between polymer units. The Cl^- counter-ions strongly influence their presence on the polymer chains. The dynamics of PVAm and PVAm intramolecular and intermolecular (with water) hydrogen bonds are investigated through hydrogen bond life time and hydrogen bond decay auto-correlation function. We will present the comparison of the equilibrium structure and relaxation dynamics properties of the chemically modified PVAm with unmodified PVAm.

Synthesis of Processable Poly(*o*-phenylenediamine) as Undoped Conducting Polymer

Siddhartha Samanta, Poulomy Roy, Pradip Kar*
Department of Chemistry, Birla Institute of Technology, Mesra, Ranchi-835215
**pradipkgp@gmail.com*

Intrinsically conducting polymers (ICP) may be used as substitute of inorganic electronic, optoelectronic, semiconducting materials due to advantages like processability, architecture flexibility, tailorability, versatility, light weight, environmental stability etc.[1]. For these applications some higher conductivity is required than that of the undoped conjugated polymers. The conductivity of conjugated polymers, which are either weak semiconductors or insulators, increases by several folds due to 'doping'. The majority of problems and disadvantages like processability, conductivity, stability, reproducibility, repeatability etc. associated with conjugated polymers are related to doping problems [2]. Among those ICPs polyaniline and its derivatives have distinct place due to readily inter-convertible redox form containing wide range of conductivity and the redox state of those polymers are easily changed by acid (doping) or base (dedoping) treatment. The synthesis of polyaniline derivatives containing free active functional groups (e.g., $-NH_2$, -OH etc.) in the backbone chain that can offer better solution processability, better induce doping by metal nanoparticles and good performances towards various applications. However, the polymers have been reported to be insoluble in organic solvents resulting poor processability as well as conductivity due to formation of ladder polymer.

After an extensive literature survey it appears that poly(o-phenylenediamine) (PoPD) is not a well-established polymer and there are controversies about polymerization mechanism, final structure and characteristics of the polymer [3]. PoPD was synthesized from the monomer o-phenylenediamine in dimethyl sulfoxide (DMSO) media using ammonium per sulphate as a radical initiator. The synthesized polymer was completely soluble in common organic solvent like DMSO, N,N-dimethyl formamide etc. The polymer was characterized by various standard characterization techniques. The structure of the polymer confirmed from the spectral analysis, was just like polyaniline derivative with free =NH functional groups. The average DC conductivity of undoped polymer film cast from DMSO was 2.21×10^{-6} S/cm. In conclusion, processable PoPD was successfully synthesized form DMSO medium and the moderate conductivity was observed for undoped polymer.

References:

[1] Handbook of Conducting Polymers, Vol. 2, Skotheim, T.A. (Ed.), Marcel Dekker, New York **1986**.
[2] Kar, P. Doping in Conjugated Polymers, Wiley-Scrivener, New Jersey **2013**.
[3] Li, X.G.; Huang, M.R.; Duan, W.; Yang, Y.L. Chem. Rev. **2002**, 102, 2925-3030.

Poor Solvent and Thermal Annealing Induced Enhanced Crystalline Order in Poly(3-dodecylthiophene) Films.

Ishani Roy* and S. Hazra
Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata.
*Ishani.roy@saha.ac.in

Poly(3-alkylthiophenes) or P3ATs belong to the large family of semiconducting polymers and provide appreciable charge carrier mobility due to their high conjugation length. They are semicrystalline in nature having lamellar stacks and amorphous interlamellar regions. The degree of crystallinity and orientational order is largely responsible for the field effect mobility of P3AT based devices.

In this work we study the influence of a poor solvent and annealing temperature on the ordering of crystallites in Poly(3-dodecylthiophene) (P3DDT) films formed by using mixed solvents. P3DDT films prepared from a mixture of a good and a poor solvent, chlorobenzene and anisole in this case, have a greater degree of *edge-on* orientation compared to those from a pure good solvent (chlorobenzene). The poor solvent is responsible for a conformational transition from coil-like to rod-like state of the P3DDT chains, as is evident from UV-Visible spectroscopy[1,2]. On annealing above the melting temperature (60°C) of the alkyl side chains a further enhancement of rod-like conformation is observed. On further increasing the annealing temperature these free chains undergo π-stacking to form lamellar aggregates. A greater proportion of poor solvent in the solution results in the formation of a greater number of rod-like conformations but not necessarily a greater degree of crystallinity. These rod-like chains stack to form crystalline domains on annealing the film. So, on annealing, a film cast from a solution containing greater proportion of poor solvent has a higher degree of crystallinity, which is clear from XRD and GISAXS[3] results. X-ray diffraction mapping[4] shows that the amount of crystallites in the perfectly *edge-on* direction increases upto 130°C, which is below the melting temperature (165°C) of the backbone, and decreases beyond that temperature. However, the amount of crystallites in directions other than the perfect *edge-on* direction keeps increasing with temperature. The size of these crystallites increases in all directions with annealing temperature. AFM images show that the P3DDT films are composed of 0.6-0.8 μm sized islands, which further consist of smaller domains, and remain almost unaffected by annealing. This means that the evolution of crystallites takes place essentially within the smaller domains.

References:

[1] N. Kiriy *et. al.*, *Nano Lett.*, 2003, **3**, 707–712.
[2] W. Zu *et. al.*, J. Phys. Chem.B, 2011, **115**, 6412–6420.
[3] S. V. Roth *et. al.*, J. Phys.: Condens. Matter, 2011, **23**, 254208.
[4] S. Hazra, Appl. Surf. Sci., 2006, **253**, 2154–2157.

Core-subsituted Naphthalenediimide copolymers for Optoelectronic application

Nagesh Kolhe and S.K. Asha*
Polymer Science and Engineering Division
CSIR-National Chemical Laborartory, Pune-411008 (India)
**sk.asha@ncl.res.in*

Organic semiconducting oligomers and polymers have shown great promise for application in optoelectronic devices like organic field effect transistors (OFETs), Organic Light emitting diodes (OLEDs) and solar cell owing to their low cost, solution processability, mechanical flexibility and large area fabrication. Although the majority of materials reported are p-type with high performance parameters in terms of hole mobility and air stability, the scenario for n-type and ambipolar materials are also improving steadily, due to accomplishment of rational molecular design and solution processable polymeric semiconductors. Among typical class of rylenedimide polymers, those based on core-substituted naphthalenedimide (NDI) copolymers are rapidly increasing in literature and their charge transport nature is found to be dependent upon the donor co-monomer used in the core position. The majority of core substituted NDI polymer exhibits n-type charge transport with electron mobility as high as ~ 0.85 cm^2/Vs reported by A. Fachetti's group. Because of their high mobility, crystalline nature and solution processability, they also find application in all –polymer solar cell as non-fullerene acceptor and recent reports showed the highest power conversion efficiency of > 4.5 %. There are very few reports showing the ambipolar mobility in NDI based polymer using single donor in alternating fashion which required exact tuning of band energy level (HOMO and LUMO) to transport both hole and electron within same material. In this context, we have reported exactly alternating copolymer based on core- substituted NDI comprising of oligo(phenylenevinylene) as donor co-monomer which exhibited balanced ambipolar charge transport in OFET due to the favorable LUMO (-3.75 eV) and HOMO (-5.44 eV) energy level. Furthermore, the effect of side chain engineering on inter-chain packing and thereby the charge transport properties in OFET have been demonstrated by changing branched alkyl to oligoethyleneoxy (TEG) chain at imide position of NDI. The crystalline nature with lamellar ordering facilitated high molbility ambipolar charge transport in OFET which promises to open up opportunity for their application in all-polymer solar cells as acceptor materials.

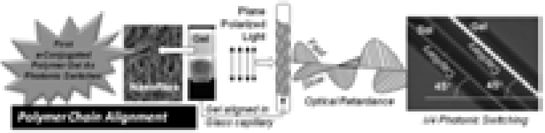
References:

[1] Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679.
[2] N. B. Kolhe, A. Z. Ashar, K. S. Narayan and S. K. Asha, Macromolecules 47, **2014**, 2296.

π-Conjugated Polymer Anisotropic Organogel Assemblies for Photonic Switches

Karnati Narasimha and Manickam Jayakannan*
Department of Chemistry
Indian Institute of Science Education and Research (IISER)
Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.

Photonic switches (or photonic wave plates) are materials that are capable of transforming the wavelength of light or trafficking optical information for doing specific job or storage. Commercial photonic wave plates are made up of silica (quartz) or inorganic crystals and they are routinely employed as half wave plates (λ/2) or quarter wave plates (λ/4) with respect to their function and applications. To demonstrate the first π-conjugated photonic switch concept; new classes of semi-crystalline and segmented π-conjugated polymers designed with rigid aromatic OPV π-core and flexible alkyl chains. These polymers found to be self-assembled as semi-crystalline or amorphous with respect to the number of carbon atoms in the alkyl units. These semi-crystalline polymers produce organogels having nano-fibrous morphology. The polymer organogel aligned in a glass capillary and this anisotropic gel device is further demonstrated as photonic switches. The glass capillary device behaves as typical λ/4 photonic wave plates upon the illumination of the plane polarized light. The λ/4 photonic switching ability found to be maximum at θ = 45° angle under the cross-polarizers. The orthogonal arrangements of the gel capillaries produce dark and bright spots as on-and-off optical switches. The organic photonic switch concept can be adapted to large number of other π-conjugated materials for optical communication and storage.



References:
1. Narasimha, K.; Jayakannan, M. *ACS Applied Materials & Interface*, **2014** (Just Accepted)
2. Goel, M.; Narasimha, K.; Jayakannan, M. *Macromolecules,* **2014**, *47,* 2592-2603

Development of Functional π-Conjugated-Polycaprolactone Amphiphilic Block Copolymers for Optoelectronics

Bhagyashree Kulkarni and Manickam Jayakannan*
Department of Chemistry, Indian Institute of Science Education & Research (IISER-Pune)
Dr.HomiBhabha Road, Pune 411008, Maharashtra, INDIA
E-mail: jayakannan@iiserpune.ac.in

Self-assembly of amphiphilic block copolymers has attracted wide interest since they offer the potential to form nanostructured materials for advanced applications in electronics, optoelectronics, biotechnology, environmental technology, etc. Among the reported block copolymers, conjugated rod–coil block copolymers have been recognized of great importance since they provide a powerful route towards supramolecular objects with novel architectures, functions, electronic and optoelectronic properties. Rod-coil block copolymer approach has been exploited in which conjugated polymer is used as rigid block and a coil segment as flexible block. The present work highlighted the synthesis of caprolactone and carboxyl substituted caprolactone polymers with different no of repeating units synthesized by controlled ring opening polymerization by hydroxyl end functionalized OPV. These polymers have hydrophobic OPV unit and hydrophilic carboxyl substituted caprolactone. The structures of monomers and polymers were confirmed by NMR, GPC and MALDI-TOF.The molecular weights of the polymers were determined by the ratio of monomer/initiator as well as catalyst concentration.The caprolactone polymers and substituted caprolactone polymers are thermally stable up to 300 °C and 230 °C, respectively. The caprolactone polymers were crystalline and their crystalline nature was confirmed by PLM whereas Substituted caprolactone polymers were found to be amorphous in nature. The photo-physical properties were also studied. The self-assembled structures of polymers were analyzed by FESEM and the substituted caprolactone polymers show the spherical particles. The substituted caprolactone polymers can be deprotected to have carboxylic functional groups which can form self- assembled structures in water. It can be used to study donor-acceptor self-assembly by physical in capsulation or by donor-acceptor anchoring.

Synthesis of Novel BMP capped Tetaraniline (TANi) based Polyurethane

Ravi Arukula, Chepuri R. K. Rao*, Ramanuj Narayan and KVSN Raju
Polymers and Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India
*E-mail: ramchepuri@iict.res.in

There has been tremendous increase in the research and developmental activity on synthesis and exploring applications for oligoanilines [1-4]. This stems mainly as oligoanilines have good solubility in common organic solvents with monodispersed molecular weights and easy synthesis in contrast to processability difficulties encountered with polyanilines. This work studied the electrical, morphological, and thermal characteristics of polyurethane (PU) derived from 2, 2-bis (hydroxymethyl) propionicacid (BMP) capped tetraaniline (TANi) and the diisocyanate HMDI as a new material for various applications. The product is synthesized from 2, 2-bis (hydroxymethyl) propionicacid Tetraaniline amide (BMP-TANi) and HMDI in 1:1 ratio. The synthesized polyurethane showed good conducting and electrical properties. The conductivities can be increased from less than 10^{-10} S/cm for pure PU to 2.49×10^{-3} S/cm for BMP caped TANi containing polyurethane, independently of the length of the soft segment in the BMP-TANi backbone chain. Conducting polyurethane composites were prepared by simple doping with p-toluene sulphonic acid (p-TSA). The results showed that thermally stability of the polyurethane was very good with BMP-TANi. This material is useful as anti-corrosive coatings and other conducting based sensors.

References:

[1] Wei, Y.; Yang, Ch.; Wei, G.; Feng, G. Synth. Met. 1997, 84, 289.
[2] Gao, J.; Li, K.; Zhang, W.; Wang, C.; Wu, Z.; Ji, Y.; Zhou, Y.; Shibata, M.; Yosomiya, R. Macromol. Rapid Commun. 1999, 20, 560.
[3] Kulszewicz-Bajer, I.; Rozalska, I.; Kurylek, M. New J. Chem. 2004, 28, 669.
[4] C. U. Udeh, N. Fey, C F J Faul, J. Mat. Chem., 2011, 21, 18137

Synthesis and Characterization of Conducting Co-polymer poly (DA-T) and their application

Apparao Thota, Chepuri R. K. Rao*, Ramanuj Narayan and KVSN Raju
Polymers and Functional materials Division,
CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India
*ramchepuri@gmail.com

Polyaniline has been extensively studied polymer for various applications such as sensors, supercapacitors and corrosion protection[1]. Conducting and electrochemically active co-polymers are synthesized and studied for their thermal and electrical properties along with anti-corrosion properties. Conducting copolymer based on N-phenyl-p-phenylenediamine and o-toluedine, poly (DA-T) has been synthesized chemically. The co-polymer been evaluated for corrosion protection of mild steel. Anti-corrosion performance of poly (DA-T) coated carbon steel (mild steel) sample exposed to 3.5 % of NaCl aqueous solution was evaluated by electrochemical corrosion measurements. The conductivity of Poly (DA-T) hydrochloride ranged from 1.14×10^{-1} to 1.87×10^{-2} S/cm. The poly (DA-T) has been confirmed by the characterization of UV-VIS, FT-IR, CV, TGA and ^{1}H NMR.

The chemical structure of Poly (DA-T)

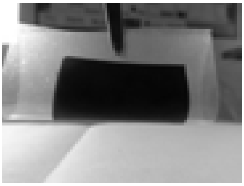
References:

(1) T. A. Skotheim, Editor, *Handbook of Conducting Polymers*, Vols. I and II, Marcel Dekker, New York, 1986.

Benzoyl peroxide oxidation route to poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)film

K. Sangam Naidu and S. Palaniappan*
Polymers& Functional Materials Division,
CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India
*palaniappan@iict.res.in

3,4-ethylenedioxythiophene is oxidized to poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) [PEDOT:PSS] using benzoyl peroxide as oxidant in presence of poly(styrenesulfonic acid) via aqueous polymerization pathway. Formation of PEDOT:PSS is confirmed from Infrared, electronic absorption and X-ray diffraction spectral results. Higher pellet conductivity iss obtained in this work (6.5 S/cm) compared to the literature report of the polymer sample (<1 S/cm) prepared using ammonium persulfate oxidant. PEDOT:PSS sample in water is processed into film, which shows a conductivity of 0.06 S/cm. PEDOT :PSS sample is stable upto 225°C. Electrochemical properties of PEDOT : PSS is being measured using cyclic voltammogram, charge-discharge and impedance spectral measurements. Initial results show that rectangular spectrum is obtained in CV and a phase angle close to 90° is observed in impedance spectrum. The results of this study will be discussed.



PEDOT: PSS coated on L-folder sheet

Acknowledgements:
We thank the Department of Science & Technology, New Delhi for funding under the project (DST/TSG/PT/2011/179-G). We are thankful to Dr. M. Lakshmi Kantam, DirectorCSIR-IICT for her support and encouragement. KSN is thankful to UGC, India for financial assistance.

References:
[1] Sondergaard, RR.; Hosel, M.; Krebs, FC. J. Polym. Sci. Pt-B-Polym. Phys. 2013, 51 (1), 16-34.
[2] Maria. N.; George G. M. The Chem. Rec. 2008, 8 (1), 13-22.
[3] Sun, J.; Gerberich, WW.; Francis, LF. Prog.Org. coat. 2007, 59 (2), 115-121

High Electromagnetic Interference Shielding Hybrid Composites Based on Carbon Nanohorn/Graphene Nanoplates and Polystyrene

Ranadip Bera, and B. B. Khatua[1]
Materials Science Centre, Indian Institute of Technology, Kharagpur-721302, India

Here, for the first time, we report the preparation of carbon nanohorn (CNH)/graphene nanoplates (GNP)/polystyrene (PS) composites through in-situ bulk polymerization of styrene monomer in the presence of CNH, followed by the addition of suspension polymerized GNP/PS beads during polymerization of styrene, as next generation multifunctional material for high electrical conductivity and electromagnetic interference shielding effectiveness (EMI SE) applications. CNH consisting of flower like architecture of sp^2 hybridized carbon with high electrical conductivity. Morphological analysis revealed selective dispersion of CNH in bulk polymerized PS matrix where GNP/PS beads were randomly distributed and formation of continuous conducting hybrid network of GNP-CNH-GNP or CNH-GNP-CNH throughout the PS matrix at exceptionally low loading of the CNH and GNP, leading to high electrical conductivity and EMI SE in the composites. Thus, an electrical conductivity of 6.24×10^{-2} $S.cm^{-1}$ and EMI SE value of ~24.8 dB were achieved in the composites even at 1.0 wt% CNH and 0.15 wt% of GNP, when the composites was prepared in the presence of 75 wt% GNP/PS bead. The GNP-CNH-GNP conductive network and the nonconductive GNP/PS beads creating dielectric mismatch in the composite influences the reflection and internal multiple reflection property of the composites.

References:

[1] Shrivastava, N. K.; Khatua B. B.; Carbon. 2011; 49(13): 4571–4579.

[2] Maiti, S.; Shrivastava, N. K.; Suin, S.; Khatua, B. B.; ACS Appl. Mater. Interfaces. 2013; 5(11): 4712–4724.

Synthesis and characterization of high molecular weight Poly (*p*-phenylene vinylene) for optoelectronic application

Shraddha Chhatre, Dr. S. B. Ogale, Dr. P. P. Wadgaonkar
Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory, Pune-411008, India
Email: sy.chhatre@ncl.res.in

Poly(*p*-phenylene vinylene) (PPV) contains alternating units of p-phenylene and trans-vinylene and shows many interesting properties like electrical conductivity, nonlinear optics, electroluminescence and photoluminescence. A small optical band gap and bright yellow fluorescence makes PPV a potential candidate for many electronic applications such as light-emitting diodes (LED) and photovoltaic devices. Some issues need to be addressed like synthesis of high molecular weight PPV, insolubility and infusibility because of its extended planar topology. This limits post synthesis fabrication. Here the synthesis of high molecular weight soluble PPV is undertaken by using Ring Opening Metathesis Polymerization (ROMP). The strained ring monomer [3.3] dithiacyclophane with solubilizing alkyl groups has been successfully synthesized and characterized. This is then converted into the paracyclophane diene and the polymerization was attempted by the opening of [2.2] paracyclophane 1,9 diene using Grubb's first generation catalyst.

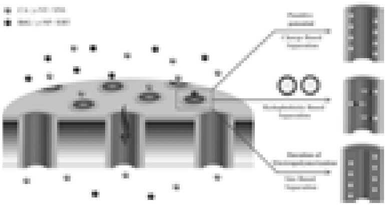
References

1. V. P. Conticello, D. L. Gin and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 9708–9710.
2. *Org. Biomol. Chem.*, 2011, **9**, 5018–5020
3. C. Y. Yu, M. Horie, A. M. Spring, K. Tremel and M. L. Turner, *Macromolecules*, 2010, **43**, 222–232
4. M. Montanari, A. Bugana, A. Sharma, D. Pasini, Org. Biomol. Chem., 2010, **9**, 5018

Disassembly of Micelles in Nanoscopic Space to Prepare Concentric Nanotubes with Variable Hydrophobic Interiors

Chayanika Das[a] and Kothandam Krishnamoorthy*[a]
[a]Polymer Science and Engineering Division, NCL, Pune
*k.krishnamoorthy@ncl.res.in

Amongst various approaches towards the preparation of hydrophobic surfaces, roughness and nanostructures are imperial. In this work we present an approach to prepare nanotubes with tunable hydrophobicity which is used to study separation of small molecules. Amphiphilic assemblies interact with oppositely charged rigid conjugated polymers and get disassembled.[1] Considering this concept, we have prepared positively charged PEDOT (oxidized) nanotubes, which interact with anionic SDS micelles.[2] This disassembly results in the adherence of negatively charged SDS head groups with the positive charges of oxidized PEDOT. Hydrophobic tails pointing towards the interior of nanotubes cause the nanotubes to be hydrophobic. This array of hydrophobic nanotubes has been used to separate small molecules with different hydrophobicity. Molecules with higher hydrophobicity pass through the nanotubes due to hydrophobic interactions. Before SDS modification, nanotubes of oxidized PEDOT were used to separate dyes with different charges. Positively charged dyes get repelled by the positive charges of PEDOT and negatively charged dyes pass through. Also these nanotubes were used to separate molecules based on size.



References:

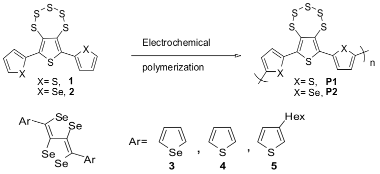
[1] Dutta, K.; Mahale, R.Y.; Arulkashmir, A.; Krishnamoorthy, K. Langmuir. **2012**, 28, 10097-10104

[2] Das, C.; Krishnamoorthy, K. Chem. Comm. **2014,** 50, 5905-5908

Sulfur and selenium containing new building blocks for conjugated systems

Sashi Debnath, Anjan Bedi, Sanjio S. Zade*
Department of Chemical Sciences,
Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246
*sanjiozade@iiserkol.ac.in**

The evolution of new conjugated organic materials for dyes, light emitting diodes, field effect transistors, sensors and electrochromic devices has largely relied upon assembling π-conjugated molecules and polymers from a limited number of building blocks. The synthesis of new conjugated building blocks, thiophene and selenophene capped C_4S_6 derivatives (compounds **1** and **2**) and diselenolodiselenole (C4Se4) derivatives (compounds **3-4**), is described for the first time. Here, we introduce two new synthetic approaches to synthesize these building blocks from their diyne precursors with elemental sulphur and selenium. Crystal structures of compound **3-5** show planar conjugated backbone with resolute intermolecular interactions through heteroatoms. Compounds **1** and **2** undergo electrochemical polymerization to produce new conjugated polymers **P1** and **P2**, respectively. Optoelectronic properties of these polymers are studied.



References:

[1] D. J. Schipper, L. C. H. Moh, P. Müller, T. M. Swager, Angew. Chem. Int. Ed. **2014**, 53, 5847.
[2] A. Bedi, S. Debnath, S. S. Zade, Chem. Commun. **2014**, 50, 13454- 13456.
[3] S. Das, S. S. Zade, Chem. Commun. **2010**, 46, 1168.

Thieno- and Seleno[3,2-*b*]pyrrole Donor Fused with Benzotriazole Acceptor: Microwave Assisted Synthesis and Electrochemical Polymerization

Sirina Ghosh, AnjanBedi and Sanjio S. Zade*
Department of Chemical Sciences, Indian Institute of Science Education and Research,
Kolkata, Mohanpur 741252, Nadia, West Bengal, India.

Thieno-/selenopyrrole fused benzotriazoles were synthesized by microwave assisted cyclization that dramatically reduces the reaction time. Incorporation of benzotriazole as an acceptor moiety in a fused ring system was studied for the first time. X-ray crystallographic studies were done for thienopyrrole and selenopyrrole fused benzotriazoles**1**, **2**, **6** and **7**. Compounds**6** and **7** crystalizes via hydrogen bonding with solvent ethyl acetate molecule. *N*-methyl substituted compounds **1** and **2** were electrochemically polymerized and characterized by spectroelectrochemistry. Introduction of more electron rich fused selenophene rings in compound **2** resulted in the elevation of HOMO level compared to that of compound **1**. Thus photophysical and electrochemical properties of these fused systems can be tune by changing the heteroatom of the terminal aromatic rings. Compound **1** and **2** showed solvatochromic effect.Increasing the solvent polarity, the emission maxima were shifted to longer wavelengths in the emission spectra of compound **1** and**2**.

Scheme: synthesis of thieno- and seleno[3,2-*b*]pyrrolefused benzotriazole

References:

[1] Cheng, Y.-J.; Chen, C.-H.; Ho, Y.-J. ; Chang, S.-W. ; Witek, H. A.; Hsu, C.-S. Org. Lett., **2011**, 13, 5484-5487.

[2] Kato, S.-i.; Furuya, T.; Kobayashi, A.; Nitani, M.; Ie, Y.; Aso, Y.; Yoshihara, T. ; Tobita, S.; Nakamura, Y. J. Org. Chem., **2012**, 77, 7595-7606.

A modified Polymerization technique of Polymer/MWCNT Nanocomposites with High Electrical Properties

Nilesh K. Shrivastava and B.B. Khatua*
Materials Science Centre
Indian Institute of Technology, Kharagpur
Kharagpur 721302, India

Ample of researchers are dedicated to the research on conducting polymer composites (CPCs) since few decades due to its large industrial demand. CPCs can be prepared by incorporating carbon black, carbon fiber, conductive metal fillers and recently carbon nanotube (CNT) into insulating polymer matrix above percolation threshold. Abundant research has been done using CNTs asfiller in making multifunctional nanocomposites, due to their high aspect ratios and excellent electrical properties. Polymer-CNT nanocomposites are usually prepared by solution casting, in-situ polymerization and melt mixing. There is no solvent removing problem like solution casting and non-uniform dispersion like melt mixing are the advantages of in-situ polymerization. In this work we report a modified in-situ polymerization technique for preparation of PMMA/CNT nanocomposites. Through this process, matrix conductivity of $\approx 2.5\times10^{-3}$ Scm^{-1} was obtained in PMMA/CNT nanocomposites with CNT loading close to 0.5wt%. Whereas, solution casted and melt mixing processes required 2wt% and 3 wt% CNT respectively to achieve the same level of electrical conductivity in the nanocomposites.

Key word: Nanocomposites, MWCNT, Electrical Properties.

Novel Water Dispersible Polyaniline based Electrode for Organic Field Effect Transistor

Shiny Nair[1], M.Yasir[2], M. Kathiresan[1], V. Natarajan[1], T. Mukundan[1],
[1]Naval Physical and Oceanographic Laboratory, Kochi, India
[2]Department of Mechanical Engineering, NIT Calicut, India

Organic field effect transistor (OFET) amplifiers are ideal candidates for flexible large area acoustic sensors to create the proximity electronic interface. Solution processable conducting and semiconducting polymers are a requirement to print these OFETs on flexible substrates. These processable conducting polymers have been used in the organic field effect transistors as electrodes in place of metal. Water dispersible polyaniline (PANi) that is template polymerized in the presence of polymer acids, poly (2-acrylamido-2methyl-1-propanesulfonic acid), or PAAMPSA and poly (styrene sulfonic acid) (PSS) has been developed. Conducting polymers that are not typically processable can be deposited from solution and conductivities enhanced by a simple solvent annealing process. Utraviolet Photoemission Spectroscopy (UPS) is used in the present study to determine the energy level alignment at interfaces between two electroactive conjugated organic materials, i.e., 1. copolymer of poly (3-hexyl thiophene) and poly (t-butyl acrylate); 2. pentacene and high work function electrode materials, palladium, synthesized PANi-PAMPS and PANi-PSS. Interfacial barrier properties were studied by first principle density functional theory calculations. UV-vis-NIR spectroscopy was used to examine the electronic structures of PANi-PAMPSA and PANi-PSS. Structure conductivity relationship was established by four probe conductivity measurement and XRD analysis. These OFET systems with polymeric electrode and active materials are being used in large area flexible acoustic sensors.

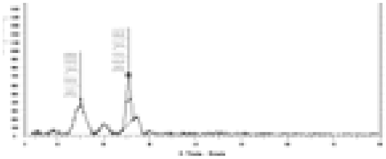


Fig. 1 XRD analysis of PANi PAMPS

References:
[1] Mi-Ri, C.; Seong-Hoon,; et al. W ChemSusChem **2011**, 4, 363-368.
[2] Koch, N.; Ghijsen, J.; et al. Appl. Phys.Lett. **2003**, 82, 70-72.
[3] Dawen, L.; Jay, L. G.; Appl. Phys.Lett. **2006**, 88, 635131-635133
[4] Yinhua, Z.; Canek, F.H.; et al. Science. **2012**, 336, 327-332
[5] Saranya. G.; Shiny N.; Natarajan, V.; et al. Comp. Mater. Sci. **2014**, 89, 216-223

Synthesis, Characterization, Optical and Electrochemical Properties of Phenothiazine, EDOT and Fluorene based Conjugated Polymers

E. Ramachandran and R. Dhamodharan*
Department of Chemistry, Indian Institute of Technology Madras,
Chennai - 600 036, Tamil Nadu, India.
Email: ramchandrane@gmail.com

The worldwide energy consumption is expected to double within next three decades since the world population is constantly growing. The main energy source for meeting the global energy needs is fossil fuel (coal, oil and natural gas) but there are two main disadvantages in using fossil fuels: (i) the limitation of resources and (ii) the environmental impact. So it is very important to develop sustainable energy solution. Among the all forms of alternate energy sources that exist today (nuclear, hydroelectric, geothermal, wind, biomass and solar), solar energy is considered to be clean and potential. Therefore the development of smart material which can harvest the solar energy very efficiently with relatively low cost is of current interest to the scientific community.

Narrow band-gap polymers have attracted enormous interest since they can effectively harvest the solar energy since nearly 50 % of the solar photons are in the near infrared (NIR) region. In order to achieve a very low band-gap polymer, the donor should be more electron rich with high-lying HOMO (highest occupied molecular orbital) energy levels and the acceptor should be highly electron deficient with low-lying LUMO (lowest un-occupied molecular orbital) energy level. Phenothiazine is a well known donor molecule used in synthesizing low band-gap polymers due to its electron rich nature owing to the presence of sulphur and nitrogen. Cyano-containing fluorene is one of the best acceptors used in narrow band gap polymers.

In the present study we have synthesized six narrow band-gap polymers containing phenothiazine as an electron donor and cynao-fluorene as electron acceptor. Moreover in order to improve the photon absorption from the solar spectrum, it is necessary to incorporate a molecule with high molar absorptivity; so we have included ethylenedioxythiophene (EDOT), which has a very high molar absorption co-efficient (ε) into the monomers and it showed improved molar absorption values for the corresponding polymers. The synthesized polymers showed broad absorption and very low-band gap (< 2.0 eV) and hence they can be used as potential candidates for solar cell and other application.

References

1. Boyle, G., Open, U., *Renewable energy: power for a sustainable future*. Oxford University Press in association with the Open University: Oxford, **1996.**
2. Cheng, Y-J; Yang, S-H; Hsu, C-S. *Chem. Rev.* **2009**, *109,* 5868–5923
3. Gibson, G. L; McCormick, T. M; Seferos, D. S. J. Am. Chem.Soc. **2012**, *134*, 539–547.
4. Hwang, D-H; Kim, S-K; Park, M-J; Lee, J-H; Koo, B-W; Kang, I-N; Kim, S-H; Zyung, T. *Chem. Mater.* **2004,** *16,* 1298- 1303.

Synthesis, Characterization and Optoelectronic Properties of Fluorene and Carbazole based Conjugated Polymers

Vivek Anand, Ramachandran Elumalai and Dhamodharan Ragavachari*
Indian Institute of Technology Madras
e-mail: damo@iitm.ac.in

Since the discovery of conjugated polymers (CPs) by Shirakawa and co-workers[1], they have been widely investigated for use as electronic and optoelectronic devices like organic light emitting diodes (OLEDs), electrochromic materials (ECs), field effect transistors (FETs) and solar cells[2]. Among these, application as electrochromic materials is quite diverse because these CPs have various stable oxidation states and the colours corresponding to these states are quite persistent moreover the switching time is also fast which leads to rapid colour change[3]. Plastic electronics are attractive and advantageous alternative to their inorganic counterparts because of their low cost, proccesability, and flexibility. But designing novel CPs having planar architectureπ, no -π stacking, high solubility and stability is a challenging task.

We here present the design, synthesis, and electrochemical and optoelectronic properties of new EDOT-Fluorene-Carbazole based conducting polymers. The combination of these moieties can have potential applications in the field of electochromics and electroluminescence

References

1. McEntee , G. J; Skabara, P. J.; Vilela, F.; Tierney, S.; Samuel, I. D. W.; Gambino, S.; Coles, S. J.; Hursthouse, M. B.; Harrington, R. W.; and Clegg, W.; *Chem. Mater.* **2010**, 22, 3000.
2. Sassi, M.; Salamone, M. M.; Ruffo, R.; Mari, C. M.; Pagani, G. A.; and Beverina, L.; *Adv. Mater***. 2012**, *24*, 2004–2008 .
3. a) Witker, D.; and Reynolds, J. R.; *Macromolecules* **2005,** *38,* 7636-7644. b) Mortimer, R. J.; Aubrey L. Dyer, A. L.;. Reynolds, J. R.; *Displays* 2006, *27*, 2–18.

An amphiphilicthermoresponsive conjugated block copolymer comprising regioregularpoly (3-hexyl thiophene)

Pallavi Kumari[1], Manas Kumar Bera[2], Sudip Malik[2] and Biplab K. Kuila[1*]
[1]Centre for Applied Chemistry, Central University of Jharkhand, Brambe,Ranchi, India
[2]Polymer Science Unit, Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick Road, Kolkata-700 032, India
Email: biplab.kuila@cuj.ac.in

Design and synthesis of new conjugated polymeric materials with new functionality and wide processibility has attracted a great deal of research attention because of their enormous potential applications in sensors, energy storages, corrosion inhibitors, enzyme catalysts, and optoelectronic devices etc.[1,2].Particularly, there is a great demand of highly water soluble conjugated polymeric materials for applications centred on biological environments[3]. Block copolymers where the functionality of the blocks can be varied independently, self-assemble into fascinating set of periodic nanostructures and are very attractive targets to device new materials where precise control over nanoscale organization is crucial[4].Application of the block copolymer strategy by synthesizing new conjugated block copolymer is one of the most convenient ways to manipulate optical and electronic properties of the conjugated polymer in the rapid optimization manner. Her we have reported a novel class of amphiphilic, thermoresponsive rod-coil conjugated block copolymer consist of regioregularpoly(3-hexyl thiophene) and Poly(N-isopropyl acrylamide). The block copolymer is synthesized by facile click reaction (scheme-1). The successful synthesis of the individual end functionalized polymer and the block copolymer were further confirmed by NMR, FTIR and MALDI-ToF MS.

In nonselective solvent, the block copolymer self-assemble into two phase separated nanostructure whereas in polar solvent like water or ethanol, P3HT-b-PNIPAM, self-assembled into core/shell–type nanostructure. The optical and luminescence property of the block copolymer is different from its pure analogue and highly depends on the nature of the solvent or composition in a mixed solvent. The temperature dependent UV-vis and photoluminescence study clearly indicates that between 30 to 350C in water, this polymer undergoes a reversible phase transition from a collided structure to collapsed globule. We believe that the unique optical and electronic properties of this block copolymer with thermoresponsive and amphiphilc characteristics will make it promising for many applications like sensor, fluorescence thermometer, and optoelectronic and bioelectronics devices.

Scheme 1 Total Reaction Scheme for the synthesis of P3HT-b-PNIPAM

References:

[1] Sirringhaus,H.Tessler, N.Friend, R. H. Science**, 1998**, 280,1741-1744.
[2] Heeger, A.J. Angew. Chem. Int. Ed.,**2001**,40,2591-2611.
[3] Nilsson K.P.R. ,Inganas. O, Nat. Mater. **2003**, 2, 419-424.
[4] Kuila B. K, Chakraborty C.,. Malik S, Macromolecules,**2013**, 46, 484-492.

Nonlinear Second harmonic generation of polymeric materials

M. Das[1*], P. Sen[2], S. K. Dolui[3] and B. Q. Khattak[4]
[1]Department of Physics, Medi-Caps Institute of Science and
Technology & Science, Indore-453331
[2]School of Physics, Devi Ahilya Vishwavidyalaya, Takshashila Campus, Indore - 452 017
[3]School of Science & Technology, Tezpur University, Tezpur, Napaam - 784028
malyaj08@gmail.com

Highly efficient Second-harmonic generation (SHG) polymers films are frequently used in waveguide applications[1]. SHG in organic molecules and polymers originate from a strong donor-acceptor intermolecular interaction via π-conjugated system with lack of symmetry[2]. We have reported FTIR and SHG analysis polymeric materials in the present abstract. The chemical structure was shown in Figure 1.

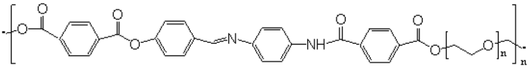


Figure 1: Chemical structures of polymer

The FTIR spectra of the polymer in the range of 4000–500 cm^{-1} as shown in Figs. 2 was recorded at room temperature using Jasco 660 plus an FTIR infrared spectrophotometer in KBr cells.

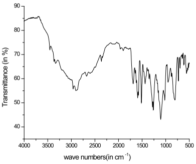


Figure 2: FTIR Spectra of Polymer

We have used Kurtz powder technique[3] to study the SHG activity. The SHG measurement is performed using 15 ns pulsed Nd: YAG laser at 1064 nm wavelength. The presence of N-H group and increased conjugation length is one of the reasons of SHG activity of polymer.

References:
[1] J. Zhang, E. Cassan, D. Gao, and X. Zhang, Optics Express, Vol. 21, Issue 12, pp. 14876-14887 (2013).
[2] D. S. Chemla, and J. Zyss, *Nonlinear Optical Properties of Organic Molecules & Crystals*,(Academic Press, New York), **1-2,** (1987).
[3] S. K. Kurtz and T. T. Perry, J. Appl. Phys. **39** (1968) 3798.

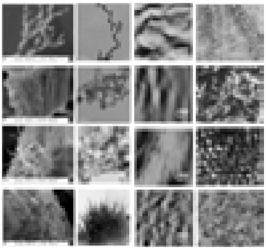
Tuning the photophysical properties of π- conjugated copolymer based on thiophene-benzothiadiazole by controlling the solvent induced aggregation.

[1]Renjith S, [1]T Prasada Rao, and [1]Sudha J D*

[1] Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum, Kerala, 695 019 India

*sudhajd2001@yahoo.co.in

Research on solution processableπ - conjugated polymers are receiving attention because of their unique optoelectronic properties which find applications in photovoltaics, super capacitors, thin film transistors, sensors and so forth. Active layer morphology, exciton conjugation length and crystallinity are the crucial factors which govern the efficient performance of such devices. Literature reports reveals that the relative solubility parameter of solvent used for the fabrication of active layer plays a key role in the modulation of optoelectronic properties via tuning the conformational changes effected by inter- or intra-chain aggregations. It is possible to tune the conformational order, dichroism as well as the charge carrier mobility by varying the relative solubility parameter. In the present work, we are addressing the role of solvent/nonsolvent ratio in tuning the photophysical properties of a copolymer based on 3-hexylthiophene and benzothiadiazole (PDHTBT). Molecular aggregation studies performed by changing non-solvent/solvent ratio reveals that significant non-solvent in solution makes solute-solvent interaction, energetically less favorable and forcing polymeric chain segments to approach each other resulting in aggregation. Sudden variation of solubility parameter also results in the coiling of polymeric chains and even transition from extended chain to collapsed helical coil conformations. Inter-chain interactions induced by solvent polarity results in birefringent lyotropic mesophases which further improves the charge carrier ability of the polymeric layer. The results generated in the present work can be exploited for the fabrication of photovoltaic devices with efficent performance.



References:

[1] Choudhury, P. K.; Bagchi, D.; Sangeeth, C. S.; Menon, R. J. Mater. Chem.**2011**, 21, 1607-1614.

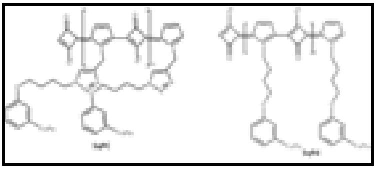
[2] Scharsich, C.; Lohwasser, R. H.; Sommer, M.; Asawapirom, U.; Scherf U.; Thelakkat, M.; Neher, D.; Ko¨ hler, A. J. polym.Sci.B **2012**, 50,442-453.

[3] Traiphol, R.; Sanguansat, P.; Srikhirin, T.; Kerdcharoen, T.; Osotchan, T. Macromolecules **2006**, 39, 1165-1172.

Self-Assembled Conjugated Polymers for Multifunctional Applications: Structure and properties

Molji C, Narayanan Unni K. N, and Sudha J D*
Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum, Kerala, 695 019 India
sudhajd2001@yahoo.co.in

Conjugated conducting polymers have attracted lot of scientific urge due to their intriguing properties arising from their tuneable electronic structure, low energy band gap, high optical damage thresholds, ultrafast optical responses and architectural flexibility along with processability and thermo mechanical stability. Such properties make them suitable candidates for photovoltaic applications mainly organic solarcells, OLEDs, OFETs etc. NIR absorbing conducting polymers are widely explored for photovoltaic systems since the photo induced charge generation has direct correlation with optical absorptivity. As the extent of absorption increases, the band gap become narrow and the photo excited electron density become enhanced. Designing Donor- Acceptor copolymers with NIR absorbing dye segments is an important strategy to tune bandgap and carrier density. Squaraine dye is one such ideal building block for tweaking the bandgap of polymers. Squaraine dyes typically contain an electron-deficient central four membered ring and two electron donating groups in a donor-acceptor–donor (D-A-D) fashion. In addition to band gap, the conformations adopted by polymeric chains in the active layer also play a crucial role in the device performance. Quasi ordered liquid crystalline conducting polymer (LCPs) systems are important in this respect as they inculcate both order and charge generation in a single system. Here, we present the preparation and characterisation of two LCPs (SqPc and SqPd) based on squaraic acid and pyrrole as acceptor and donor monomers, respectively. They were characterised for LC behaviour by DSC and PLM. Later, photo physical and electrochemical analyses revealed their utility in photovoltaic systems.



References:

[1] Ajayaghosh, A; Eldo, J.Org. Lett.**2001**, 16, 2595-2598.
[2] McEwen, J.J.; Wallace, K. J. Chem Comm, **2009, 6339**-6351
[3] Ajayaghosh, A; Chenthamarakshan, C. R.; Das, S.; George, M. V.Chem. Mater.**1997**, 9,644-646.

Preparation and anticorrosive properties of Polythiophene/Stretched Graphene composite

K. V. Yeole, S. T. Mhaske*
Department of Polymer and Surface Engineering,
Institute of Chemical Technology, N. P. Marg, Matuga (E), Mumbai-400019
*kvyeole@gmail.com

The synthesis of Poly (thiophene)-Stretched Graphene (PTh-SGR) conducting nanocomposite obtained by in situ polymerization of thiophene with ammonium persulphate as initiator by the addition of SGR. SGR was obtained by the treatment of Graphene with acids. The synthesized materials were characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible absorption (UV-visible), X-ray diffraction (XRD), morphological study, electrical conductivity and corrosion measurements. FTIR spectroscopy determines the interaction between the PTh and graphene. The band gaps of PTh & PTh-SGR measured by UV-visible spectroscopy. Morphological study shows the improvement in the graphene structure as well as in the composite. PTh-SGR nanocomposites thus synthesized were incorporated into epoxy based coating formulation and its anticorrosion property was studied. The aim of this study was to develop a facile method for the synthesis of eco-friendly anticorrosive coating.

Keyword: Poly (thiophene), Graphene, Conductivity, Anticorrosion.

Synthesis and Characterization of Conducting Polymer/Chitosan Semi Interpenetrating Polymer Network (Ipns) Hydrogels

Kanupriya Nayak[1*], Dr. Irfan Ahmad Mir[2]
Central Institute of Plastic Engineering and Technology, Lucknow
ratannayak23@gmail.com

Biocompatible hydrogel materials have emerged as potential matrix materials for development of Conducting Interpenetrating Network systems. Semi interpenetrating network (IPNs) of chitosan and conducting polymers have been developed. Chitosan was used as matrix material and conducting polymers, Polyaniline and Polypyrrole were used to prepare conducting IPNs by *in-situ* polymerization technique. The characteristics of these conducting polymer/chitosan semi interpenetrating polymer network (IPNs) hydrogels were investigated by Scanning electron microscopic (SEM), Thermo Gravimetric Analyzer (TGA), Fourier transform infrared (FT–IR) spectroscopy and swelling studies. It was observed that incorporation of conducting polymer network inside the chitosan network does not affect the basic characteristics of hydrogel. The swelling properties of chitosan network and those of IPNs show similar trend. FTIR analysis shows that basic chemical characteristics of chitosan and Polypyrolle and Polyaniline are intact. Thus no significant chemical interaction takes place. Thermal characteristics of the IPNs are similar to the thermal stability of chitosan matrix. SEM shows that the morphology of chitosan network remains intact with filler phase embedded uniformly. These materials are essentially conducting biocompatible substances which may have application in drug delivery, tissue engineering, sensing etc.

Keywords: Conducting polymer, IPNs Hydrogels , Chitosan , Plyaniline , Polypyrrole , Swelling.

References

[1]. Guan Y L, Shao L, Liu J and Yao K D **1996** *J. Appl. Polym.Sci.* **61** 2325
[2]. Oliverira W D and Glasser W G **1996** *J. Appl. Polym. Sci.* **61** 81
[3]. Rathna G V N, Rao D V M and Chatterji P R **1996** *JMS-Pure Appl. Chem.* **A33** 1199
[4]. Hoffman A S **2002** *Adv. Drug Delivery Rev.* **43** 3
[5]. Castel D, Richard A and Audebert R **1990** *J. Appl. Polym. Sci.* **39** 11
[6]. Gupta P, Vermani K and Garg S **2002** *Drug Discov. Today* **7**569

One-Pot Microbial Method to Synthesize Reduced Graphene Oxide and Intracellular PHA biopolymer

Nilkamal pramanik[1, 2] Patit Paban Kundu1*,Ranjan Kumar Basu*2
[1]Advanced Polymer Laboratory, Department of Polymer Science & Technology,
University of Calcutta,
[2] Department of Chemical Engineering, University of Calcutta, Kolkata- 700009, India
E-mail: nilkamal.can@rediffmail.com

In the present study, we have investigated the microbial reduction of an novel compound, graphene oxide into graphene and intracellular accumulation of biodegradable, biocompatible and nontoxic biopolymer, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)copolymer through one pot synthesis strategy. It avoids the use of toxic and environmentally harmful reducing agents commonly used in the chemical reduction of GO to obtain graphene. The microbial reduction and intracellular accumulation of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer were performed by *Alkaliphilus oremlandii ohILAs* strain at temperature of 32°C and pH 8 for 36 hours under a orbital shaking at 105 rpm. The microbially reduced graphene demonstrates significantly improved electro-catalytic properties and electrochemical sensing performances in comparison with chemically reduced graphene. Both the reduced graphene and biopolymer were characterized using FTIR, XRD, DLS, TEM, AFM and Raman spectroscopy analysis. Transmission electron microscopy and atomic force microscopy images provide clear evidence for the formation of few layer graphene. Characterization of the resulting microbially reduced GO by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy shows partial reduction of GO to graphene. Raman spectroscopy data also indicates the partial removal of oxygen-containing functional groups from the surface of GO and formation of graphene with defects.

References

[1]. Nilkamal Pramanik, Khushi Mukherjee, Arpita Nandy, Shritama Mukherjee, Patit Paban Kundu, Comparative analysis of different properties of polyhydroxyalkanoates isolated from two different bacterial strains of *Alkaliphilus oremlandii OhILAs* and recombinant *E.coli* XL1B, Journal of Applied polymer Science, 2014.

[2] Pornpa Suriyamongkol, Randall Weselake, Suresh Narine, Maurice Moloney, Saleh Shah, Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plants — A review, Biotechnology Advances 25 (2007) 148–175.

Improved Performance of Solution-Processed n-type Organic Field-Effect Transistors by Regulating the Intermolecular interactions and Crystalline Domains on Macroscopic Scale

Suresh Vasimalla[1], Satyaprasad P. Senanayak[2], Meenakshi Sharma[1], K. S. Narayan[2], Parameswar Krishnan Iyer[1,2*]
[1]Department of Chemistry, Indian Institute of technology,Guwahati, Guwahati, Assam, India
[2]Centre for Nanotechnology, Indian Institute of technology,
Guwahati, Guwahati, Assam, India
[3]Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore, India

The development of four new n-channel naphthalene diimide (NDI) and perylene diimide (PDI) copolymers and their solution processed thin film transistor (TFT) devices are reported. Remarkable enhancements in the electron transport behavior for all the four copolymers were achieved on improving the intermolecular interactions in their thin film structures. These solution processable n-type copolymers were synthesized by palladium catalyzed Suzuki coupling reactions, and their excellent solubility in several organic solvents allowed their deposition in OTFT devices from solution directly. Since these copolymers possess crystalline domains, annealing their films induced crystalline phases in the thin film structures with a very high degree of enhancement in crystallinity that was more prominent for PDI copolymers as compared to NDI derivatives.

This resulted in significant enhancement in the intermolecular interactions in the thin film state on the macro scale, facilitating improved and higher charge carrier transport in annealed devices as compared to the as-spun devices that have lesser crystalline phases. The transport measurements performed helped us to understand the difference in transport mechanism between D−A and A−A moiety and confirmed that tuning the backbone structures as well as annealing them at appropriate temperature has profound implications on the level of improvement in electron transport behavior. It is observed that the extended conjugation in the four copolymer structures, the efficient intermolecular interactions in the thin film state, and the formation of crystalline domains in the copolymers after annealing are, in principle, responsible for the enhanced device performance. These copolymers demonstrated electron mobility enhancement of several orders and are reported to be as high as 0.8 $cm^2\ V^{-1}\ s^{-1}$ and 0.2 $cm^2\ V^{-1}\ s^{-1}$with I_{on}/I_{off} ratios 10^5 for NDI-Ph and NDI-BT, while those of PDI-Ph and PDI-BT are 0.04 $cm^2\ V^{-1}\ s^{-1}$ and 0.032 $cm^2\ V^{-1}\ s^{-1}$, respectively, with I_{on}/I_{off} ratios of 10^3–10^4.

References:

[1] H. Yan, Z. Chen, Y. Zheng, C. Newman, J.R. Quinn, F. Dotz, M. Kastler, A.Facchetti, *Nature* **2009,** *457,* 679.

[2] R. Kim, P. S. K. Amegadze, I. Kang, H. J. Yun, Y. Y. Noh, S. K. Kwon, Y. H. Kim, *Adv. Funct. Mater.***2013**, *23*, 5779.

[3] P. M. Alvey, R. J. Ono, C. W. Bielawski, B. L. Iverson, *Macromolecules***2013**,*46*, 718.

[4] V. Suresh, S. P. Senanayak, M. Sharma, K. S. Narayan, P. K. Iyer. *Chem. Mater* **2014**, *26*, 4030.

Functional Materials ForNew Technologies: Designs at Nanoscale

Prasad Raut[1], Andrew Shinko[1], Sepideh Niknezhad[1], and Sadhan C. Jana[1]*
[1]Department of Polymer Engineering, University of Akron, Akron, OH 44325, U.S.A.
**janas@uakron.edu*

We currently look at the design of a number of functional bulk materials, e.g., aerogels and multicomponent nanofibers in our laboratory where the investigation focuses on how the nanoscale crystalline polymer strands[1], crosslinked thermoset gel networks, polymeric nanofibers[2,3], and 5-10 nm diameter pearl-necklace silica strands[4]hierarchically construct the bulk structures with nanoscale features. In one example, mesoporous polymer gels filled with ionic liquids are used as separators cum electrolytes of lithium ion batteries offering high ionic mobility, expanded operating temperature window, and strong mechanical performance. A second example focuses on the design of core-shell and side by side nanofiber structures that offer fine balance between burst and timed-release of drugs in wound dressing materials. A third example considers screening of airborne nanoparticles(100 nm or smaller) using polymeric aerogel monoliths with filtration efficiency approaching 100%at an order of magnitude higher air permeability than found in HEPA filters.In all these examples, the interplay between chemistry, phase separation dynamics, and development of nanometric building blocks are investigated with the objective of meeting some of the grand technological challenges faced by our generation.

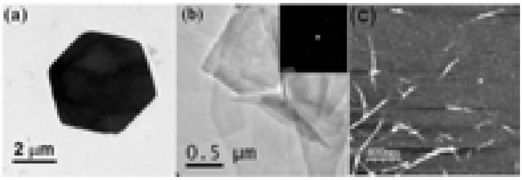
References:

1. Wang, X., Jana, S.C. *ACS Appl. Mater. Interfaces*, 2013, 5, 6423–6429
2. Benavides, R., Jana, S.C., Reneker, D.H. *Macromolecules*, 2013, 46, 6081-6090.
   Benavides, R., Jana, S.C., Reneker, D.H. 2012 *ACS Macro Letters*, 2012, 1, 1032-1036.
3. Duan, Y., Jana, S.C., Reinsel, A.M., Lama, B., Espe, M.P., *Langmuir*, 2012, 28, 15362–15371.

Highly Exfoliated Polymer/Surfactant-Free LDH Nanocomposites: Structure, Morphology and Crystallization Behavior

E. Bhoje Gowd
Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India – 695 019
bhojegowd@niist.res.in

Polymer-inorganic nanocomposites have evolved and attracted great interests from both in industry and in academia during the last two decades. In particular, exfoliation of layered materials in polymer matrices has been shown to spectacularly improve the flame retardancy, optical, thermal and rheological properties of base polymer. Layered double hydroxides (LDH) are one such potential inorganic nanofillers with an advantage to vary the composition of both inorganic layers as well as balancing anions in the interlayer space. Because of the tremendous flexibility in tuning the properties of LDH, these materials are considered as a new emerging class of nanofillers for the preparation of multifunctional polymer/LDH nanocomposites. Preparation of highly exfoliated polymer nanocomposites using LDH is always a great challenge because of the stronger electrostatic interlayer interactions due to their higher charge density. A number of approaches have been reported for the preparation of exfoliated nanocomposites, mainly in the context of surfactant modified LDH. However, high level of surfactant loadings could lead to negative impact on costs, procesability and also possible to inferior thermal properties of the polymer nanocomposites. The end-use applications of polymer nanocomposites would be greatly expanded with surfactant-free materials. The present talk mainly highlights the new strategies to prepare highly exfoliated polymer/ surfactant free LDH nanocomposites using syndiotactic polystyrene and isotactic polypropylene. In addition to that, the effect of LDH on the crystallization behavior, polymorphism, thermal stability and flame retardancy of polymer/LDH nanocomposites will be discussed.



TEM images of (a) as-prepared Mg-Al LDH, (b) delaminated Mg-Al LDH and (c) AFM image of iPP nanocomposite film containing 10 wt% of LDH

Nanoscale Functionalization of Surfaces with Polymers: Self-assembled Monolayer Formation and related techniques

P. Murugan, P. Nagaraju, M. Krishnamurthy, A. B. Mandal,
* Debasis Samanta*
Polymer Division, CSIR-CLRI, Adyar, Chennai-20, India
debasis.samanta@gmail.com

Polymer functionalized surfaces are of wide interest for sensors, solar cells and molecular electronic device fabrication. Utilization of self-assembled monolayer (SAM)[1] formation technique is very useful to functionalize surfaces in a controlled manner. For example, polymer can be immobilized on SAM by "grafting to" approach in which case a polymer is synthesized in solution possessing a reactive group at one end that reacts with complementary functional group on SAM. Another approach is "grafting from" technique where initiator is immobilized on surface first followed by the reaction of this surface bound species with monomer in solution. However, "graft from" technique is limited to living chain-growth polymerization and needs difficult experimental set up. An intermediate approach is "grafting through" polymerization method in which case, solution polymerization is performed in the presence of a surface functionalized with groups react in the polymerization It often has the advantage of simplicity like "graft from" polymerization, but with improved performance in terms of grafting density.

In the presentation we report our recent result on "graft through" click polymerization[2] and Sonogashira polymerization[3] reaction that was performed by using functionalized SAM. We will discuss about the thickness, grafting density of the polymers on surfaces. The results obtained from various characterization techniques such as XPS, FTIR, AFM will also be discussed. We will extend our discussion to other techniques of functionalization of surfaces such as chromium assisted immobilization of thermoresponsive polymers to leather surfaces[4] and copper catalyzed "click" polymerization on fullerene surfaces. Finally, we will present our results on functionalization of carbon nanotube surfaces for targeted drug delivery applications.[5]

Acknowledgement: Financial assistance from DST (SR/FT/CS-104/2009) and DBT (BT/PR6433/GBD/27/413/2012) is gratefully acknowledged.

Reference:

1) Samanta, D. Sarkar, A. Chem. Soc. Rev. **2011**, 40, 2567.
2) Samanta, D. Murugan, P. Ananthakrishnan, S. J. Somanathan, N. Das, S. K. Jaisankar, S. N. Mandal, A. B. Chem. Commun. **2012**, 48, 12068.
3) Murugan P. Ananthakrishnan, S. J. Somanathan, N. Samanta, D. Mandal, A. B. RSC Adv. **2015**
4) Samanta, D. et al. RSC Adv. **2013**, 3, 16626.
5) Samanta, D.; Sankar, R. M; Jaisankar, S. N.; Alam, M. S; Mandal, A. B. *Chem. Commun.* **2011**, 47, 11975.

Carbon Quantum Dot-Polymer Nanocomposites: Their Optical and Conducting Properties

Lopamudra Bhattacharjee and Rama Ranjan Bhattacharjee*
PSG Institute of Advanced Studies, Coimbatore, Tamil Nadu
**ramaranjanb89@gmail.com*

With the advent of controlled preparation of inorganic semiconductor Nano-Crystals (NCs) with tunable electronic and spectroscopic properties [1-4], they are readily used, in composition with polymers, for light-emission, energy generation, sensing and memory applications [3,4]. However, the known toxicity associated with many of these NCs, in particular, the use of heavy metals such as cadmium and tellurium limits large-scale applications.

We synthesized water dispersible carbon-based quantum dots (CQDs) in gram-scale using a single step pyrolysis process. Most importantly we have shown that we can control the conductivity of the CQDs by optimizing the size and crystalline property of the CQDs. The tuning of the property was achieved through careful choice of precursor to stabilizer ratio. We have also shown the I-V characteristics of a single CD. For this, we spin coated a very dilute aqueous solution of CD over an ITO coated glass substrate. It can be printed on flexible surfaces, can be easily spin coated on ITO and easily made into freely suspendable polymer films with water soluble polymers like Polyvinyl alcohol (PVA). Conducting AFM show symmetrical current-voltage characteristics exhibiting linear behavior in the low voltage regime and saturates at higher voltages. Under solar simulator, the CQD-PVA film shows a maximum voltage of 25 mV which do not drain in dark. Presence of polymer stabilizer on the CQD surface makes it highly water dispersible and easily blends with polymers like PVA through inter-polymer complex formation. The CQDs thus can be suspended in any polymer matrix.

References:

[1] Sun Y. P., Zhou B., Lin Y., Wang W., Fernando K. A. S., Pathak P. J. Am. Chem. Soc. **2006**, 128, 7756-7757.
[2] Cao L., Meziani M. J., Sahu S., Sun Y. P. Acc. Chem. Res. **2013**, 46, 171-180.
[3] De B., Karak N. A. RSC Adv. **2013,** 3, 8286-8290.
[4] Wang J., Wang C. F., Chen S. Angew. Chem. Int. Ed. **2012,** 51, 1-6.

New Generation Luminescent Nanomaterials Based on Polymer Nanoparticles

Amitava Patra
Department of Materials Science,
Indian Association for the Cultivation of Science, Kolkata 700 032, India,
E-mail: msap@iacs.res.in

Considering the emerging field of organic molecules encapsulated polymer nanoparticles, we have highlighted few important fundamental photophysical aspects in details. Here, we will discuss the photo-physical behaviors of polymer nanoparticles encapsulated fluorophore dye molecules and their restricted rotational behaviors inside polymer nanoparticles. Details time resolved spectroscopic investigations have been carried out to unveil the effect of micro environmental rigidity on rotional diffusion of dye. Steady state and time-resolved fluorescence spectroscopic studies are used to investigate the energy transfer between host-guest and the local environments of dye molecules when encapsulated within the polymer nanoparticles. In case of multiple fluorophores encapsulated polymer nanoparticles, we observed multistep cascaded energy transfer. We demonstrate π-conjugated polymer nanoparticles-photosensitizer conjugates for singlet oxygen generation via FRET cascade which would be useful for photodynamic therapy.

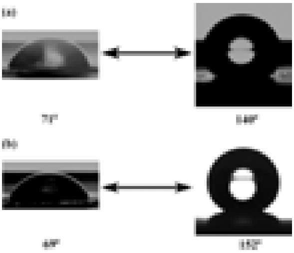
References:

1. S. Bhattacharyya, and A. Patra, J. Photochem. and Photobiol. C: Photochemistry Reviews, (**Review article**) 2014, 20, 51–70.
2. S. Bhattacharyya, M. K. Barman, A. Baidya, A. Patra, J. Phys. Chem. C. 2014, 118, 9733-9740.
3. S. Kundu, S. Bhattacharyya and A. Patra, Materials Horizons, 2014 (accepted).
4. C. Martin, S. Bhattacharyya, A. Patra, and A. Douhal, Photochemical & Photobiological Sciences, 2014, 13, 1241-1252 .
5. S. Bhattacharyya, S.Prashanthi, P. R. Bangal and A. Patra, J. Phys. Chem. C 2013, 117, 26750–26759.
6. M. K. Barman, S. Bhattacharyya and A. Patra, Phys. Chem. Chem. Phys, 2013, 15, 16834-16840.
7. S. Bhattacharyya, B. Paramanik, S. Kundu and A. Patra, ChemPhysChem. 2012, 13 , 4155.
8. S. Bhattacharyya, B. Paramanik and A. Patra, J. Phys. Chem. C, 2011 115, 20832.
9. S. Bhattacharyya, T. Sen, and A. Patra, J. Phys. Chem. C, 2010, 114, 11787]

Designing of a Simple Temperature Responsive Coating by Simple Physical Blending

[1]Swapan K. Ghosh*, [1]K. Rajesh Kumar, [1]Faisal Ansari, [2]Dhriti Ranjan Saha,
[2]Dipankar Chakravorty, [3]Anindya Datta
[1]Nova Surface-Care Centre Pvt. Ltd., Unit Nos. D107 to D112, Kailash Industrial Complex,
Vikhroli-Hiranandani link road, Vikhroli (W), Mumbai 400 079, India.
[2]Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick road, Jadavpur, Kolkata 700 032, India
[3]University School of Basic and Applied Sciences,
Guru Gobind Singh Indraprastha University, Delhi 110 078, India
*Email: swapan.ghosh@nsccindia.com

In this presentation we shall be reporting a very simple design philosophy of a coating which response to temperature-rise to change its nature from hydrophilic to superhydrophobic. The developed material can be applied to variety of surfaces simply by brush or roller, thereby becoming hugely applicable as a base of a smart paint. Low surface energy fluoro and amino monomers were introduce to prepare the polymer backbone, which was then used as a binder for nano-micro dual particle morphology, pre-functionalised with hydrophobic siloxane, by simple physical blending, inspired by so called lotus effect. The resulting material show a water contact angle of 152° with a roll of angle as low as 2° in response to elevated temperature, changing its hydrophilic nature. This reversible switching is ascribed to formation and breaking of hydrogen-bond between amine group (secondary or tertiary) in polymer backbone and water. We also show that the response temperature can be tuned, which shows future possibility of designing country specific self-cleaning exterior paints.



Reversible switching of contact angle due to change in temperature of the substrate

Novel ordered meso patterning of thin polymer films by Self Organization

Rabibrata Mukherjee
Instability and Soft Patterning Laboratory, Department of Chemical Engineering
IIT Kharagpur, Pin 721302, West Bengal, India
e-mail: rabibrata@che.iitkgp.ernet.in

Topographically patterned films and surfaces with sub micron and meso scale lateral resolution find wide application in host of important and interesting areas such as micro electronics electronics, thin film transistors (*TFT*), biological sensors, structural color, super hydrophobic, super wetting and self cleaning surfaces, materials with surface gradient etc. For many of the above applications, rapid prototyping of surfaces with the pattern extending over large areas (~ cm^2) are necessary. To cater to this segment, various polymer specific patterning methods have been developed in last couple of decades, which are simple and easy to execute. These methods are broadly classified as "Soft Lithography" (SL). Majority of the SL methods rely on replicating a "master" pattern by some mechanisms which include molding and visco plastic deformation, embossing or pattern replication by capillary driven flow. Consequently, majority of these techniques are capable of producing a perfect negative replica of the original mold, thus depending heavily on the availability of the original, lithographically fabricated mold or stamp. We have been investigating the possibility of creating structures that are distinct from being a mere positive or negative replica of the original stamp, thereby allowing more flexibility and control over pattern morphology. In this context we will present some of our recent work that allows creation of different ordered patterns by utilizing the interplay of different forces at the meso scale. First, we will discuss how stress relaxation in a visco elastic thin film to create patterns that have the same periodicity as that of the master but have programmable feature height using a single stamp.[1] We have subsequently extended this technique to create patterns with a topography vis – a – vis wettability gradient.[2]We then discuss how partially or completely ordered structures can be obtained by spin coating on a topographically patterned substrate,[3]and highlight how sequential spin dewetting has been utilized in fabricating a novel alternating binary droplet array.[4]

References:

1. Bhandaru, N.; Roy, S.; Suruchi, P.; Harikrishnan, G.; Mukherjee, R. Lithographic Tuning of Polymeric Thin Film Surfaces by Stress Relaxation, *ACS Macro Letters***2013**, 2, 195 – 200.
2. Roy, S.; Bhandaru, N.; Das, R.; Harikrishnan, G.; Mukherjee, R. Thermally Tailored Gradient Topography Surface on Elastomeric Thin Films, *ACS Applied Mater Interface***2014,** 6, 6579–6588.
3. Roy, S.; Ansari, K. J.; Jampa, S. S. K.; Vutuluri, P.;Mukherjee, R. Influence of Substrate Wettability on the Morphology of Thin Polymer Films Spin–Coated on Topographically Patterned Substrates, *ACS Applied Mater Interface***2012,** 4, 1887–1897.
4. Bhandaru, N.; Das, A.; Salunke, N. Mukherjee, R. Ordered Alternating Binary Polymer Nano Droplet Array bySequential Spin Dewetting, *Submitted* 2014.

Chitosan-Curcumin Nanoparticles on Proliferation of Human brain Carcinoma cell lines

B. Garnaik*
Division of Polymer Science and Engineering,
CSIR-National Chemical Laboratory, Pune - 411008, India
Email: b.garnaik@ncl.res.in

Chitosan nanoparticles are good drug carriers because of their biocompatibility, biodegradability, and can be readily modified. Nanoparticles have been widely investigated to enable drug delivery due to their low toxicity, sustained drug release, molecular targeting, and additional therapeutic and imaging functions. Turmeric contains a major polyphenolic compound, named curcumin was chosen because it eliminates cancer cells derived from a variety of peripheral tissues. Although in vitro experiments have addressed its anti-tumour property, no in vivo studies have explored its anti-cancer activity in the brain. Oral delivery of this food component has been less effective because of its low solubility in water. This study has developed a chitosan-based delivery system to locally administer curcumin for brain cancer treatment. We prepared chitosan/curcumin nanoparticles and characterized by UV-visible, SEM, transmission electron microscope (TEM) and light scattering (DLS) analysis techniques. In vitro release study was performed by using a UV spectrophotometer, and enzymatic degradation rate was determined by analyzing the increased free amino groups. Viability of brain cancer cells (human U87 glioblastomas and rat C6 glioma cells) was measured via direct and indirect cell culture on nanoparticles by MTS assay. Curcumin-Chitosan nanoparticles effectively inhibited the proliferation of human U87 glioblastomas through multiple mechanisms, and may be a beneficial agent against human carcinoma. These results will be highlighted.

References:

1] Duan J.; Mansour HM.; Zhang Y. Int. J. of Pharmaceutics. **2012**, 426, 193-201.
2] Tang H.; Murphy CJ. ; Zhang B.; Shen Y.; Van Kirk EA.; Murdoch WJ. ; Radosz M. Biomaterials. **2010,** 31, 7139-7149.
3] Vinogradov S.; Wei X. Nanomedicine. **2012,** 7, 597–615.
4] Holland EC. Synthesis. **2000**, 97, 6242-6244.

Synthesis of Nanoparticles in Polymer Hydrogels for Catalytic and Drug Delivery Applications

Manohar V. Badiger Ph. D.
Polymer Science and Engineering Division, CSIR-National Chemical Laboratory (NCL)
Dr. Homi Bhabha Road, Pune – 411 008, India
e-mail:mv.badiger@ncl.res.in

Nanoparticles (NPs) have been extensively used in a wide range of applications, such as, catalysis, biomedicine, sensors and opto-elctronics due to their unique electronic properties and high surface to volume ratios. However, issues like aggregation, non-dispersibility of NPs frequently crops up. In order to overcome these problems, research efforts are being made to stabilize NPs in various ways. In-situ synthesis of metal NPs in the polymer matrices is an excellent alternative.

In the present work, a simple and convenient method for generating and immobilizing Gold NPs (Au-NPs) into polyethylene glycol-polyurethane (PEG-PU) hydrogel matrices is reported. The Au-NPs immobilized PEG-PU hydrogel matrices are easy to handle and can be used as catalysts. The efficiency, reusability and durability of the Au-NP-PEG-PU catalyst matrices were investigated using a model reaction of reduction of 4-nitroaniline (4NA) to *p*-phenylenediamine (*p-PDA*) by sodium borohydride. The Au NPs-PEG-PU matrix showed excellent catalytic efficiency without any aggregation, leaching or degradation. The reusability of the catalyst for 28 cycles yielding a total turnover number of 3220 and turn over frequency is $0.152 s^{-1}$ is demonstrated.

We also worked on the synthesis and characterization of Silver NPs (Ag-NPs) using a thermo-associating polymer namely, carboxymethyl guar grafted poly(ethylene oxide-co-propylene oxide) [CMG-g-PEPO]. The polymer acts as both reducing agent as well as stabilizing/capping agent. This polymer was used for drug delivery applications. These aspects will be discussed during the presentation.

Dispersion and Dynamics of Polymeric Nanoparticles in Polymers: Role of Confinement and Interface Wettability

Jaydeep K Basu*,
Department of Physics, IISc, Bangalore
*basu@physics.iisc.ernet.in

Dispersion of nanoparticles in polymers to create new polymeric materials is a key challenge in polymer science. In this regard polymeric nanoparticles, with minimal enthalpic interactions, especially with a homologous matrix polymer was deemed to be the most effective strategy to enhance dispersion. However, it turns out that entropy plays a major role in such blends and nanocomposites leading to auto-phobic interfacial wetting/de-wetting and hence failure of such strategies in several cases. Here we will discuss the issues involved in circumventing this problem with polymer grafted gold nanoparticles embedded in polystyrene especially how confinement can aid in the dispersion. We will also discuss how the dynamics of these embedded polymeric nanoparticles show apparent anisotropic diffusivity and significantly reduced drag as well as enhanced hydrodynamic interactions while moving through the viscous polymer medium and its connection to the glass transition temperature of the polymer.

References:

[1] Chandran, S.; Begam N.; Padmanabhan V.; and Basu, J.K. Nature Communications (**2014**) 5, 3697.
[2] Chandran, S.; Mukhopadhyay M.K.; and Basu, J.K. J. Chem. Phys. (**2013**) 138, 014902.

Development of Multi-Functional Nanobiocomposites: A One-stage Process through Reactive Blending

Vincent Ojijo and Suprakas Sinha Ray*
DST/CSIR National Centre for NanostructuredMaterials, Council for Scientific and IndustrialResearch, Pretoria 0001, South Africa
**rsuprakas@csir.co.za*

Polylactide (PLA) and poly[(butylene succinate)-*co*-adipate] (PBSA) were reacted by being blended in a batch mixer in the presence of a chain extender, triphenylphosphite (TPP), and two different types of organically modified clays – a montmorillonite clay (C20A) and a synthetic mica (MEE) – to enhance the thermal stability, impact toughness and barrier properties of the PLA. An accelerated increase in the torque during processing indicated catalyzed chain-extension reactions in the clay-based compatibilized blends. The rate and extent of the increase in the chain extension/coupling were dependent on the type of organic surfactant used to modify the pristine clays. Enhanced chain extension/coupling and char formation resulted in dramatic thermal-stability increases of 17 and 26 °C for composites with 2 and 6 wt% C20A loadings, respectively. Similarly, the oxygen and water-vapor permeabilities were improved with the addition of the clays. At 4 wt% MEE loading, the oxygen and water-vapor permeabilities were reduced by 60 and 50%, respectively. Unlike the MEE-based blends, C20A-based compatibilized blends resulted in higher toughness than the neat PLA due to the lesser crystallinity of the PLA component and enhanced chain extensions/coupling in the C20A - based samples. Therefore, this work demonstrates the possibility of enhancing the thermal stability, toughness and barrier properties of PLA in a one-stage process through reactive blending with PBSA in the presence of clays.

References

[1] Ojijo, V.; Ray, S. S.; Sadiku, R.ACS Appl. Mater. Interfaces**2013**, 5, 4266–4276.
[2] Ray, S. S. Acc. Chem. Res. **2012**, 45, 1710−1720.
[3] Ojijo, V., Ray, S.S. Prog. Polym.Sci. **2013**, 38, 1543−1589.
[4] Ojijo, V.; Ray, S.S.; Sadiku, R. Macromol. Mater. Eng. **2014**, 299, 596-608

Cobalt Metal Nanoparticle Embedded Polymer based Magnetic Materials

G. S. Mukherjee[1], P. Sachdeva[2] and M. Banerjee[2]
[1]Defence Research & Development Organization, Metcalfe House
DRDO Complex, New Delhi-110054
[2]Nano Science & Technology Lab., School of Physics, Devi Ahilya University, Indore - 452 017
gsmukherjee.drdo@gmail.com

Cobalt (Co) exhibits ferromagnetic behaviour even at ultra thin level. But its nanostructures are prone to oxidation. Thus, we felt interesting to work towards protecting the Co nanostructures. Our approach to overcome the problem of oxidation of Co was done by creating a polymer under-layer to enable proper growth of Co magnetic nanostructure followed by applying an overlayer to protect the Co nanostructure. Here magnetic materials in the form of films namely PVA/Co/C, PVA/Co/Ag were prepared by using ion beam sputtering technique where particles of different characteristics – magnetic metal (Co), followed by non-magnetic non-metal (C overlayer) and non-magnetic metal (Ag overlayer) were applied in the PVA matrix as per sequence referred above. Similarly nanocomposite film, PVA/Co was also prepared by embedding Co nanoparticles onto PVA film without applying any overlayer. Microstructural investigation was done using GIXRD, XPS, MOKE, AFM and MFM to understand features of such magnetic materials. GIXRD reveals the formation of nanocrystalline Co with *hcp* phase and that there is no change in the crystalline structure of PVA even after sputtering. Role of polymer, thickness of embedded Co as well as the overlayer and its nature are discussed. Interestingly, it has been observed that the magnetic property of PVA/Co film retains its magnetic properties even after 2 years.

References

1. Kharmouche A.; Chérif S-M.; Bourzami A.; Layadi A.; Schmerber G. J. Phys. D: Appl. Phy. **2004,** 37, 2583
2. 3. Su C.W.; Tsay J.S.; Hwang C.H. Yao Y.D. J. Appl. Phys. **2005**, 97, 10J111
3. Chen Y-Y, Wang P.W.; Hsu J-C.; Lee C-Y. Vacuum, **2013,** 87, 227–231
4. Mukherjee G.S. J. Materials Sci. **2005**, 40, 3017-3019

Plasma Polymerization of Tetrafluoroethane for Nano-scale Surface Modification of Cellulosic Substrate

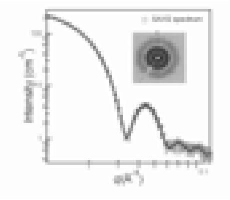
Kartick K. Samanta*, S. Saxena, S. Basak, P. G. Patil,
A. Arputharaj, and Gayatri T. N.
Plasma Nanotech Lab, Chemical and Bio-chemical Processing Division
Central Institute for Research on Cotton Technology (CIRCOT),
Adenwala Road, Matunga, Mumbai - 400019, India
** karticksamanta@gmail.com*

Plasma polymerization of hydrocarbon, fluorocarbon, and other molecules is important for nano-scale surface engineering of polymeric substrates for its improvement in dyeing, printing, adhesion strength, hydrophilic, hydrophobic, flame retardant, and UV protective properties in dry state using a minimal amount of chemical. In this study, surface modification of cellulosic substrates (cotton textile) was carried out by plasma polymerization of tetrafluoroethane with a small admixture of difluoromethane at atmospheric pressure. In-situ plasma polymerization is a complex process due to the fragmentation of a precursor molecule and numbers of recombination reactions. When the tetrafluoroethane gas was introduced in helium (He) plasma, it gets fragmented into various molecules as detected in gas chromatography-mass spectrometry of the plasma exhaust, such as CF_3, C_2F_5, $C_2F_2H_3$, C_3F_5H, C_2F_4, C_3F_6H, etc. Some of the low molecular weight species that were not detected in GC-MS, were also detected by their atomic lines in optical emission spectrometer, such as F at 429, 357, 341, 325 nm and $–CF_2$ line at 318 nm. After the plasma reaction of such fluorocarbon species with a cellulose substrate, highly hydrophilic cotton turned into hydrophobic cotton. As a result of this, a water droplet of 37 μl did not get absorbed by the fabric even after 3600 s, whereas in the untreated sample, it was absorbed within 3 s. Water contact angle was found to increase from≈0° to 142° in the untreated to plasma treated samples, respectively. The Raman spectra of the treated sample showed the stretching vibration of C–F at 734 cm^{-1} and deformation vibration of C–C in fluorocarbon polymer and other fluorocarbon at 293 cm^{-1} and 387 cm^{-1}, which are the indication of PTFE like structure formation. Similarly the D and G bands at 1575 cm^{-1} and 1360 cm^{-1} were the typical features of a highly amorphous fluorinated carbon film. SEM-EDX showed the presence of 4% fluorine atom in the plasma treated sample. Secondary ion mass spectrometry (SIMS) of the treated sample showed the presence of strong molecular peak of F^- at 19 amu in addition with significant decrease of O^- and OH^- molecular peaks. Some of the higher molecular weight fluorocarbon species that were detected in SIMS are 39, 43, 69 (CF_3^-), 85, 93, 109, 119 (C_2F_5), 131 ($C_8H_{16}F$), 143 ($C_5H_7F_4$) amu, and such on. The physical image in SEM and molecular image in SIMS showed there was no blockage of inter or intra fibres spacing/feature in the fibre, yarn or fabric structure due to the possibly nano-level surface modification of cellulose.

Key words: Plasma polymerization, Cellulose, Surface functionalization, Hydrophobic, SIMS

Application of Small Angle Scattering (X-ray and neutron) on Soft Materials

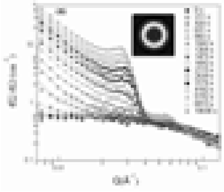
Narayan Ch. Das
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302



Small-angle scattering (SAS), either X-ray or neutron (SAXS or SANS) unveils invaluable information about the nanoscale size and structural profile in the bulk of systems. As such SAS has been applied to topics ranging from soft materials, such as polymer crystallization, phase behaviour of polymer blends, molecular self-assemblies, structure, size and size distribution of nanomaterials, size and structural characterization of micelles, gels, protein and virus, etc. One major advantage is the ability to determine a statistically significant bulk average particle size in the nanoscale of the order 1nm to over 100nm. A minimum quantity as low as 60 μL sample is sufficient for the SAXS experiment. A vast number of scatters, e.g. over 10^5 can be probed in a single experiment with SAS whereas imaging such a number using microscopy would be inconceivable, even with the aid of image analysis software.In addition, SAS can visualise the internal structure, such internal pore structure of porous materials and capsid protein and biomolecules.

In this talk, we will discuss basic principle of SAS including source and facilities available around the world. In addition, wealso review the recentworkson soft materials using both X-ray and neutron scattering. 1. We will see how SAXS techniques are used to study anisotropic characteristic and structure of aligned carbon nanotubes array.2.How SAS is used to investigate early stage crystallization of polymers and phase behaviour of polymer blends?. 3. The application of SAS to investigate the size and structure of biomolecules like capsid protein or virus. 4. How SAS provides the Size and structure of highly concentrated polymeric micelles and so on?.For example, Fig. 1 shows time resolve SANS spectrum of isothermal polymer (PE) crystallization in the solution. Quantitative analysis of the SANS spectrum provides differential structural parameters such as crystal size, lamellae stacking, long period, crystallization kinetics, etc.

Brome mosaic virus(BMV) is a small icosahedral of the alpha virus-like superfamily of RNA with a segmented positive-strand RNA genome and a mean diameter ~ 268Å that offers high levels of RNA synthesis and virus production in plants. SANS and SAXS were applied to study the size, shape and protein-RNA organization of BMV. For example,Fig. 2 shows typical SAXS spectrum of BMV virus. Model fitting/analysis and the radial distribution of BMV from the Fourier transform of scattering spectrum gives a clear indication of size, size distribution of capsid protein and RNA packing, itsdistribution and their structure in the BMV.



References

1. R. J. Roe, Method of X-ray and Neutron Scattering in Polymer Science, Oxford University Press, New York, 2000.Das et al. J. Chemical Physics, 123, 204906 (**2006**).
2. N.C. Das, K. K. Yang,Y. Liu, P. E. Sokol,Z.GWang, H. Wang, J. Nano. Sci. Nanotechnology, 11(6), 4995-5000 (**2011**).
3. N.C. Das, H. Cao, H. Kaiser, J. Gladden, P.E. Sokol, Langmuir, 28, 11962-11962 (**2012**).

Hybrid hydrogel based polymer nanocomposite with superior properties

Devasish Chowdhury*
Material Nanochemsitry Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Guwahati, Assam, India
devasish@iasst.gov.in

Natural polymers, or polymers derived from living creatures, are of great interest in the field of biomaterials. As these polymers are biodegradable, non-toxic, easy and cheap to manufacture they are used in various applications as in food, textiles, cosmetics, plastics, adhesives, paper, drug delivery systems, gene therapy and tissue engineering. In this presentation, I would like to discuss development of hybrid hydrogel based polymer nanocomposite with superior properties. In the first example, I would like to show carbon dots rooted agarose hydrogel film as a hybrid solid sensing platform for detection of heavy metal ions and novel chitosan-carbon dots nanocomposite hydrogel films. The fabrication of the solid sensing platform is centered on simple electrostatic interaction between NH_3^+ group present in carbon dots and OH^- groups present in agarose. As a second example, I want to discuss a preparation of chitosan-carbon dot hydrogel films using a green source "tea" as precursor for carbon dots (CDs). The electrostatic interaction of positive charge on chitosan and negative charge on CDs prepared from tea was used for the successful preparation of a stable and robust chitosan-carbon dots nanocomposite hydrogel film. It was observed that chitosan- carbon dots hydrogel films are soft but tough with superior UV/visible blocking, swelling, thermal and mechanical properties in comparison to chitosan hydrogel film. Moreover chitosan- carbon dots films are more water repellant (hydrophobic) as indicated by their high contact angle values. Thus, fabrication of such green soft but tough biocompatible chitosan- carbon dots nanocomposite hydrogel films offers tremendous bio-medical and industrial applications.

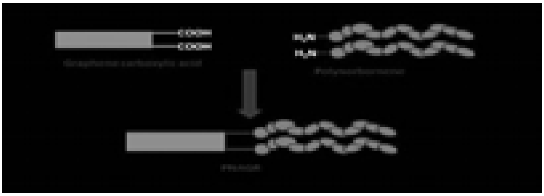
References:

[1] Konwar, A, Gogoi, N, Majumdar, G, Chowdhury**,** Devasish Carbohydrate Polymers, **2015**, 115, 238-245.

Polynorbornene Grafted Graphene as Hybrid Functional Materials

Madhumita Mukherjee, Mutyala Naidu Gonivada, and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

Grpahene has attracted considerable attention over recent years due to its excellent mechanical thermal and electrical properties. In this study, graphene functionalized polynorbornene has been developed with three different weight fraction of graphene carboxylic acid. Polynorbornene has been synthesized by ring opening metathesis polymerization (ROMP) method. Formation of the monomer and the polymer has been confirmed by ^{1}H NMR, MASS and FTIR spectroscopy and GPC Technique. Graphene carboxylic acid has been attached to the polynorbornene backbone via amine functionality to get the polymer grafted graphene (PNAGR). Formation of PNAGR is confirmed by FTIR. Thermal stability of PNAGR has been studied by TGA and DSC with three different weight percentage of the graphene carboxylic acid. Self aggregation of PNAGR in different polarity has been studied using DLS, SEM and TEM techniques. As per our knowledge, this type of self aggregation on a unique hybrid material has been studied for the 1st time. The resulting composite is expected to be useful in aircraft application.



References:

1. D. Lee, M. C. Choi, and C. S. Ha, *Journal of Polymer Science Part A: Polymer Chemistry*, **2012,** 50, 1611-1621.

Polymer Assisted Synthesis of Metal Oxide Nanostructures

Md. Harunar Rashid
Department of Chemistry, Rajiv Gandhi University, Rono Hills,
Doimukh – 791 112 (Arunachal Pradesh), India
E-mail: mhr.rgu@gmail.com

Research on transition metal oxide nanostructures have become increasingly interesting to scientists because of their unique size– and shape–dependent physicochemical and optoelectronic properties which makes them suitable for application in various fields. However, to realize these potentials, it is very important to develop a synthetic method that produces metal oxide nanostructures of tunable size, shape and composition. Compared to different physical approaches, chemical methods are simple and are very efficient in size tenability and dispersibility of the nanomaterials. Recently, we have developed synthesis techniques to prepare metal oxide nanostructures such as ZnO, SnO_2 and Fe_xO_y nanostructures in presence of polymer additive to tune the size or shape of the nanostructures. Our synthesis method is based on aqueous based co-precipitation reactions at relatively low temperature. We observed that addition of polymer controlled the growth of nanostructure formation. The synthesized nanostructures were characterized by different spectroscopic, microscopic and diffractometric techniques.

Photophysical Study of P3HT/NDI Based Hybrid Nanoparticles

Soumitra Satapathi,[1, 2,a]MijanurRahaman Molla,[3] Santanu Bhattacharyya,[2]Suhrit Ghosh,[3]Amitava Patra[2,]
[1]Department of Physics, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India
[2] Department of Materials Science,
Indian Association for the Cultivation of Science, Kolkata,India
[3] Polymer Science Unit, Indian Association for theCultivation of Science, Kolkata ,India
Soumitra.satapathi@tufts.edu,

Electron donor-acceptor based hybrid novel structure remains a frontier area of research to design optoelectronic, photovoltaic, and light harvesting devices. Here, we reportthe synthesis of interdyad and intradyad nanoparticles by using the electron donating polymer Poly-3-(hexylthiophine)) (P3HT) and the electron accepting molecule1, 4, 5, 8 naphthalene tetracarboxylicdiimide (NDI). The intradyad nanostructures are fabricated in situ by adding donor and acceptor molecules simultaneously whereas interdyad nanoparticles are fabricated by attaching the donor and acceptor nanoparticles electrostatically. The differential scanning calorimetry (DSC) confirms the segmental motion of the polymer chain and the uniform packing in intradyad nanostructures which is absent in the interdyad system. The photoluminescence quenching and the shortening of decay time of the excited state of the donor molecule were observed with increasingthe concentration of acceptor molecule in the intradyad system which is attributed to the photoinduced electron transfer from donor to the acceptor molecule. However, in the case of the interdyad system, thechange in photoluminescence quenching and the decay time is less significant due to different photophysical processes.

Polymer anchored oxo-vanadium(IV) complex: An efficient catalyst for oxidation reactions in aqueous medium

Sk. Manirul Islam*, Kajari Ghosh, Rostam Ali Molla,
Noor Salam, Susmita Roy
Dept. of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W. B., India
E-mail: manir65@rediffmail.com

Modern chemistry has been inseparably linked with green chemistry. It has been still gaining importance in all aspects of chemistry. Sustainable development in all stages from the development to the final production cycle has become a practical need in an over-polluted world. Oxidation of olefins, primary and secondary alcohols and sulfides is a very useful reaction in industrial organic synthesis and in the pharmaceuticals. A 30% aqueous solution of H_2O_2 is a non-toxic, environmentally benign, cheap and effective oxidizer, and its only residue is water. Besides oxygen, it is one of the most 'green' oxidants and its oxidative power and positive properties have been highlighted in several publications [1, 2]. Application of polymer supported catalysts in oxidation reactions has been received attention in recent years due to their potential advantages over the homogeneous ones [3-5]. The present work consists of synthesis, characterization and catalytic evaluation of polymer anchored oxo-vanadium(IV) complex towards oxidation reaction. This complex was prepared by reacting chloromethyl polystyrene with anthranilic acid followed by loading of vanadium metal in ethanol and characterized by various techniques such as CHN analysis, SEM-EDX, FT-IR and UV-vis spectral studies and thermogravimetric analysis. Preliminary reactions were carried out choosing styrene, benzylalcohol and methyl phenyl sulfide as model substrates. Influences of various reaction parameters were studied. Moreover, hot filtration test proved that this catalyst acted as a truly heterogeneous catalyst and can be reused for five times without significant loss in activity. Thus good catalytic activity and efficiency of this catalyst in the oxidation reaction of olefins, alcohols and sulfides suggest that the present catalytic systems would be useful to synthesize industrially important organic compounds.

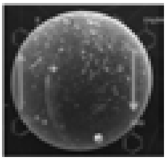


Fig. 1: Catalytic activity of polymer anchored oxo-vanadium catalyst

Reference

[1] S.M. Islam, A.S. Roy, P. Mondal. M. Mobarak, J. Mondal. Tetrahedron Lett. 53 (2012) 127.
[2] Rostam Ali Molla, Anupam Singha Roy, Kajari Ghosh, Noor Salam , S. M. Islam, Journal of Organometallic Chemistry 776 (2015) 170-179.
[3] S.L. Regen, Angew. Chem. Int. Ed. 18 **(**1979) 421.
[4] S. M. Islam, A. S. Roy, P. Mondal, N. Salam, J. Mol. Catal A: Chem. 358 (2012) 38.
[5] S. Roy, T. Chatterjee and S. M. Islam, *Green Chemistry*: Chem. 15 (2013) 2532.

L-Tryptophan Based Chiral Poly (amide-imide) / POSS Nanocomposites: Study on synthesis and characterization

S.Balaji and M.Sarojadevi*
Department of Chemistry, Anna University, Chennai-600025
E-mail: bal_jichem@yahoo.co.in

Poly (amide-imide)s (PAIs) are well known as a class of polymers with good compromise between thermal stability and processability. We can readily tune the properties of the materials for realizing the desired ones by changing the contents or type of organic compounds. From this viewpoint, polyhedral oligomeric silsesquioxane (POSS) is attractive as a cornerstone in highly ordered materials. In this study a new chiral diamine monomer methyl2-[(3,5-diaminobenzoyl)amino]-3-(1H-indol-3yl)propanoate was successfully synthesised using L-tryptophan as starting material and polymerized with different aromatic tetracarboxylic dianhydrides such as BTDA and PMDA via both thermal and chemical imidization method to produce different chiral polyimides. The synthesized diamine, polyimides and polyimide/POSS nanocomposites were characterized by Fourier transformer infrared spectroscopy (FT-IR), and Nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR). The imidization process of poly (amic acid) was monitored by FT-IR at different temperatures. The characterization of the resulting polymers was also perfomed by X-ray diffractometer, polarimeter, viscometer and solubility tests. The thermal properties of the novel poly (amide-imide)s and polyimide POSS-nanocomposites were investigated by TGA and DSC. Surface morphology of the polymeric particles was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

References

[1] Iwao Tabushi, Yasuhisa Kuroda, Masahiko Yamada, and Hideyuki Higashimura, *J. Am. Chem. SOC.* 1985, *107,* 5545 - 5546.
[2] Saeed Zahmatkesh, Polym. Bull. 2012, 68, 693–703.
[3] Guey-Sheng Liou , Sheng-Huei Hsiao and Hwei-Wen Chen, J.Mater.Chem., 2006, 16, 1831-1842.
[4] Der-Jang Liaw, Feng-Chyuan Chang, Jui-Hsiang Liu, Kun-Li Wang, Khalil Faghihi, Kueir-Rarn Lee, Juin-Yih Lai, Journal of Applied Polymer Science, 2007, Vol. 104, 3096–3102.

New Benzoxazines Containing Polyhedral Oligomeric Silsesquioxane from Eugenol, Guaiacol and Vanillin

P. Thirukumaran and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai – 600025
msrde2000@yahoo.com

Three octafunctional benzoxazines were synthesized from amine functionalized POSS, formaldehyde, and three phenols, namely eugenol, guaiacol and vanillin. The structure of the monomer has been confirmed by Fourier transform infrared spectroscopy (FT-IR) and ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). The benzoxazine monomers were cross-linked to form polybenzoxazines via thermal treatment to produce tough thermosetting materials without using any external initiators, accelerators, catalysts or reactive diluents. Differential scanning calorimetry (DSC) and FT-IR were used to study the curing behavior/ring-opening polymerization of the monomers. Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) have been employed to study the phase behavior of the nanocomposites, whose elemental composition was studied by Energy dispersive X-ray analysis (EDXA). Thermal properties of the cross-linked polymers have been studied by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

Keywords: Eugenol, guaiacol, vanillin, amino-POSS

References

[1] Holly, F.; Cope, A. C. J. Am. Chem. Soc. **1944**, 66, 1875−1879.
[2] Ning, X.; Ishida, H. J. Polym. Sci. Part A: Polym. Chem. **1994**, 32, 1121−1129.
[3] Agag, T.; Arza, C. R.; Maurer, F. H. J.; Ishida, H. Macromol. **2010**, 43, 2748−2758.
[4] Agag, T.; Arza, C. R.; Maurer, F. H. J.; Ishida, H. J. Polym. Sci. Part A: Polym. Chem. **2011**, 49, 4335−4342.
[5] Zhang, K.; Zhuang, Q.; Liu, X.; Yang, G.; Cai, R.; Han, Z. Macromol. **2013**, 46, 2696−2704.

Superhydrophobicity of polybenzoxazine-silica hybrids

Shakila Parveen and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai – 600025
msrde2000@yahoo.com

Superhydrophobic polybenzoxazine nano-SiO_2 hybrids [Pbz/SiO_2] were prepared from thermal curing method. The chemical structures of the benzoxazine monomers were confirmed by FTIR, ^{1}H and ^{13}C-NMR spectral analysis. Microscopic analysis (SEM) performed on polybenzoxazine/nano-SiO_2 hybird surface indicated homogeneous distribution of the nano-scaled silica in the polybenzoxazine matrix. Moreover, the wettability (from contact angle measurement) of the hybrids could be controlled by tuning the composition. The results from thermogravimetric analysis (TGA) and Dynamic mechanical analysis (DMA) indicates that the Pbz/SiO_2 hybrids possess excellent thermal and mechanical stability.

Keywords: Superhydrophobic Pbz-SiO_2 hybrids, Contact angle measurements

References:

[1] Dueramae, I.; Jubsilp, C.; Takeichi, T.; Rimdusit, S. Composites Part B **2014**, 56, 197–206.
[2] Shena, L.; Dinga, H.; Wanga, W.; Guob, Q. Appl. Surf. Sci. **2013**, 268, 297–301.
[3] Raza, A.; Si, Y.; Ding, B.; Yu, J.; Sun, G. J. Colloid Interface Sci. **2013**, 395, 256–262.
[4] Kao, T-H.; Chen, J-K.; Cheng, C-C.; Su, C-I.; Chang, F-C. Polym. J. **2013**, 54 258–268.
[5] Liu, J.; Lu, X.; Xin, Z.; Zhou, C. Langmuir **2013**, 29, 411–416.

Preparation and Characterization of Self-photostabilizing Nanocomposite Membranes

Omkar S. Kushwahaa[b], C. V. Avadhania[b],
Namrata S. Tomer[c] and R. P. Singh[c]
[a]Polymer Science and Engineering Division, CSIR-National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune 411008, India
[b]Academy of Scientific and Innovative Research (AcSIR) 2, Rafi Marg,
Anusandhan Bhavan, New Delhi – 110001, India
[c]Bharati Vidyapeeth University, Advanced Research Centre in Pharmaceutical Sciences and Applied Chemistry, Erandawane, Pune - 411038, India
E-mail: os.kushwaha@ncl.res.in

We report a durable and UV resistant nanocomposite membrane of chitosan with effective Photostabilization ascribed to ZnO nanoparticles. Zinc oxide nanoparticles were successfully dispersed in the solution of chitosan polymer. The nanocomposite films with the homogenous dispersion of ZnO nanoparticles in the chitosan matrix were obtained by solution casting method and the influence of ZnO nanoparticles as a photostabilizer was studied. The nanocomposite membranes were photoirradiated by polychromatic radiations with $\lambda > 300$ nm using mercury vapour lamps in SEPAP instrument. The resulting nanocomposite material exhibited excellent UV-resistance in very low percentages of ZnO nanoparticles. The chitosan membranes without ZnO nanoparticles showed fast degradation attributes than nanocomposite membranes. ZnO nanoparticles effectively absorbed UV radiations, thus protecting polymer from radiation degradation. The neat and irradiated nanocomposites of Chitosan / ZnO were characterized by FT-IR spectroscopy for the chemical changes / degradation taking place. Chitosan composites were further characterized for tensile properties, contact angle measurements and surface morphology.

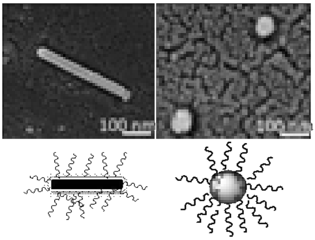
References

1. Kumar, A. P., Depan, D., Singh Tomer, N., & Singh, R. P. (2009). Nanoscale particles for polymer degradation and stabilization—trends and future perspectives. Progress in Polymer Science, 34, 479-515.
2. **Kushwaha, O. S.**, Avadhani, C. V., & Singh, R. P. (2013). Photo-oxidative degradation of polybenzimidazole derivative membrane. Advanced Materials Letters, 4, 762-768.
3. **Kushwaha, O. S.**, Avadhani, C. V., & Singh, R. P. (2014). Effect of UV rays on degradation and stability of high performance polymer membranes. Advanced Materials Letters 5, 272-279.
4. Lonkar, S. P., **Kushwaha, O. S.**, Leuteritz, A., Heinrich, G., & Singh, R. P. (2012). Self photostabilizing UV-durable MWCNT/polymer nanocomposites. RSC Advances, 2, 12255-12262.
5. Rana, V. K., **Kushwaha, O. S.**, Singh, R., Mishra, S., & Ha, C. S. (2010). Tensile properties, cell adhesion, and drug release behavior of chitosan-silver-gelatin nanohybrid films and scaffolds. Macromolecular Research, 18, 845-852.
6. Rao, C. N. R., & Cheetham, A. K. (2001). Science and technology of nanomaterials: current status and future prospects. Journal of Materials Chemistry, 11, 2887-2894.

Facile Controlled Synthesis of Amino-Acid Based Tadpole-Shaped Amphiphilic Organic/Inorganic Hybrid Polymers and Their Self-assembly in Aqueous Media

Ujjal Haldar, Mridula Nandi and Priyadarsi De*
Department of Chemical Sciences, Indian Institute of Science Education and Research
Kolkata, Mohanpur - 741246, Nadia, West Bengal, India
**p_de@iiserkol.ac.in*

Recently, considerable attention has been remunerated to the design and effortless synthesis of amphiphilic block copolymer having distinct chain architectures due to their large involvement of macromolecular properties, self-assembling behavior and employed both in bulk as well as solution state. The self-assembly behavior of such amphiphilic block copolymer in aqueous media is currently an area of intense research for many application fields such as biomedicine, cosmetology, and waste treatment. In this Study, we have synthesized a series of tadpole-shaped amphiphilic organic/inorganic hybrid polymers *via* reversible addition-fragmentation chain transfer (RAFT) polymerization technique using polyhedral oligomeric silsesquioxane (POSS) capped RAFT agent at ambient condition. Boc protected leucine methacryloyloxyethyl ester (Boc-L-Leu-HEMA) was utilized as a precursor for RAFT polymerization. The polymerization kinetics followed first order kinetics with controlled molecular weight and narrow polydispersity index (PDI) (< 1.3). Solution phase FT-IR and circular dichroism (CD) spectroscopy established that the POSS moiety did not perturb the secondary helical conformation of P(Boc-L-Leu-HEMA), attained due to the presence of side chain leucine moiety. Complete hydrolysis of Boc group produced pH responsive amphiphilic cationic polymers, which exhibited self-assembly in aqueous medium at room temperature. The self-assembling behavior in aqueous media was investigated by dynamic light scattering (DLS), atomic force microscopy (AFM) and scanning electron microscopy (SEM), to confirm well-defined core-shell nanostructure micelles with POSS moiety in the hydrophobic core. The content of POSS moiety of the polymeric matrix was enabled to transform Spherical micelles to rod shape.

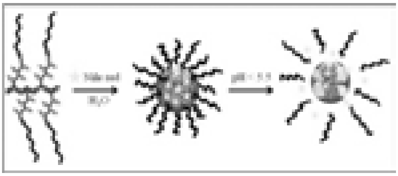


References:

[1] Zhang, W. A.; Fang, B.; Walther, A.; Muller, A. H. E. Macromolecules **2009**, 42, 2563-2569

Peptide-Polymer Conjugates: A Potential Nano-Reservoir for pH Triggered Drug Delivery

Sonu Kumar, Malay Kumar Singh, Lakshmipriya Datta and Priyadarsi De*
Department of Chemical Sciences, Indian Institute of Science Education and Research
Kolkata, Mohanpur - 741246, Nadia, West Bengal, India
**p_de@iiserkol.ac.in*



Recent advancement in exploiting peptide based biomolecules for material science application have paved the route to tailor-made polymer-peptide bioconjugates.[1] Appropriate combination of peptide moieties with synthetic polymers reinforce an attractive strategy to synergistically combine the features of these different classes of materials and to overcome some of their limitations.[2-6] In this context, side-chain peptide based polymers were documented *via* reversible addition-fragmentation chain transfer (RAFT) polymerization comprised of hydrophobic sequence of amyloid-β peptide $A\beta_{17-20}$, Leu-Val-Phe-Phe. The terminal of pendant peptides of synthesized homopolymer can be successively transformed to primary amino groups to exhibit pH based stimuli-responsiveness. Circular dichroism (CD) spectroscopy was employed to assess the ordered conformation of these tetrapeptide based polymers in solution. Subsequently, amphiphilic graft copolymer conjugates were prepared utilizing monomethoxy poly(ethylene glycol) (mPEG) polymer by implementing dynamic covalent bond. Field emission-scanning electron microscopy (FE-SEM) exemplified the self-assembly behaviour of this polymer bioconjugates to construct micellar aggregation which can further accommodate a cargo of small hydrophobic molecules, Nile red. Fluorescence spectroscopy studies facilitates the pH- triggered release behaviour of the dye-loaded nanoparticles around the acidic tumoral environment, implying that these nanoparticles via dynamic covalent linkage have promise as therapeutic nanocarrier in a drug delivery system.

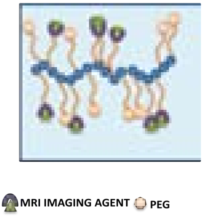
References:

[1] Hentschel, J.; Krause, E.; Börner, H. G. J. Am. Chem. Soc. **2006**, 128, 7722-7723.
[2] Kumar, S.; Roy, S. G.; De, P. Polym. Chem. **2012**, 3, 1239-1248.
[3] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. J. Mater. Chem. B **2013**, 1, 946-957.
[4] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. Langmuir **2013**, 29, 15375-15385.
[5] Kumar, S.; De, P. Polymer **2014**, 55, 824-832.
[6] Kumar, S.; Acharya, R.; Chatterji, U.; De, P. Polym. Chem. **2014**, DOI: 10.1039/C4PY00620H.

Amphiphilic Magnetic Copolymers for Dual Imaging Application

Litesh Shasank, Saikat Mukherjee , Diptendu Patra and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata
E-mail: sraja@iiserkol.ac.in

Magnetic resonance imaging (MRI) offers the potential of true three-dimensional imaging of biological structures and processes at cellular resolution. Random copolymer and triblock copolymer with norbornene backbone having cobalt complex, doxorubicin and polyethylene glycol, have been synthesised using ring opening metathesis polymerisation (ROMP). All the polymers are characterized by ^{1}H NMR, IR, GPC and TGA techniques. The morphology of the copolymer nano composites has been evaluated with DLS, TEM and AFM techniques. The cobalt complex functionalization to the polymer is monitored by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. To prove the paramagnetic nature of copolymer nanocomposites, SQUID experiment is performed at room temperature. Newly designed copolymers having paramagnetic nature are expected to be MRI agent.



References:

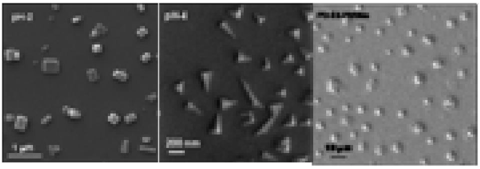
[1] Zoha M.AL-Badri and Gregory N.Tew*, Macromolecules. 2008, 41, 4173-4179.
[2] Martina, M. S.; Fortin, J. P.; Menager, C.; Clement, O.; Barratt, G.; Grabielle-Madelmont, C.; Gazeau, F.; Cabuil, V.; Lesieur, S. J. Am. Chem. Soc. 2005, 127, 10676–10685.

Morphological Tuning in Aqueous Self-Aggregation of

Semi-Telechelic POSS-Poly (vinylimidazole) and POSS-Poly(ionic liquid) Hybrids

Madhab Dule, Mrinmoy Biswas, Tapas K. Paira and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata 700 032, India

Polyhedral oligomeric silsesquioxanes (POSS) are known to be a useful nanoscale building block to prepare different varieties of superior polymer-based hybrid materials.[1] Recently, several reports deal with the hydrophilic functionalization of hydrophobic POSS moiety mainly with hydrophilic polymers for the improvement of its dispersibility in polar solvents, such as water.[2,3] The interactions between POSS units sometimes impart phase segregation due self-assembly of the POSS hybrid in water depending upon temperature, nature of the hydrophilic monomer and the polymer chain length. In this context, POSS-poly(vinyl imidazole) hybrids of varying molecular weights are prepared using thiol-POSS as chain transferring agent as well as initiator and vinylimidazole as monomer by radical polymerization technique. The POSS-polymer hybrid molecules undergo self-aggregation into spherical aggregates of nanometer dimensions (~70 nm) in water as can be seen from FESEM image. Furthermore, the formation of other anisotropic secondary aggregated structures such as cone and cube are also observed in water with the delicate variation of pH. Finally, the study is further extended to prepare POSS-poly(ionic liquid) hybrids by post-modification of POSS-poly(vinyl imidazole) with 1-bromoalkane of different chain length. The resulted hybrid poly(ionic liquid)s containing different length alkyl chain also show self-aggregated structures of various shapes in water. Finally, we propose an aggregation mechanism of the POSS-polymer hybrid as well as POSS-poly(ionic liquid) hybrids in water.



References:
[1] Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. Macromolecules **1995**, 28, 8435-8437.
[2] Ma, L.; Geng, H. P.; Song, J. X.; Li, J. Z.; Chen, G. X.; Li, Q. F. J. Phys. Chem. B **2011**, 115, 10586-10591.
[3] Zhang, W.; Fang, B.; Walther, A.; Muller, A. H. E. Macromolecules **2009**, 42, 2563-2569.

Nanojacketing and Dejacketing of ds-DNA: A Non-destructive Characterization of Nanojacketed Sample by Impedance Spectroscopy

Sudipta Nandi, Aniruddha Kundu, Tanmoy Paul and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India

Deoxyribonucleic acid (DNA), a long polymer chain of nucleotide units, having unique double-helical structure with the stack of π electrons in the base pairs, conquers a significant position in nano-technology utilizing the “molecular conduit” formation ability of DNA. Furthermore, DNA can act as excellent template for the directed growth of not only conducting polymers but also metal nanoparticles. Although DNA is easy to modify for such novel, tailor-made applications, it suffers from major limitation because of it’s poor solubility in organic solvent where it loses its base pairing recognition properties. To overcome this problem cationic amphiphiles, lipid molecules, cationic copolymers have been used which solubilise DNA in organic solvents with retention of its biologically important properties. We have tried to transfer DNA to organic medium with retention of its configuration via nanojacketing of DNA utilizing in-situ polymerization of *o*-methoxyaniline (OMA) at 30^{0}C using $HAuCl_4$ as oxidant and DNA as a soft template which leads to concomitant synthesis of Au nanojacket encapsulating DNA and poly(*o*-methoxyaniline) [POMA] at the outer layer of this nanojacket. Furthermore, digestion of nanojacketed system with saturated I_2 solution, dejackets DNA with retention of its conformation leaving hollow POMA nanotube. The nanojacketing and de-jacketing phenomena are established by several microscopic and spectroscopic studies. The impedance study of the nanojacketed DNA reveals both resistive (388 KΩ) and capacitive (13.74 pF) property.

References:

[1] Lassalle, N.; Mailley, P.; Vieil, E.; Livache, T.; Roget, A.; Correia, J. P.; Abrantes, L. M. *J. Electroanal. Chem.* **2001**, *509*, 48-57.
[2] Nagarajan, R.; Liu, W.; Kumar, J.; Tripathy, S. K.; Bruno, F. F.; Samuelson, L. A. *Macromolecules* **2001**, *34,* 3921–3927.
[3] Ganguli, M.; Jayachandran, K. N.; Maiti, S. *J. Am. Chem. Soc.* **2004**, *126,* 26-27.
[4] Huang, K.; Zhang, Y.; Long, Y.; Yuan, J.; Han, D.; Wang, Z.; Niu, L.; Chen, Z. *Chem. Eur. J.* **2006**, *12,* 5314–5319.
[5] Nandi, S.; Mukherjee, P.; Kundu, A.; Nandi, A. K. *J. Phys. Chem. B* **2014**, *118*, 2649–2661.

Photocatalytic & Sonocatalytic Degradation of Rhodamine B Using in-Situ Synthesized Ceo2/Zno Composite Nanoparticles

Nidhi H. Shah[1], S. T. Mhaske[1*]
1Department of Polymer and Surface Engineering, Institute of Chemical Technology (ICT), Matunga, Mumbai, Maharashtra, India 400019
st.mhaske@ictmumbai.edu.in

Individual CeO2, ZnO and bimetal oxide core shell CeO2/ZnO nanoparticles are synthesized without any stabilizers using in-situ precipitation technique. In this process cerium nitrate hexahydrate and zinc acetate dehydrate as precursor for the formation of CeO2 core and zinc oxide as shell. The structure, morphology and particle size of the synthesized nanoparticles were analyzed by using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). XRD results reveal that the phase structures of CeO2/ZnO nanoparticles are composited by cubic (fluorite) phase of CeO2 and hexagonal (wurtzite) phase of ZnO. The Average Particle sizes obtained for CeO2/ZnO nanoparticles were observed to be below 15 nm. Structure characterization of core/shell particles by TEM indicates that the ZnO shell is around 5 nm in thickness and CeO2 core is 9 nm in diameter. The effectiveness of the synthesized CeO2/ZnO used as catalysts for the photocatalytic as well as sonocatalytic degradation of Rhodamine B (RhB) dye, has also been investigated. It has been observed that the catalytic activity of CeO2 has been effectively increase by coating with a more photoactive ZnO. Photocatalysis was more efficient than sonocatalysis in degradation of Rhodamine B.

References:

[1] Yue Lin ⍰, Zhang Xiaoming, Preparation of highly dispersed CeO2/TiO2 core-shell nanoparticles, Materials Letters 62 (2008) 3764–3766Minton, A. P. J. Biol. Chem. 2001, 276, 10577-10580.
[2] I-TsanLiua, Min-HsiungHona, Lay GaikTeoh, The preparation, characterization and photocatalytic activity of radical-shapedCeO2/ZnO microstructures, Ceramics International, 2013.
[3] Y. He, X.Yu, T.Li,L.Yan, B.Yang, Preparation of CeO2/ZnO nanostructured microspheres and their catalytic properties, Powder Technology166(2006)72–76.

Hard confinement effect on polymer crystallization

PratickSamanta, Rajiv Srivastava, Bhanu Nandan
Department of Textile Technology, Indian Institute of Technology Delhi,
New Delhi-110016, India
Email:-Praticksamanta@gmail.com

Polymer crystallization is a topic which has been extensively studied in the past. The kinetic and thermodynamic aspect of polymer crystallization, in bulk, is more or less known very well. However, the situation becomes complex when the polymer is allowed to crystallize in confined environments where the length-scale of the confinement is only few times that of the long period of polymer crystal lamellae. Such confinement may frustrate the polymer crystallization process resulting in significant deviation from the crystallization as known for the bulk conditions.In the present investigation, we study the crystallization of poly(L-Lactic acid) (PLLA), an important biodegradable polymer, under two-dimensional confinement. The two-dimensional confinement was imposed on the PLLA crystallization by infiltrating it in the pores of nanoporous alumina membrane where the pore diameter was less than 150 nm. The samples were characterized by DSC, WAXD, and SEM. The knowledge gained through these studies will be significant in understanding polymer crystallization in polymer nanofibres which recently has been attracting lot of attention.

References:

[1] Duran, H.; Steinhart, M.; Butt, J. H.; Floudas, G. *Nano Lett*ers, **2011**, 11, 1671–1675.
[2] Maiz, J.; Martin, J.; Mijangos, C. *Langmuir*, **2012**, 28, 12296−12303
[3] Bishopa, C.; Teeters, D. *ElectrochimicaActa*, **2000**, 54, 4084–4088.
[4] Nojima, S.; Ohguma, Y.; Kadena, K.I.; Ishizone, T.; Iwasaki, Y.; Yamaguchi, K. *Macromolecules***, 2010**, 43, 3916–3923.
[5] Bujans, B. F.; Alonso, F. F.; Cerveny, S.; Parker, F.S.; Alegr,A.; Colmeneroacd, J. *Soft Matter*, **2011**, 7, 7173–7176 .
[6] Kulb, B.; Pennings, J. A. *Polymer*, **1980**, 21,607-611.
[7] Vasanthakumari, R.; Pennings, J. A. *Polyme*r, **1983**, vol-24,174-178.
[8] Cartier, L.; Okihara, T.; Ikad, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. *Polymer*, **2000**, 41, 8909–8919.
[9] Alema, C.; Lotz, B.; Puiggali**,** J. *Macromolecules*, **2001**, 34, 4795-4801.
[10] Yasuniwa, M.; Tsubakihara, S.; Iura, K.; Dan, Y. O. Y.; Takahashi, K. *Polymer* ,**2006**,47, 7554-7563.

Carbon nanotube based composite nanofibers as polymeric membrane for water purification

Debmalya Roy*[1],Abhai Kumar[1], Neeru Tiwari[1],
Kingsuk Mukhopadhyay[1], A. K. Saxena[2]
[1]Nanoscience and Technology Division, DMSRDE, GT Road, Kanpur - 208013
[2] DMSRDE, GT Road, Kanpur-208013
*droy@dmsrde.drdo.in

The composite nanofibers of polysulfone has been prepared by electrospinning technique where by changing the concentration of solid content, voltage and flow rate the different diameters, lengths and orientations have been achieved. The different weight percentage of silver nanoparticles (AgNPs) on functionalized multiwalled carbon nanotube (MWCNT) were mixed with polysulfone to prepare the composite fibers to tailor make the chemical and physical property of polymeric membrane for decontamination and disinfection of drinking water. The role and nature of different functional groups on nanotube surface were thoroughly studied for Ag loading and on mechanism of decontamination and disinfection of water. The best performing functionalized MWCNT for the removal of toxic metal ions and Escherichia coli bacteria was selected for synthesis of composite nanofibers. The detailed structure property relationship of the nanofibers has been studied by the morphological characterization, surface area and contact angle measurements. The modified surface of MWCNTs by Ag nanoparticles and polar functional groups placed on the polymeric nanofibers were enhanced the interfacial interaction with the decontaminated and disinfect water which in turn enhances the efficiency of filtration of drinking water.

References:

[1] Gopal, R.; Kaur, S.; Feng, C. Y.; Chand, C.; Ramakrishna, S.; Tabe, S.; Matsuura T. J. Membr. Sci. **2007**, 289, 210-219
[2] Pendergast, M. T. M.; Hoek, E. M. V. Energy Environ. Sci. **2011**, 4, 1946-1971
[3] Roy, D.; Tiwari N.; Mukhopadhyay K.; Saxena A. K. J. Membr. Sci. (revised version submitted)

Chemical Functionalization of Graphene Oxide: Reaction Kinetics and Property Evaluation

Jyoti Prakash Singh, Uttam Saha, Rimpa Jaiswal,
Anurag Srivastava and T.H. Goswami*
Defence Material and Store Research and Development Establishment,
Kanpur GT Road, DMSRDE PO, Kanpur, India

Graphene, the one atom thick planar structure of sp^2 bonded carbon, has emerged as a novel material in the field of material science owing to its excellent electrical & thermal conductivities, high crystal & electronic quality, strong mechanical strength and high surface area (2630 m^2/g). In spite of its exotic properties, the key issues for the successful commercial applications largely depends on the development of suitable methods for the synthesis of processable functionalized graphene at low cost in bulk quantity. Among the several approaches tried so far, the solution phase chemical method is most promising owing to its low cost, ease of control, and bulk production capability. In addition, there is an immense scope to improve subsequent processing through chemical modification and also has an opportunity to introduce suitable functionalities required for different end-use applications. Oxidation of graphite provides a suitable precursor material for chemical treatment, primarily due to the generation of several reactive oxygenated functionalities; namely, the sp^3-hybridized carbon containing hydroxyl (OH) and epoxide/ether functional groups on the top and bottom surfaces of basal plane and sp^2-hybridized carbons containing carboxyl and carbonyl groups at the edges of the sheet. Hydrophilic nature of GO allows easy dispersion in water to form stable colloidal suspension. The organic/polymeric functionalized GO nanosheets are however, required for broad range applications. The detail kinetic study was carried out using three different class of diisocynates, namely, aliphatic (hexamethylene diisocyanate, HMDI), alicyclic (isophorone diisocyanates, IPDI), and aromatic (toluene diisocyanates, TDI). Extent of functionalization in different locations are predicted from relative ratio of hydroxyl and carboxyl groups participated in diisocyanate reaction and N 1s XPS spectra show nearly 3:1, 2:1, 1.3:1 in HMDI, IPDI, and TDI respectively. TDI, the most sterically hindered diisocyanate among the reported one, shows slowest reactivity and minimum disorder in the final structure compared to long chain aliphatic diisocyanate, HMDI. Similar reaction is extended with diamines and dihydroxy compounds also. The selection of reagents, its concentration and reaction parameters are paramount important in getting desired functionalized GO. This is particularly important for bi-functional reagents, as change of concentration can yield two different products. For example, bimolecular reaction (low concentration of organic reagents) form cross-linked network structure, whereas, pseudo-unimolecular reaction yield functionalized processable graphene oxide (fGO). Also, the nature of reagent plays an important role on controlling the rate of reaction and the steric factor dominates over the electronic factor in controlling the rate of reaction. However functionalization with monofunctional organic moiety gives processable graphene. The processable functional hybrid materials are evaluated for their potential application.

Keys Words: GO, cross-linked network structure, chemically functionalized graphene.

Fullerene-graphene nanohybrid and fluorescent conducting polymer nanocomposites for supercapicitor and optoelectronic application.

Rimpa Jaiswal, Jyoti Prakash Singh, Uttam Saha,
Anurag Srivastava and T.H. Goswami*
Defence Material and Store Research and Development Establishment,
Kanpur GT Road, DMSRDE PO, Kanpur-208013, India
E-mail ID of the corresponding author

Fullerene and graphene, the two important members of carbon family, have generated tremendous research interest to the entire scientific community owing to their excellent exotic properties & potential large scale applications. Also, the concepts of multifunctional hybrid materials are gaining interest for broad range applications. Preparation of pristine fullerene-graphene hybrid material does not yield stable product and forms agglomeration during its use. Oxygenated derivatives of fullerene and graphene, i.e., fullerenol and graphene oxide (GO), may however be easily chemically combined to form stable hybrid material. Further, the nano-hybrid material is used to prepare nanocomposites with different fluorescent conducting polymers (FCPs) for wide range of optoelectronic applications. The present work highlights the preparation, characterization and property evaluation of three different nanocomposites based on fullerenol-graphene nanohybrids and neat graphene with conducting polymer. Fullerenol graphene nanohybrid (FGO) is synthesized by treating GO with fullerenol and is further reduced to get reduced hybrid product (rFGO). In another approach, the processable reduced graphene oxide (rGO-P) is synthesized by two times repetition of oxidation and reduction of GO. Ternary nanocomposite of FGO and rFGO is prepared by taking PU as matrix and 5% thiophene phenylene copymer and varied the percentage of FGO and rFGO respectively. The third nanocomposite was prepared by blending fluorine-bithiophene copolymer and processable reduced graphene oxide (rGO-P). All the composites were characterized by IR, UV, PL, TGA, DSC and electronic properties were evaluated by I-V characteristics, CV and conductivity measurement. The LED device prepared by third composite shows excellent result and there is 5 times increase in maximum device efficiency (Cd/A) and three times increase in maximum brightness (Cd/m^2). The conductivity measurement indicates an increase for rFGO compared to FGO. The conductivity, electrochemical property and capacitance results of composites provide interesting conclusions.

Keys Words: Fullerenol, Graphene Oxide, Nano-hybrids, fluorescent conducting polymers, Nanocomposites

Thermoresponsive polymer coated gold nanoparticles (AuNPs)

Samarendra Maji[1], Zhiyue Zhang[2], Bruno G. De Geest[2]and Richard Hoogenboom[1]
[1]Supramolecular Chemistry Group, Department of Organic and Macromolecular Chemistry,
[2]Faculty of Pharmaceutical Sciences, Department of Pharmaceutics,
Ghent University, 9000 Ghent, Belgium
*Richard.Hoogenboom@UGent.be

In the last few years gold nanoparticles (AuNPs) have receivedpopularity inresearchfor their interesting optical properties owing to surface plasmon resonance (SPR), resulting in wide applications ranging from optoelectronics to biology [1].Upon association of the AuNPs in solution, a red-shift of SPR can be observed due to the change of interparticle distance. Thermoresponsive polymer coated AuNPs have attracted much interest due to their response to external stimuli, such as temperature, pH and salt [1,2] and open up a new area of intense research.

In the current contribution we report our recent efforts to develop thermoresponsive polymer coated AuNPs that are stimulated by temperature and salt. In the first part of the presentation we will demonstrate the preparation of poly(N-isopropyl acrylamide) (PNIPAM) coated AuNPs and the effect of temperature and salt on the phase transition behavior and hydrogen bonded layer-by-layer assembly [3].UV-Vis, DLS, TEM and AFM characterization techniques were used to characterize the materials.The phase transition results in a color change from red to blue-purple due to the change in the SPR. Moreover, the synthesized responsive particles were further tested with two different salts of the Hofmeister salt series. We used spectroscopic investigations to elucidate the salt sensing properties of the PNIPAM@AuNPs of the Hofmeister series.In the second part of this contribution we will demonstrate the preparation of P(NVP-*stat*-PNVCL) decorated gold nanoparticles and their temperature and salt induced aggregation behavior.Transmission electron microscopy (TEM) revealed distinct corona surrounding the gold nanoparticles, thereby indicating the successful modification with polymers. More recent work on the thermoresponsive polymer coated AuNPs will also be highlighted.

References:

[1] Liu, X.Y.; Cheng, F.; Liu, Y.; Li, W. G.; Chen, Y.; Pan, H.; Liu, H. J. J. Mater. Chem. **2010,** 20, 278–284.
[2] Yusa, S. I.; Fukuda, K.; Yamamoto, T.; Iwasaki,Y.; Watanabe, A.; Akiyoshi, K.; Morishima, Y.Langmuir **2007**, 23, 12842–12848.
[3] Zhang, Z.; Maji, S.; da F. Antunes, A. B.; De Rycke, R.; Zhang, Q.; Hoogenboom, R.; De Geest, B. G. Chem. Mater. **2013,** 25, 4297–4303.

Carbon Dots rooted Agarose Hydrogel Hybrid Platform for Optical Detection and Separation of Heavy Metal Ions

Neelam Gogoi,[a] Mayuri Barooah,[a] Gitanjali Majumdar[b]
and Devasish Chowdhury[a]*
[a]Physical Sciences Division, Polymer Unit, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Garchuk, Guwahati, 781035, India
[b]Department of Chemistry, Assam Engineering College, Jalukbari, Guwahati, 781013, India

We introduce chitosan based carbon dots rooted agarose hydrogel film as a robust hybrid solid sensing platform for on-site detection of heavy metal ions. The fabrication of the solid sensing platform is centered on simple electrostatic interaction between NH_3^+ group present in carbon dots and OH^- groups present in agarose. Simply on dipping the hydrogel film strip into heavy metal ion solution, in particular Cr^{6+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+} the strip displays color change, viz., Cr^{6+}→yellow, Cu^{2+}→blue, Fe^{3+}→brown, Pb^{2+}→white, Mn^{2+}→light brown. The optical detection limit of the respective metal ion is found to be 1 pM by studying the changes in UV-visible reflectance spectrum of the hydrogel film. Moreover, the hydrogel film finds applicability as an efficient filtration membrane for separation of these quintet heavy metal ions. The strategic fundamental feature of this sensing platform is the successful capability of chitosan to form colored chelates with transition metals. This proficient hybrid hydrogel solid sensing platform is thus the most suitable to employ as an on-site operational, portable, cheap colorimetric-optical detector of heavy metal ion with potential skill in their separation.

Keywords: agarose hydrogels, chitosan carbon dots, solid sensing platform, heavy metal ions, ion separation

References

(1) Ye, B. C.; Yin, B. C. Highly Sensitive Detection of Mercury (II) Ions by Fluorescence Polarization Enhanced by Gold Nanoparticles. *Angew. Chem. Int. Ed.* **2008**, 47, 8386.
(2) Zhang, J. F.; Zhou, Y.; Yoon J.; Kim, J. S. Recent Progress in Fluorescent and Colorimetric Chemosensors for Detection of Precious Metal Ions (Silver, Gold and Platinum ions). *Chem. Soc. Rev.* **2011**, 40, 3416.
(3) Hossain, M. Z; Brennan, J. D. β-Galactosidase-Based Colorimetric Paper Sensor for Determination of Heavy Metals. *Anal. Chem.* **2011**, 83, 8772.

Polyethylene Oxide Adsorption to Graphene Oxide Surface Probed by Small Angle Neutron Scattering

Kiranmai Yellam[1], Sanjay Kumar[1], Chandan Sharma[1],
Vinod K. Aswal[2], G. Harikrishnan[1*]
[1]Department of Chemical Engineering,
Indian Institute of Technology Kharagpur, West Bengal, India
[2]Solid State Physics Division, Bhabha Atomic Research Centre Mumbai,India
*hari@che.iitkgp.ernet.in

This work estimates the adsorbed layer thickness and density of polyethylene oxide (PEO) as a function of concentration and molecular weight on to graphene oxide (GO) surface. Small angle neutron scattering experiments were employed to investigate this. The selection of geometry of GO for neutron scattering analysis was facilitated by complementary tools such as particle size analyzer and atomic force microscopy. SANS data were analyzed by selecting a model with proper modifications incorporated to account for GO polydispersity.

References:

[1] Emily, M.M.; Neal, T.S.; Christopher, A.H.;Milo, S.P.S.; David, J.B,; Rahnejat, K.A.; Cullen, P.L.; Heenan, R.K.; Linder, P.; Schweins, R.; J. Am. Chem. Soc. **2012**, 134, 8302–8305.
[2] Bongiovanni, R.; Ottewill, R.H.; Rennie, A.R.; Progr. Colloid Polym. Sci. **1991**, 84, 299-304.
[3] Andrew, N.; Terence, C.; Langmuir **2004**, 20, 2298-2304.

Physicochemical studies on local anesthetic loaded second generation nanolipid carriers

Prasant Nahak, Amiya Kumar Panda
Department of Chemistry, University of North Bengal, Darjeeling-734013, India
Email: prasant.nahak@gmail.com

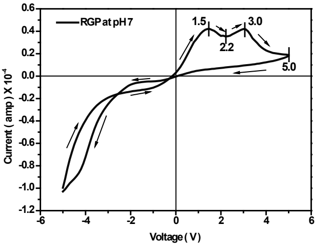
The effect of nonionic surfactants (Tween 40 and Tween 60) hydrocarbon chain length on the physicochemical properties of nanostructured lipid carriers (NLCs) were investigated in the absence and presence of two local anesthetics, lidocaine (LIDO) and procaine hydrochloride (PRO.HCl). Sorbitan tristearate (Span 65), soy lecithin (SLC) and stearic acid (SA) in 2:2:1 molar ratio were used in formulating the NLCs. Combined dynamic light scattering, differential scanning calorimetry (DSC) and spectroscopic studies were adopted in the physicochemical characterization of the NLCs. NLC formulations were found to be stable for at least 60 days (when kept at 4oC). Tween 60 stabilized NLCs exhibited superiority than the Tween 40 stabilized systems. DSC and polarity studies indicated altered crystallinity of the lipid matrices induced by LIDO as it could insert into the core of the NLC; PRO.HCl could only get interfacially adsorbed for its ionic nature. Tween 60 stabilized NLCs exhibited better drug loading capability than the Tween 40 based formulations as revealed from the entrapment efficiency studies. Sustained drug release was experienced by Tween 60 stabilized NLCs as studied by in vitro release kinetics. The developed NLCs could thus be considered to have prospects as novel drug carrier for controlled/sustained release to improve the time duration of anesthesia.

Keywords: NLC, anesthetics, DLS, calorimetry, entrapment efficiency, drug release

pH sensitive optoelectronic properties of amphiphilic reduced graphene oxide grafted by poly (dimethylaminoethyl methacrylate)

Nabasmita Maity, Atanu Kuila and Arun K. Nandi *
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India
*psuakn@iacs.res.in

Poly(N,N′-dimethylaminoethyl methacraylate) (PDMAEMA) is synthesized by atom transfer radical polymerization, followed by attachment to reduced graphene oxide (rGO) via diazonium coupling. The rGO-PDMAEMA (RGP) is characterized by ^{1}H NMR, UV-Vis, FTIR and Raman spectroscopy. Then molecular brushes of PDMAEMA chains over rGO surface are demonstrated by TEM and AFM. The TGA thermograms indicate 55 wt% grafting of PDMAEMA. RGP is dispersible in the widest spectrum of solvents from CCl_4 to water [solubility parameter ($\delta p + \delta h$), 0.6 to 58][1]. The pH dependent fluorescence properties of RGP is interesting: at pH 4, it exhibits two emission peaks, but at pH 7 and pH 9.2, a single and broad emission peak is observed. Two emission peaks at pH 4 are attributed to radiative decay of excitons to two kinds of holes in the rGO originating from illumination and p-type doping, which is also characterized by a blue shift of the Raman D band. Moreover, n-type doping of RGP at pH 9.2 is also evident due to a similar Raman shift. The I–V characteristic curve at pH 7 exhibits a bimodal negative differential resistance (NDR) property with a rectification ratio of 5.5[2].



References:

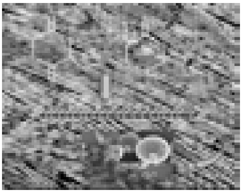
[1] Layek, R. K.; Kuila, A.; Chatterjee, D. P.; Nandi, A. K. J. Mater. Chem. A. **2013**, 1, 10863-10874.

[2] Kuila, A.; **Maity, N**.; Layek, R. K. Nandi, A. K. **J. Mater. Chem. A**. **2014**, **2**, 16039-16050.

Synthesis and Characterization of Biodegradable Nanolamellar Triblock and its Application in Drug Delivery

Nibedita Kasyapi[1*], Anil K. Bhowmick[2]
[1]Department of Materials Science and Engineering,
Indian Institute of Technology Patna, Patna 800013, India.
[2]Rubber Technology Centre, Indian Institute of Technology Kharagpur,
Kharagpur-721302, India
*nibedita.polymer@iitp.ac.in

A series of biodegradable lactone based triblock copolymers, was synthesized by varying feed composition, monomer/ initiator (1, 6-hexanediol) ratio and monomer/ catalyst (tin 2-ethyl hexanoate) ratio in a sequential ring opening polymerization for drug delivery. The structure of the copolymers was established through ^{1}HNMR, ^{13}C NMR, Raman and Fourier transform infrared spectroscopy techniques. ^{13}C NMR was used to study the block sequencing and extent of transesterification. The crystallinity and lattice strain of the copolymers were changed on variation of lactones and the glass transition temperatures of the two blocks shifted depending on the ratio of the two monomers.The morphology of the triblock was investigated by transmission electron imaging and atomic force microscopy, showing alternating stripes of nanolamellae. Long range order of lamellae in the triblocks was guided by their composition.The triblock, fabricated into microsphere having average diameter of 17μm, was used for encapsulation of drug molecules. After the release of drug, formation of pores on the surface of the microsphere was observed. The release profile exhibited the characteristic of a potential carrier.



References:

[1] Kasyapi, N.; Bhowmick, A. K. J. Phys. Chem. C. **2014**, 118, 22325-22338.
[2] Kasyapi, N.; Bhowmick, A. K. RSC Adv. **2014**, 4, 27439-27451.

Synthesis of functionalized Poly(vinyl chloride)/Layered double hydroxide nanocomposite

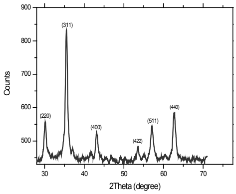
Monika and Nira Misra
School of Biomedical Engineering, Indian Institute of Technology
(Banaras Hindu University), Varanasi 221005
monika.rs.bme10@iitbhu.ac.in

Polymer composite- poly(vinyl chloride) (PVC)/layered double hydroxide(LDH)- was prepared. PVC was functionalized with thiosulphate using phase transfer catalyst. LDH was synthesized by co-precipitation method. Thiosulphate-PVC/LDH was physically mixed. The structural and compositional informations were determined by Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy, X-ray diffraction and thermal properties by Thermo gravimetric analysis (TGA). Biocompatibility was evaluated and compared with that of pure PVC by measuring of hydrophilic nature, hemolysis assay. Lastly, in vitro cell viability and cell adhesion of mouse mesenchymal stem cell on developed polymer composite was examined for definite biocompatibility. The results showed better haemolytic property, cell viability and cell adhesion in polymer composites as compared to pure PVC. Therefore, these polymer composites were developed to improve existing grouting material.

Highly flexible, light weight natural rubber latex/Fe_3O_4 nanocompositesfor EMI shielding application

Omorogbe S.O.[1, 3], Ikhuoria, E.U.[2], Kallayi, N. [1], Aigbodion, A. I.[3],
Warrier K.G.K.[1], Pillai S. [1*]
[1]Materials Science and Technology Division,
CSIR-National Institute for Interdisciplinary Science and Technology, Kerala, India-695019
[2]Department of Chemistry, University of Benin, Benin City, Nigeria
[3]Product Development Laboratory, Research Operations Department,
Rubber Research Institute of Nigeria, P. M. B. 1049, Benin City. Nigeria.
pillai_saju@niist.res.in

Magnetic nanoparticlespossesswide range of application in various areas,such aselectromagnetic shielding, magnetic filters,information storage and biomedicines. Herein, we aimed to synthesize highly crystalline,nano-sizedmagnetite (Fe3O4) particles using a modified co-precipitation methodand to fabricate natural rubber latex/Fe3O4 nanocomposites.The particle morphology,structural and magnetic properties of as-synthesised Fe3O4nanoparticles wasinvestigatedusingboth TEM and XRD techniques. The size of Fe3O4 synthesized was10 – 20 nm range as revealed in TEM images. XRD pattern of synthesized powder corresponds to that of pure Fe3O4 and was highly crystallinein nature (JCPDS no.01-075-0033). This was supported by higher resolution TEM images and their corresponding SAED patterns.Further, natural rubber latex (NRL)/Fe3O4 nanocomposite of high saturation magnetization for electromagnetic interference shielding capability was fabricated by solution processing and compression moulding. Electrical conductivity, thermal property, and electromagnetic shielding efficiency were investigated. The interaction between Fe3O4 and the NRL matrix were elucidated using both spectroscopy and microscopic techniques. The NRL/Fe3O4 nanocompositesbased composites showed superior electrical conductivity, excellent thermal stability and good EMI shielding effectiveness (SE) properties and may be apromising material for EMI shielding application antistatic discharge matrix for miniature devices encapsulation.



References

[1.] A. A. Al-Ghamdi, E. H. El-Mossalamy, Omar A. Al-Hartomy, A. M. Abdel Daiem, F. Al-Salamy, Farid El-Tantawy Attieh A. Al-Ghamdi. Journal of Applied Polymer Science, Vol. 125, 2604–2613 (2012)

[2.] Shen Wu, Aizhi Sun, Fuqiang Zhai, Jin Wang, Wenhuan Xu, Qian Zhang, Alex A. Volinsky. Materials Letters 65 (2011), 1882–188

Functional porous organic polymers: fabrication and properties in different physical states

Sujoy Bandyopadhyay, Pragyan Pallavi,
Amith G. Anil and Abhijit Patra*
Department of Chemistry, IISER, Bhopal
*abhijit@iiserb.ac.in

In the last few years porous organic polymers have emerged as an important class of materials. Synthetic flexibility, possibility to incorporate desired functionalities into the porous framework as well as light weight are the advantages with microporous organic polymers (MOPs).[1, 2]We have designed monomer 4,4',4'',4'''-(5,5-dioctylcyclopenta-1,3-diene-1,2,3,4-tetrayl) tetrakis (bromobenzene) (DCTB). Network polymers were synthesized bypalladium-catalyzed Sonogashira cross-coupling reactions.Fine tuning of fabrication conditions led to the formation of polymers in the form of amorphous solid, strongly fluorescent solution as well as in the form of nanoparticles. Gas adsorption studies reveal that the amorphous polymer possesses pore size mostly in the range of microporous region (< 2 nm) with surface area 295 m^2/g. Molecular dynamic simulations has been carried out; surface areas, gas adsorption capabilities were simulated and structure-property correlation was established (Figure1). Solution processable polymer was obtained by varying the reaction conditions. Direct fabrication of nanoparticles in aqueous dispersion was achieved through miniemulsion polymerization. [3]Solution processable polymer and nanoparticles exhibit cyan fluorescence and their detailed photophysical properties were investigated.

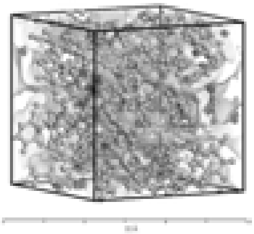


Figure1. Illustration of amorphous cell of DCTB based MOP at 77K (dots: adsorbed N_2 molecules, shades: solvent accessible surface area).

References

[1] Patra, A.; Scherf, U. *Chem. Eur. J.***2012**, *18*, 10074-10080.

[2] Cheng, G.; Bonillo, B.; Sprick, R. S.; Adams, D. J.; Hasell, T.; Cooper, A. I. *Adv. Funct. Mater.***2014,***24*, 5219-5224.

[3] Patra, A.; Koenen, J. M.; Scherf, U. *Chem. Commun.***2011**, *47*, 9612-9614.

Green Emitting Nanotubular Assembly from Folded Polyurethane Containing Pendant Naphthalene Diimide Chromophores

Tathagata Mondal and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the Cultivation of Science
2A and 2B Raja S. C. Mullick Road, Jadavpur, Kolkata - 700032
psusg2@iacs.res.in

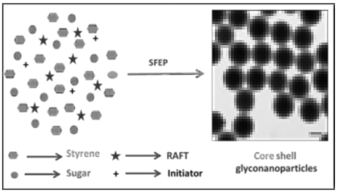
Folding of synthetic macromolecules has been a topic of immense interest in the recent past owing to their relevance with biopolymers in structural elegance. Recent reports describe effects of structural nuances on foldamers including mainly short oligomers and rigid polymers. However, organization of flexible polymer chains remains to be a daunting task primarily because the entropy cost associated with formation of a single folded structure among many possibilities. We envisaged classical polyurethane (PU) scaffold might provide ample opportunities for functional foldamers due to (*i*) easy synthesis (*ii*) enthalpy driven folding by intra-chain H-bonding and (*iii*) possibility of manipulation the monomer structure for exploring diverse functionalities.

To test such possibilities we have synthesized a PU by condensing hexamethylene-di-isocyanate and a di-ol containing a pendant naphthalene-diimide (NDI) in presence of a chiral alcohol as a “mono-functional impurity” to achieve the desired PU with predictable molecular weight and chiral end groups. The polymer was characterized by ^{1}H NMR, FT-IR and GPC measurements. Self-assembly was studied by solvent, concentration and temperature dependent UV/vis which showed intra-chain pi-stacking among the pendant NDI chromophores in solvent such as methyl-cyclohexane (MCH) due to the intra-chain H-bonding (among the urethanes) induced folding of the PU. Photoluminescence studies showed intense green emission in MCH unlike the blue emitting unfolded polymer in $CHCl_3$). Intense Cotton effect was noticed in MCH due to helicity induction by the chiral end groups. Powder XRD data revealed a strong Bragg’s diffraction corresponding to the width of the folded PU along with successive peaks confirming lamellar packing of the foldamer. TEM studies showed initially formed spherical assemblies upon aging for 24 h were converted to 1D nanotubes resulting in macroscopic gelation. Synthesis, folding induced structure gelation mechanism and modulation of photophysical properties of this novel PU will be the topic of this presentation.

Glyconanoparticles with tunable core-shell morphology via RAFT polymerization

S. N. Raju Kutcherlapati, Niranjan Yeole, Madhusudhan Reddy Gadi,
Ramu Sridher Perali and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad-500 046
E-mail: tusharjana@uohyd.ac.in

Here we report simple and one-pot method for the synthesis of core-shell glyconanoparticles using reversible addition fragmentation chain transfer (RAFT) agent in surfactant free emulsion polymerization (SFEP) where, 2-allyl-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (sugar)used as hydrophilic comonomer and styrene as a hydrophobic monomer. As the results suggest that, the comonomer (sugar) concentration as well as length of hydrophilic sugar block play vital role in forming monodisperse core-shell glyconanoparticles. The formation of core-shell glyconanoparticles in which PS was the core and glyco molecule (sugar) is in the shell are characterized by scanning electron microscopy, transmission electron microscope, thermo gravimetric analysis, differential scanning calorimetry, UV-Visible spectroscopy, nuclear magnetic resonance spectroscopy. The particle size, core-shell dimension tunability are achieved by altering the RAFT agent concentration, hydrophilic monomer (sugar) concentration in the polymerization mixture.Zeta potential measurements of these synthesised nano particlesproves the colloidal stability of nanoparticles. This work also proves the utility of RAFT method for the synthesis of core shell nanoparticles when compared to the conventional polymerization. This methodology allows a new, simple route for the synthesis of polymeric glyconanoparticles which has potential applications in targeted drug delivery and as antigen mimicking sugar coated polymeric material.



References:

[1] N. R. Yeole, S. N. Raju Kutcherlapati, T. Jana, RSC Adv. **2014**, 4, 2290-2296.

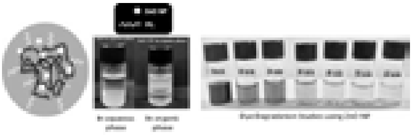
[2] S.C. Abeylath, E. Turos, Carbohydrate Polymers. **2007**,70,32–37.

[3] S. N. Raju Kutcherlapati, N. R. Yeole, M. Reddy Gadi, R. Sridher Perali, T. Jana (Manuscript under preparation).

A Real time Application of Poly(ionic liquid)s stabilized ZnO nanoparticles: As Antimicrobial Agents and Degradation of Organic Dye

K. T. Prabhu Charan[1], K. Manojkumar, Sadhana Venkatesh[1],
Yenuganti Mahesh, Akella Sivaramakrishna[1], Kari Vijayakrishna[1]*
Organic Chemistry Division, School of Advanced Sciences,
VIT University, Vellore 632014, Tamil Nadu, India
*Kari@vit.ac.in

Poly(ionic liquid)s (PILs) have properties of both ionic liquids (ILs) and polymers, its applications has triggered in all the corners of science and technology,[2] due to its hydrophilic and hydrophobic nature of the PILs. One can tune its solubility behavior of the polymer based on need and necessities.[3] PILs have tremendous applications in various fields of chemistry such as catalysis,[4] gene delivery vectors,[5] antimicrobial agents,[6] polymersomes,[7] polymer electrolytes,[8] stabilizing agents for different metal nanoparticles.[9] Researchers still facing difficulty in stabilization of Znic Oxide nanoparticles (ZnO NP) with time in solution phase, such NP may form bulk metals which will lose its potential antimicrobial and catalytic applications. We have synthesized six different PILs and used for stabilization ZnO NP in solution phase, here we have clearly demonstrated the importance of PILs, as carriers towards reversible "**solubility switch**" for synthesized ZnO NP between aqueous and organic media by simple anionic metathesis reaction. Initially we have studied real time application of ZnO NP thin films as antimicrobial agents in addition to this we have successfully degraded organic dye[1]in presence of PIL stabilized ZnO NP and photo light.



(a). (b). (c).

Figure : (a) PIL-Br stabilized ZnO NPs, **(b)** PIL-Br ZnO NP a round trip from water to organics, **(c).**Images of degradation of EBT

References

1. Charan, K. T. P.; Manojkumar,K.;Venkatesh, S.; Vijayakrishna, K.; Sivaramakrishna, A., Unpublished Results, **2014.**
2. (a) Yuan, J.; Mecerreyes, D.; Antonietti, M. Prog. Polym. Sci.**2013,** 38, 1009-1036; (b) Vijayakrishna, K.; Jewrajka, S. K.; Ruiz, A.; Marcilla, R.; Pomposo, J. A.; Mecerreyes, D.; Taton, D.; Gnanou, Y., Macromolecules **2008,** 41, 6299-6308.
3. (a) Charan, K. T. P.; Pothanagandhi, N.; Vijayakrishna, K.; Sivaramakrishna, A.; Mecerreyes, D.; Sreedhar, B., Eur. Polym. J.**2014**, 60, 114-122. (b) Marcilla, R.; Curri, M. L.; Cozzoli, P. D.; Martínez, M. T.; Loinaz, I.; Grande, H.; Pomposo, J. A.; Mecerreyes, D., Small **2006,** 2, 507-512.
4. Green, O.; Grubjesic, S.; Lee, S.; Firestone, M. A., Polymer Reviews **2009,** 49, 339-360.
5. Zhang, Y.; Chen, X.; Lan, J.; You, J.; Chen, L., Chem. biol.& drug design **2009,** 74, 282-288.
6. Choi, S. Y.; Rodríguez, H.; Mirjafari, A.; Gilpin, D. F.; McGrath, S.; Malcolm, K. R.; Tunney, M. M.; Rogers, R. D.; McNally, T., Green Chem.**2011,** 13, 1527-1535.
7. Vijayakrishna, K.; Mecerreyes, D.; Gnanou, Y.; Taton, D., Macromolecules **2009,** 42, 5167-5174.
8. Mecerreyes, D., Prog. Poly. Sci.**2011,** 36, 1629-1648.
9. Mecerreyes, D.; Lee, V.; Hawker, C. J.; Hedrick, J. L.; Wursch, A.; Volksen, W.; Magbitang, T.; Huang, E.; Miller, R. D., Adv. Mat.**2001,** 13, 204-208.

Effect of Natural Nanotubes on the Thermo-mechanical Properties of Polypropylene

Bindu Manchanda[1]*, Veena Choudhary[1], K.K. Vimal[2],
G. S. Kapur[2], Shashikant[2]
[1]Centre for Polymer Science and Engineering, Indian Institute of Technology,
Hauz Khas, New Delhi 110016
[2]Indian Oil Corporation Ltd., Research & Development Centre,
Sector 13, Faridabad, Haryana, 121007

The paper describes the effect of different natural nanotubes, which differ in morphology and chemical composition on the thermo-mechanical properties of polypropylene (PP).Nanotubes used in the study are Halloysite nanotubes(HNT) $[Al_2Si_2O_5(OH)_4.H_2O]$,a hydrated alumina silicate having hollow rod-like geometry with diameter [50-100 nm] and length [0.1µ - 500 nm] and Sepiolite $[Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O]$, a hydrated magnesium silicate having a fibrous and needle-like morphology with diameter [25–30 nm] and length of ~1–2 µm. PP/HNT, PP/Sepiolite and PP/HNT/Sepiolite nanocomposites were prepared by varying HNT and Sepiolite content by melt processing using twin screw extruder.It was observed from SEM and TEM micrographs that HNT and Sepiolite were well dispersed in the PP matrix by shearing. The effect of nanotubes on thermal properties of polypropylene was studied using Differential scanning calorimetre (DSC) and Thermo gravimetric analysis (TGA). DSC results show increase in crystallization temperature (T_c) as well as in degree of crystallinity (X_c) implying that nanotubes acts as a nucleating agent for the crystallization of polypropylene.TGA also shows increase in degradation temperature of PP nanocomposites as compared to neat PP but with differences for different nanotubes used. The nanocomposites also show enhanced mechanical properties with ~ 80-90% increase in flexural modulus, 60-70 % increase in tensile modulus and 10-20% increase in impact strength on addition of 10% Sepiolite in PP . However PP/ HNT nanocomposites show relatively lesser increase in flexural modulus and tensile modulus than PP/ Sepiolite nanocomposites with equal loadings of filler.while 25% increase in impact strength was observed upon incorporation of 5% HNT in PP. DMA results also indicate increase in Storage modulus upon adding nanotubes in PP and thus, confirming reinforcement of PP by nanotubes.

Key words: Polypropylene, nanocomposites, Sepiolite, HNT.

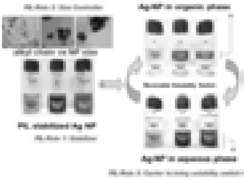
References:

1. Bilotti E, Fischer HR etal. JAppl Poly Sci, in press.
2. Giuseppina T, Daniela T.Composites Science and Technology 68 (2008) 451–460.
3. J.A.M. Ferriera, P.N.B. Reis, J.D.M. Costa, B.C.H. Richardson, M.O.W. Richardson. Composites: Part B 42 (2011) 1366-1372.
4. E. Morales, M. C. Ojeda etal. Polymer engineering and science (1992) Vol. 32.
5. E.Morales, J.R.white. J.Materials science 23 (1988) 4525-4533.
6. N.Ning, Q.Yin, F.Luo, Q.Zhang, R. Du, Q.Fu. Polymer 48: 7374-7384 (2007).
7. K. Prashantha , H.Schmitt , M. F. Lacrampe, P.Krawczak.Composites Science and Technology 71 (2011) 1859–1866.
8. M. Du, B. Guo and D. Jia..Polymer International 2010, 59, 574-582.
9. K. Prashantha, M. F. Lacrampe, P. Krawczak. EXPRESS Polymer Letters Vol.5, No.4 (2011) 295–307.
10. M.Du, B.Guo, X.Cai, Z. Jia, M. Liu, D. Jia. e-Polymers, 130: 1-14 (2008).

Ionic Polymers as a *Smart Stabilizer*for metal Nanoparticles and their applications in Organic Synthesis

Kari Vijayakrishna*
[1] Organic Chemistry Division, School of Advanced Sciences, VIT University,
Vellore-632014, TamilNadu, India
kari@vit.ac.in, vijayakrishnakari@gmail.com

The poly(ionic liquids) (PILs) which are ionic polymers finding increasing applications due to their unique yet tunable physio-chemical properties.[1-3] Recently we have demonstrated that PILs can be used as smart stabilizers for different nanoparticles.[4-5] These PIL stabilized metal NPs showed reversible solubility switch between aqueous and organic phases via simple anion metathesis. Here the size of the metal NPs can be tuned by varying the side alkyl chain length in the polymer back bone. In the synthesis of metal NPs, PILs played multiple roles such as stabilizer, size controller and carriers to bring solubility switch. Synthesized PIL-Ag-NPs exhibited good catalytic activity for the reduction of nitrobenzene to aniline with $NaBH_4$. PIL stabilized Ni-NPs were used as magnetically separable catalyst towards chemo selective reduction of carbonyl compounds under base free conditions.[6] We have also prepared different chiral-PILs and used them for asymmetric organocatalysis.[6] All our resent findings will be discussed during the presentation.



References

[1] Mecerreyes, D., Prog. Poly. Sci.**2011,** 36, 1629-1648.

[2] Vijayakrishna, K. Mecerreyes, D. Gnanou, Y. Taton, D. Macromolecules. **2009**, 42, 5167-5174;

[3] Vijayakrishna, K. Jewrajka, S. K. Ruiz, A. Marcilla, R. Pomposo, J. A. Mecerreyes, D.; Taton, D.; Gnanou, Y., Macromolecules. **2008**, 41, 6299-6308.

[4] PrabhuCharan, K. T.; Pothanagandhi, N.; Vijayakrishna, K.; Sivaramakrishna, A.; Mecerreyes, D.; Sreedhar, B. Eur. Polym. J. **2014**, 60, 114-122.

[5] Garcia, R. Vijayakrishna, K. Mecerreyes, D. React. Funct. Polym. **2014**, 79, 54-58.

[6] Vijayakrishna, K et al (unpublished and communicated results)

Development of light weight material for electromagnetic interference shielding: A study on PPCP/MWCNT/Fe_2O_3/$BaTiO_3$ composites

Pawan Verma and Veena Choudhary*
Centre for polymer science and Engineering,
Indian Institute of technology Delhi, New delhi-110016, India
*Email: veenach@hotmail.com

Polypropylene random copolymer (PPC)/multiwalled carbon nanotube (MWCNT)/iron oxide/barium titanate composites have been fabricated in the varying amount of fillers (iron oxide & barium titanate) to evaluate the potential of PPC as EMI shielding materials. For this analysis, 10 wt % CNT keep constant in all the composition while iron oxide and barium titanate were blended in varying ratio (as1:1, 1:4 & 4:1 here the total weight of Iron oxide and Barium titanate is 50wt%).The effect of dispersion and distribution were analysed using scanning electron microscopy, X-ray and Raman within the matrix. The room temperature electrical conductivity, complex permittivity and electromagnetic interference (EMI) shielding of PPC composites were studied in the frequency range of 8.2–12.4 GHz (X band). Thermal analysis is done by TGA while mechanical stability find out by tensile test The dc conductivity of composites increased with increasing MWCNT loading but no significant change is absorbed in conductivity with iron oxide and barium titanate and typical attainment of dc conductivity value of ~10^{-3} S/cm along with electromagnetic interference (EMI) shielding effectiveness (SE) value of -47 dB (>99.99 % attenuation) in the composite having barium titanate and iron oxide in the ratio 4:1.

Keywords: EMI shielding; Hybrid composites; Electrical conductivity

Reference

1. Singh, B. P.; Saini, K.; Choudhary, V.; Teotia, S.; Pande, S.; Saini, P.; Mathur, R. B., J Nanopart Res 16, 1 2013.
2. Saini, P. In Thermoset Nanocomposites; Wiley-VCH Verlag GmbH & Co. KGaA, 2013.
3. Gupta, A.; Choudhary, V., Journal of Applied Polymer Science 123, 1548 2012.
4. Gupta, A.; Choudhary, V., Journal of Materials Science 46, 6416 2011.

Electrical Conductivity of Graphene and Functionalized Graphene using chitosan as cationic binder in layer by layer assembly

Manash Jyoti Deka,

In this work we have synthesized graphene from commercially available Graphite nanopowder using surfactant exfoliation technique and incorporated different functional groups on it using different chemical reactions. Then we have made different sized lateral dimension of graphene and functionalized graphene dispersion using previously reported method and standardized the lateral dimensions. These dispersions were fabricated on silicon wafer subtrates using layer by layer assembly, where we have used chitosan as cationic binder to fabricate large area and stable graphene/functionalized graphene nanosheets. Then we have measured electrical conductivity of its dispersion fabricating layer by layer assembly on silicon wafer substrates using an impedance analyzer at room temperature at different frequencies and calculated the sheets resistance of its layer by layer assembly. We have successfully investigated that the conductivity of each dispersion fabricated on Silicon/chitosan layer by layer assembly depends on the lateral dimension of the nanosheets as well as their functionalising groups. All characterizations of graphene and functionalised graphene dispersion were performed using FT-IR, UV-Visible, Dynamic light scattering measurement, Atomic force microscope and Scanning electron microscope.

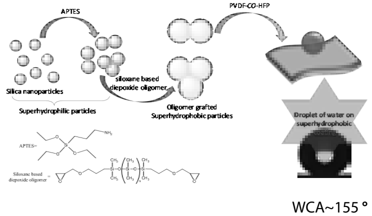
References

1. Novoselov, K. S.; Geim, A. K.; Morozov, V.; Jiang, D.; Zhang, Y.;Dubonos, S. V; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. *Science* 2004, *306*, 666–669.
2. Hofrichtr,J.;Szafranek,B.N.;Otto,M.;Echtermeyer,T.J.;Baus,M.;Majerus,A.;Geringer,V.;Ramsteiner,M.;Kurz,H. Synthesis of graphene on silicon dioxide by a solid carbon source. *Nano Lett.* 2010, *10*, 36-42.
3. Ling,L.L.;Liu,K.P.;Yang,G.H.;Wang,C.M.;Zhang,J.R.;Zhu,J.J. Fabrication of Graphene–Quantum Dots Composites for Sensitive electrogenerated chemilu-minescence immunosensing. *Adv. Funct. Mater.* **2011**, *21,* 869–878.
4. Rao,C. N. R.;Ramakrishna matte, H. S. S.; Subrahmanyam,K. S. Synthesis and selected properties of graphene and graphene mimics.*Accounts of Chem. Research*. **2013,** *46* **,**149–159.
5. Paulus,G.L.C.; Wang,Q.H.; Strano,M.S.Covalent electron transfer chemistry of graphene with diazonium salts. *Account of Chem. Researh*.**2013**,*46*,160–170 .

Oligomer Grafted Nanoparticles - Fluropolymer Surfaces; Access to Superhydrophobicity

Ramakrishna S., Santhosh Kumar K.S.*, Dona Mathew,
Reghunadhan Nair C. P.
Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum, India
*santhoshkshankar@yahoo.com

Superhydrophobic (SH) surfaces have wide range of applications in industrial and academic sectorsfrom anti-wetting, anti-corrosion, anti-icing, self-cleaning to anti-bacterialin nature.Superhydrophobic coatings can be generated from polymer/oligomer chain grafted nanoparticles dispersed in a suitable polymer. The inorganic-organic interface play crucial role in imparting excellent surface properties. In this contribution, silica nanoparticles were functionalized with amine groups.Subsequently, the amine groups were reacted with oxirane rings of a siloxane based diepoxide oligomer. This oligomer grafted silica particles were then dispersed in poly (vinylidenefluride - *co*- hexafluropropylene) flurocopolymerto yield SH coatings. The SH coating exhibits static water contact angle >155 ° and sliding angle <10 °.



Scheme1. Preparation of superhydrophobic coating.

References:
[1] X. Wang, X. Liu, F. Zhou and W. Liu, Chemical Communications, 2011, 47, 2324-2326.
[2] L. Xu, Z. Geng, J. He and G. Zhou, ACS Applied Materials & Interfaces, 2014, 6, 9029-9035.
[3] K. S. Santhosh Kumar, V. Kumar and C. P. R. Nair, Journal of Materials Chemistry A, 2014, 2, 15502-15508.

Glycopolypeptides based cationic α-Helicaltemplates for non-viral gene delivery

Vinita Dhaware,[1]Rajkumar Banerjee[2]* and Sayam Sen Gupta[1]*
[1]Chemical Engineering Division,
CSIR-National Chemical Laboratory, Dr. HomiBhabha Road, Pune – 411 008, India
[2]Department of Lipid Science and Technology,
CSIR-Indian Institute of Chemical Technology, Hyderabad
*ss.sengupta@ncl.res.in

Glycopolypeptides with a well-defined secondary structure are of significance in understanding biological phenomena. Synthetic glycopolypeptides, or polypeptides featuring pendant carbohydrate moieties, have been of particular interest in the field of tissue engineering, gene delivery and drug delivery. The carbohydrate group is known to condense DNA via hydrogen bonding which reduces the necessity to incorporate excess cationic charge which in turn decreases the toxicity of the system. Also, the carbohydrate moieties are well known to interact with specific cell receptors and hence would serve as targeting agent without further need of modification of gene delivery vehicle with receptors. We have synthesized charged water soluble charged glycopolypeptides that adopt a helical conformation in water. This was carried out by the random copolymersation of 6-deoxy-6-azido-glyco-N-carboxyanhydride and 6-OAc-glyco-N-carboxyanhydride - monomers at a feed ratio of 1:4, respectively, using n-hexylamine as initiator. This 20% azide functionality allowed for the easy attachment of a bioactive group, which could potentially enhance the biological activity of the glycopolypeptide. A library of water-soluble charged glycopolypeptides were synthesized by clicking various alkynes containing tertiary amines using CuAAC click chemistry approach with the azido group at the sixth position. These glycoplypeptides were characterised by FT-IR, NMR and GPC. Zeta potential and circular dichroism measurements studies revealed the glycopolypeptides were cationic and adopted helical conformation. The efficacy of these helical cationicglycopolypeptidesas a gene transfection vector in various cell lines will be discussed.

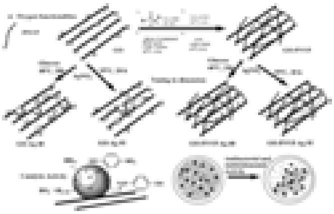
References:

[1] Discher, D. E.; Eisenberg, A. Science.**2002**, 297, 967–973.
[2] Pati, D.; Kalva, N.; Das, S.; Kumaraswamy, G.; Sen Gupta, S.; Ambade, A. V. J. Am. Chem. Soc. **2012**, 134, 7796–7802.

Green Synthesis of Silver Nanoparticles Supported on GO-/GO-grafted-Poly(*N*-Vinyl pyrrolidone) and Studies of the Condition Dependent Tuning in Dimension, Catalytic Activity and Antibacterial and Antileishmanial Activities

Shikha Singh[1], Kheyanath Mitra[1], G. Ravi Kumar[2], Biswajit Ray[1*]
[1]Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi – 221005, India
[2] Institute of Medical Science, Banaras Hindu University, Varanasi – 221005, India
[*] *Email: biswajitray2003@yahoo.co.in*

Now a day's much attention has been focused on the immobilization of nanoparticles onto suitable substrate in order to prevent their agglomeration or, to enhance their efficiencies through a proper interaction with the substrate. Herein, we report the *in-situ* synthesis of silver nanoparticles supported on graphene oxide (GO) and poly(*N*-Vinyl pyrrolidone) (PNVP)-grafted GO under different conditions (scheme). Obtained silver (Ag) nanoparticles fabricated systems have been characterized by FT-IR and UV-Vis spectra and morphology of silver nanoparticles has been studied and compared using SEM and TEM. The catalytic activity, leaching resistance and reusability of each system have been studied and compared in which GO-PNVP-Ag synthesized at 95 °C evolved as the most efficient catalytic system in all respects. GO-PNVP-Ag system has also shown superior antibacterial and antileishmanial activities compared to GO or GO-PNVP system.



Modified xanthan gum/SiO_2 hybrid nanocomposite: A promising adsorbent for selective adsorption of cationic dyes from aqueous solution

Soumitra Ghorai, Sagar Pal*
Polymer Chemistry Laboratory,
Department of Applied Chemistry, Indian School of Mines, Dhanbad – 826004, India

In the present work, we report on the development and application of a novel nanocomposite derived from hydrolyzed polyacrylamide grafted xanthan gum and silica (Hyd. XG/SiO_2) as an adsorbent to remove both methylene blue (MB) and methyl violet (MV) dyes from aqueous solution. The nanocomposite has been prepared through a simple saponification reaction followed by *in-situ* silica incorporation through a sol-gel method, where Hyd. XG promotes silica polymerization and also works as a novel template for silica formation. The efficacy and rate of dye adsorption on Hyd. XG/SiO_2 has been investigated under various parameters such as pH, temperature, time, adsorbent dosage and initial dye concentration. The kinetics data reveals that the adsorption process follows pseudo second-order kinetics and the adsorption equilibrium is in good agreement with Langmuir adsorption isotherm, indicating monolayer sorption on homogenous surface. The thermodynamic studies confirm that the adsorption is spontaneous and endothermic in nature. The desorption study confirms the excellent regeneration capacity of nanocomposite, which makes the adsorption process economically viable. The remarkably high adsorption capacity of dyes on Hyd. XG/SiO_2 nanocomposites can be explained on the basis of H-bonding interaction, dipole-dipole and electrostatic interactions. Hyd. XG/SiO_2 based nanocomposite not only shows outstanding adsorption capacity of cationic dyes (MB dye removal – 99.4%, Q_{max}- 497.5 $mg.g^{-1}$ and MV dye removal – 99.1%, Q_{max}- 378.8 $mg.g^{-1}$) but also reveals excellent potentiality for the selective removal of cationic dye pollutants from the mixture of cationic and anionic dyes.

Creation of Alternating Multi-Polymer Droplet Array on Topographically Patterned Substrate

Anuja Das, Nandini Bhandaru, Rabibrata Mukherjee*
Instability and Soft Patterning Laboratory,
Department of Chemical Engineering, Indian Institute of Technology Kharagpur,
West Bengal, Pin 721302, India

The workreports a method for creating an ordered alternating array of droplets of two different polymers on a topographically patterned substrate, by sequential spin dewetting. Polymer solution as low as 0.1% (w/v) or even less,when spin coated over a non wettable substrate undergoes in-situ de-wetting during the coating process itself, a phenomenon also known as *Spin De-wetting*. For this study, dilute solutions of polymethylmethacrylate (PMMA) and polystyrene (PS) have been used ($C_n \leq 0.1\%$ for both). First, the PMMA solution is spin coated, leading to formation of aligned array ofequal sized spin de-wetted droplets along the grooves of the topographically patterned substrate. Now the substrate is silanized and the second polymer layer is spin coated. Similar to PMMA, PS layer also breaks down into spin de-wetteddroplets aligned along the substrate grooves and position themselves between the pre-existing PMMA droplets, resulting in a multi material droplet array. The number of PS droplets between two PMMA droplets can be controlled by varying the concentration of the second casting solution. In case the substrate is not silanized after the first spin dewetting step, then the PS accumulates over the pre-existing PMMA droplets due to preferential polymer-polymer interaction, resulting in an array of core-shell droplets. Concentration of polymer solution higher than that of a critical concentration (C_n*) results in thread covering the entire groove of the patterns or a continuous filmsupressing the formation of droplets completely.

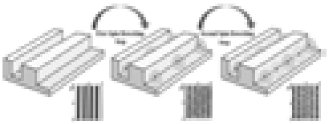


Figure: Schematic representation of the process developed to fabricate binary alternate polymer droplet arrays.

Keywords: Polymer, Spin de-wetting, Silanization, Polystyrene, Polymethylmethacrylate

References:

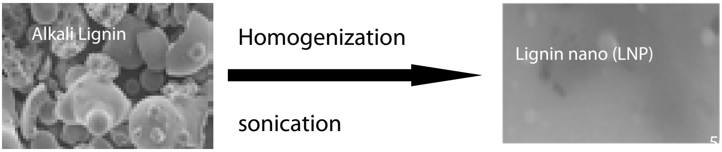
[1] Mukherjee, R.;Bandyopadhyay, D.; Sharma,A. Soft Matter**2008**, 4, 2086–2097.
[2] Roy, S.; Mukherjee, R. ACS Appl. Mater Interfaces**2012**, 4, 5375 – 5385.
[3] Cavallini,M.; Gomez-Segura, J.;Albonetti,C.; Ruiz-Molina, D.;Veciana, J.;Biscarini,F. Phys. Chem. B.**2006**, 110, 11607–11610.
[4] Redl, F. X.; Cho, K. S.; Murray, C. B.; O'Brien, S. Nature **2003**, *423*, 968–971.
[5] Bandyopadhyay, D.; Sharma, A.; Rastogi,C.Langmuir**2008**, *24*, 14048-14058.
[6] Roy, S.; Biswas, D.;Salunke, N.; Das, A.;Vutukuri, P.; Singh, R.; Mukherjee, R. Macromolecules **2013**, *46*, 935–948.
[7] Reiser, A.PhotoreactivePolymers.*The Science and Technology of Resists. Wiley*, New York **1989**.

Novel lignin/Carrageenan multifunctional green-nanocomposites for food packaging applications

Jeevan Prasad Reddy[1]* and Jong-Whan Rhim[2]
[1]Sree Vidyanikethan Engineering College, Sree Sainath Nagar,
Tirupati, A.Rangampet, Andhra Pradesh – 517102
[2]Department of Food Engineering and Bionanocomposite Research Institute,
Mokpo National University, 61 Dorimri, Chungkyemyon,
Muangun, Jeonnam 534-729, Republic of Korea
jeevansku@gmailcom

Due to eco-friendly nature, multifunctional green materials from renewable resource based polymers emerged of this century. With this motivation, the present study is aimed to synthesize multi-functional green nanocomposites from an abundantly available renewable lignin (alkali lignin) nanoparticles and carrageenan biopolymer. Lignin nanoparticles (LNP) were prepared by a green root without any chemical treatment (high speed homogenization and sonication). The effect of LNP content (3, 5 and 10 wt% based on carrageenan) on the mechanical, water vapor permeability (WVP), and antioxidant properties of the green-nanocomposites were studied.

The lignin nanoparticles (LNP) are spherical in shape and with sizes of 15 to 20 nm. Properties of carrageenan film such as mechanical and water vapor barrier properties were improved significantly ($p<0.05$) by blending with the LNP. The tensile modulus and tensile strength of Carrageenan film increased by 48% and 35%, respectively, in the composite film with 5 wt% of LNP, and the WVP of carrageenan film decreased by 22% after formation of green-nanocomposite with 3 wt% of LNP. In addition, these green-nanocomposites also significantly improved the UV- resistance and posses strong antioxidant properties. The LNP obtained from green root can be used as a reinforcing agent for the preparation of green-nanocomposites, and they have a high potential for the development of multifunctional completely biodegradable food packaging materials.



References:

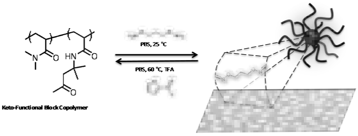
[1] Dimmel D. CRC. Press. Boca. Raton. **2010**, 1-10.

[2] Luo, S.; Netravali, A.N. Polym. Degrad. Sta. **2003**, 80, 59–66.

Oximes as reversible links in polymer chemistry: dynamic macromolecular stars

Soma Mukherjee, [1]Abhijeet P. Bapat,[2] Megan R. Hill[1],
Brent S. Sumerlin[1,*]
[1]George & Josephine Butler Polymer Research Laboratory, Center for Macromolecular
Science & Engineering, Department of Chemistry, University of Florida,
Gainesville, FL 32611, USA
[2]Southern Methodist University, Department of Chemistry, Dallas, Texas, USA 75275-0314
*sumerlin@chem.ufl.edu

The presence of a dynamic bond in a polymeric assembly, by virtue of its reversible nature, enables the system to reconfigure its molecular architecture and provides a mechanism for controlled release of small molecules such as dyes, drugs, and fragrances. We demonstrate the formation of oxime-functional macromolecular stars that are able to dissociate and reconstruct themselves upon application of a stimulus. The reversible nature of the oxime bond in the presence of externally added alkoxyamines or carbonyl compounds enables reconfiguration *via* competitive exchange. Reversible addition-fragmentation chain transfer (RAFT) polymerization was utilized to prepare well-defined amphiphilic block copolymers in which a hydrophobic keto-functional block allowed self-assembly into micelles in water. Adding a difunctional alkoxyamine small molecule to these solutions resulted in crosslinking of the micelles to yield macromolecular stars. The reversible nature of the *O*–alkyl oxime linkages was demonstrated *via* competitive exchange with excess of carbonyl compounds or monofunctional alkoxyamine under acidic conditions and at elevated temperatures to result in dissociation of the stars to unimolecular oxime-functional polymer chains.



Hydrophobic functionalisation of cellulosic fabric using atmospheric pressure pulse plasma of He/1,1,1,2-Tetrafluoroethane

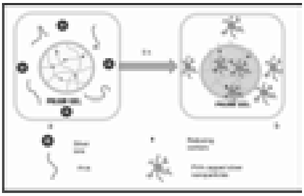
Raghav Mehra, Manjeet Jassal* and Ashwini K. Agrawal*
Smart and Innovative Textile Materials (SMITA) Research Labs
Department of Textile Technology, Indian Institute of Technology (IIT),
Hauz Khas, New Delhi -110016, India
** ashwini@smita-iitd.com*

Plasma technology has gained importance in recent years as it is a dry process and alters only the top surface of the material whereas bulk is not affected. In this study, hydrophobic functionalisation of cellulosic fabric was carried out using He/1,1,1,2-Tetrafluoroethane (He/TFE) plasma at atmospheric pressure. The effect of various parameters such as duration of pulse (duty cycle), voltage, reaction time and monomer flow rate were studied to impart hydrophobicity to cellulosic substrate. A comparison was made between continuous and pulse plasma. Hydrophobicity was evaluated in terms of water contact angle. It was found that the highest water contact angle in He/TFE plasma treated samples could be attained at a specific value of duty cycle. At this condition, a uniform deposition was formed on the treated fabric with high flourine content. The results indicate that pulsed plasma may be suitable for in-situ reaction of precursors with substrates and may be able to offer better control of reactions compared to continuous wave plasma. During a plasma pulse, monomer fragmentation and substrate activation may take place, and subsequently, these may react together during the plasma off period. The duty cyle, which determines the on and off period of the plasma, may be tuned to achieve desired functionalization of the substrate.

Fabrication of PNiAM Hydrogel Silver Nanocomposite and Its Antibacterial Study.

Anuja S.Kulkarni, Archana B.Dhumure, Vaishali S. Shinde*
Department of Chemistry, SavitribaiPhule Pune University, Pune 411007
vsshinde@chem.unipune.ac.in

Small and uniform Ag nanoparticles were prepared by *in situ* reduction of Ag ions in cross-linked poly (*N*-isopropylacrylamide)-*co*-6-acrylamide-6-deoxy-α-D-galactopyranose hydrogel (PNiAM). In this hydrogel, *N*-isopropylacrylamide (NIPAm) monomer is used in higher concentration because of its thermosensitivity, good biocompatibility and ability to stabilize *in-situ* generated nanoparticles. The PNiAM hydrogel reduces Ag ions to Ag nanoparticles (AgNPs) at room temperature and neutral pH, without any additional reducing agents. As the carbohydrates are better known to have the reducing ability, this characteristic property is used in the work to synthesize PNiAM hydrogel silver nanocomposite. These hydrogel/s were added to this solution for reduction of silver ions which was further used for the antibacterial activity.



References:

[1] (a) N. Singh and P. K. Khanna, *Mater. Chem. Phys*., **2007**,104,367. (b) M. V. Varghese, R. S. Dhumal, S. S. Patil, A. R. Paradkar and P. K. Khanna, *J. Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry*, **2009**, 39, 554. (c) M. Brust, M. Walker, D. Bethel, D. J. Schiffrin and R. J. Whyman, *J. Chem. Soc., Chem. Commun*., 1994, 801.

[2] V. S. Bhalerao, S. Varghese, A. K. Lele and M. V. Badiger, *Polymer*, **1998**,39, 2255

[3] (a) V. Pawar, V. S. Shinde, *J.Appl.Poly.Sci*.,**2003**, 111, 2607.b) M. V. Badiger, A. K. Lele, V. S. Bhalerao,S. Varghese and R. A. Mashelkar, *J. Chem. Phys*. **1998**, 109, 1175.

Drug Release Study of Ciprofloxacin-PLA nanofibers

Sharad P. Parwe and Baijayantimala Garnaik*
Polymer Science & Engineering Division, CSIR-National Chemical Laboratory, Pune (India)
E mail:b.garnaik@ncl.res.in

Ciprofloxacin (CP) is commonly used broad-spectrum fluoroquinoline antibiotic with low side effects and has also shown to have antiproliferative and apoptotic activities in several cell lines. Polylactide (PLA) polymers have attracted tremendous attention in biomedical applications because of its biocompatibility and biodegradability in nature. Synthesis of high molecular weight biocompatible PLA using biocompatible catalyst is still challenging. With an easy and cost-efficient procedure, several 7-((4-substituted) piperazin-1-yl) derivatives of CP were prepared. Five different kinds of OH-terminated poly(L-lactide) (two-, three-, four-, six-arm, star-shaped) homopolymer were synthesized by ring opening polymerization of L-lactide in the presence of dodecanol, glycerol, pentaerythritol, dipentaerythritol as initiators and zinc based catalyst. Ciprofloxacin was conjugated with PLA and non woven nanofiber mat was fabricated using electrospinning. The drug-release behaviour of the mat was studied to reveal potential application as a drug delivery system. The result shows that the ciprofloxacin release rates of the PLA conjugate nonwoven nanofiber mat could be controlled by the drug loading content and the release medium. The development of a biodegradable ciprofloxacin system, based on nonwoven nanofiber mat, should be of great interest in drug delivery system. The release of ciprofloxacin possesses antimicrobial and antitumor activities.

References

[1] M. Sobczak, European Journal of Medicinal Chemistry. **2010**, 45, 3844-3849
[2] J. Azéma et al. Bioorg. Med. Chem. **2009**, 17, 5396–5407
[3] Jianmei Pang,Yuxia Luan,Feifei Li,Xiaoqing Cai,Jimin Du,Zhonghao Li ,Int J Nanomedicine. **2011**, 6, 659-665
[4] Fatma Kayaci, Ozgun C. O. Umu, Turgay Tekinay, and Tamer Uyar. J. Agric. Food Chem. **2013**, 61, 3901–3908

Controlled drug delivery using layered double hydroxides

Sudipta Senapati and Pralay Maiti*
School of Materials Science and Technology, IIT-BHU, Varanasi 221 005, India
pmaiti.mst@itbhu.ac.in

A series of layered double hydroxides (LDHs) have been synthesized using various anions through co-precipitation techniques. A model drug raloxifene has been intercalated into layered double hydroxides using ion-exchange method. The mechanisms involved in the raloxifene release process have been studied for the series of LDH with varying metals and different anions as counter ions.

The drug intercalation was confirmed through X-ray diffraction (XRD), FT-IR spectroscopy and thermo gravimetric analysis (TGA). The *in vitro* release behavior of the drug from LDH was studied at pH 7.4 phosphate buffer solutions (PBS) at 37 ^{0}C. The results show that LDH clay materials can be used as controlled release system at sites requiring long-term drug exposure as they release effective amount of drug over a long time periods. The release pattern of the drug from these LDHs has been investigated through X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy. C127I cell viability on LDHs and drug intercalated LDHs has been examined through MTT assay at different time intervals. The cell viability was found to increase with time for pure LDHs while decrease in case of drug intercalated LDHs confirming the controlled release of drug using LDH.

References:

[1] Khan, A. I.; Lei, L.; Norquist, A. J.; O'Hare, D. Chem. Commun. **2001**, 2342-2343.
[2] Li, B.; He,J.; Evans, D. G.; Duan, X. Appl. Clay Sci. **2004**, 27, 199-207.
[3] Shi, C.; Guo, X.; Qu, Q.; Tang, Z.; Wang, Y.; Zhou, S. Biomaterials. **2014**, 35, 8711-8722.

Optical and Conducting Properties of Carbon Quantum Dot-Poly Vinyl Alcohol Composite

Lopamudra Bhattacharjee* and Rama Ranjan Bhattacharjee
PSG Institute of Advanced Studies, Coimbatore, Tamil Nadu
**lopa22b@gmail.com*

Highly fluorescent and water dispersible carbon quantum dots (CQDs) were prepared by controlled pyrolysis of citric acid in presence of poly (sodium 4-styrene sulfonate, PSS). Fourier transform infrared spectroscopy and thermogravimetry were used to study surface passivation of PSS-CQDs. Fluorescence (FL) studies revealed dependency of fluorescence maxima on inter-particle interactions. FL spectra of PSS-CQDs in powder, polymer film and printed impressions showed emission tunability in visible region [1]. Current-voltage (I-V) characteristics of individual PSS-CQDs coated on ITO were probed using spreading resistance imaging mode of atomic force microscope. I-V data of individual PSS-CQDs exhibited linear behaviour at low bias and a sudden jump in current value as the bias crossed zero voltage. Cyclic voltammetry (CV) was used to determine band gap of the CQDs. I-V behaviour was interpreted using CV data and fluorescence properties of the PSS-CQDs. Under solar simulator, the CQD-PVA film shows a maximum voltage of 25 mV which do not drain in dark. Atomic force microscope was used to study morphology of PSS-CQDs embedded in thin-films. Our study reveals promising properties of CQDs for development of cheap materials to design future LEDs.

Reference:

[1] Bhattacharjee, L., Manoharan, R., Mohanta, K., Bhattacharjee R. R. J. Mater. Chem. A, **2014**, DOI: 10.1039/C4TA05491A

“Ultrasound assisted copolymerization of polystyrene with polyvinyl alcohol and its effect on size and shape of iron oxide nanoparticles”

Prasad P. Joshi[1], Satyawati S. Joshi[*1]
[1]Department of Chemistry, S.P. P. U., Pune 411003
*ssjoshi@chem.unipune.ac.in

In our earlier studies, we have successfully synthesized cubic iron oxide nanoparticles of 12 nm by combustion method using PVA as a fuel [Prajkta R. Patil etal (1)]. From our studies, on synthesis of other nanoparticles using same method and different hydrophilic polymers we observed that the functional group of polymer, its related properties play an important role in structure, size, morphology of nanoparticles. In present study, by formation of copolymer of polystyrene (PS) with PVA, the changes in structural and morphological properties on iron oxide nanoparticles are investigated .

The PS-co-PVA samples were made by dispersing the homo polymers in water and by using ultrasound as a radical initiator source. No chemical was added for initiating the reaction. Radicals formed by cavitation process in ultrasound irradiation were sufficient to carry out this reaction. PS was synthesized by cationic polymerization and PVA (MW 1,25,000) was used as purchased. Reaction was carried out in custom build reactor. In current study, the effect of varying intensity, polymer to polymer ratio, and temperature was studied. Samples were characterized by IR, NMR, SEM and TEM. The TEM shows brush like morphology of the polymer.

Using above synthesized polymer PS-co-PVA Iron oxide nanoparticles were successfully synthesized by combustions method in air. The XRD spectra confirm the formation with high order of crystallinity(40nm particle size). SEM micrograph shows the formation of sheet like structure for as prepared samples and annelid at different temperature.

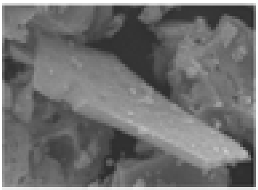


Fig. 1: SEM Micrograph of annelid sample at 300°C(**a)** Iron oxide (PS-co-PVA 1:1:1:2)

Reference

[1] Prajakta R. Patil and Satyawati S. Joshi, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, **2007, 37**:425–429

Effect of Gold Salt Concentration on P123 Mediated Gold Nanoparticle Formation at High pH

Sruti Datta*, P. Chatterjee and S. Hazra,
Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata- 700064, India
*sruti.datta@saha.ac.in

In recent time lots of work is going on to develop simple, versatile and economically viable methods for the preparation of AuNPs in a size- and shape-controlled manner, due to their huge application in fundamental science and technology. In this direction, various attempts are made to synthesize stabilized AuNPs at ambient temperature in a single step process from aqueous solution of gold salt, using water-soluble amphiphilic triblock copolymer (TBP) as both reducing and stabilizing agent [1,2].

In this work, we have systematically investigated the influence of gold salt concentration on gold nanoparticle formation, size distribution and morphology, in the presence of Pluronic stabilizers, at high pH. It is already found that high pH condition in this type of reaction is very suitable for formation of small sized, high yield nanoparticles [3]. The reactants used were hydrogen tetrachloroaureate (III) trihydrate $HAuCl_4$. $3H_2O$ as gold salt, TBP P123 $[HO(CH_2CH_2O)_{20}\ (CH_2CH(CH_3)O)_{70}\ (CH_2CH_2O)_{20}H]$ as both reducing and stabilizing agent and NaOH to raise the pH of the solution. The reactions were studied as a function of concentration of $HAuCl_4.3H_2O$ (0.5mM, 1mM, 3mM, 5mM, 7mM & 9mM) at fixed pH $\approx$ 11.5 and fixed concentration of P123 (5 wt%). Aqueous phase reduction was monitored with time at ambient temperature by simultaneous measurement of UV-visible spectra. Size distributions of the nanoparticles were investigated by DLS measurement and morphology was observed by TEM.

It was observed that at high pH condition, concentration of gold salt, in mixed solution, can be increased up to 9mM and yield of AuNPs is raised proportionally, which is interesting as it is not possible at normal pH. Correspondingly, the reaction rate is slow down with increasing gold salt concentration. At two intermediate gold salt (3mM and 5mM) concentrations, larger nanoparticles with wide size distribution is formed in comparison to lower (0.5mM and 1mM) and higher (7mM and 9mM) concentrations, which is unusual and needs proper understanding.

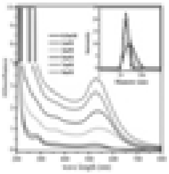


Fig 1. Uv-Vis Spectra and DLS Measurements (inset) of all Six Reaction Mixture after Completion of Reaction

References:

1. T. Sakai and P. Alexandris, Langmuir, 2004, 20, 8426.
2. P. Khullar et al., J. Phys. Chem. C, 2011, 115, 10442.
3. Q. Shou et al., J. Colloid Interface Sci., 2011, 363, 481.

Preparation of chitosan biopolymeric nanoparticles using ionic gelation technique

[1]Ankit Agarwal, [1]Sudarsan Neogi*
Department of Chemical Engineering, Indian Institute of Technology,Kharagpur
*sneogi@che.iitkgp.ernet.in

Chitosan is a natural biopolymer which is obtained by the deacetylation of chitin. Chitosan nanoparticles find wide applications in the food industries due to its small size which imparts characteristic functional and biological properties to it. In this work, Chitosan nanoparticles have been prepared using ionic cross-linking of chitosan with tripolyphosphate. The crosslinking reaction was allowed to take place for 2 hours under constant magnetic stirring.Two set of samples were prepared: one with surfactant and another without surfactant. The resulting precipitates were washed and dried and analysed for surface morphology using Scanning Electron Microscope (SEM), particle size was assessed using Transmission Electron Microscope (TEM), chemical composition and bonds were determined using X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) and elemental analysis was carried out using CHNS analyser. It was found that the particles stabilized using surfactant (Sample 1) were uniformly dispersed with negligible agglomeration compared to that without surfactant (Sample 2). The particle size of Sample 1 was approximately 40 nm whereas that of surfactant stabilized nanoparticles yielded particles almost of the size of 3 nm. The synthesized chitosan nanoparticles were assessed for their antimicrobial activity using zone of inhibition test using 1% acetic acid as the solvent for dispersing the nanoparticles. The presence of a clear zone around the chitosan nanoparticles in disc diffusion test was observed for the gram positive bacteria S.aureus which is an indication of the antibacterial activity of the synthesized chitosan nanoparticles.

References:

[1] Nadesh, R. et al J Biomed Res. A **2012**, 101, 2957-2966.

[2] Koukaras, E. N., Papadimitriou, S. A., Bikiaris, D. N., Froudakis, G. E.Mol. Pharmaceutics **2012,** 9, 2856–2862

Functionalised Nanomaterials: Effective fillers to tailor the properties of Polyfluoroalkylsiloxanes

Rinu Elizabeth Roy, K. Indulekha, R. S. Rajeev*
Polymers and Special Chemicals Group, Vikram Sarabhai Space Center,
Thiruvananthapuram-695006
*rs_rajeec@vssc.gov.in

Carbon nanotubes (CNTs) and graphene which are representatives of one and two dimensional nanostructures have attracted considerable attention due to their ultrahigh mechanical properties and electrical conductivity.These nanomaterials have been incorporated in various polymers to improve specific properties to meet the end use requirements. For e.g, CNT and graphene are known to increase the electrical conductivity of polymers to use them as electrostatic charbe mitigating films. Fluorosilicones are high performance polymers that exhibit broad operating temperatures, fuel resistance and long-term reliability. Properties of fluorosilicones can be tailored using functional fillers to meet specific requirements such as thermal conductivity, mechanical properties, high temperature stability and electrical properties. The present research focuses on the development of fluorosilicone based nanocomposites using single walled carbon nanotubes (SWCNTs) and graphene oxide (GO). However, systematic and fundamental studies are required to properly utilize the exotic properties of CNT and Graphene when they are incorporated in fluorosilicone polymer matrix. In order to have adequate interfacial adhesion between the nanomaterial and polymer matrix to transfer the properties of the former to the latter, functionalization of the nanomaterial, mainly through chemical routes, is required. But the extent of functionalization needs to be controlled so that only minimal defects are introduced on their surface for the complete transfer of properties of these nanomaterials to the polymer matrix. Here in we have studied functionalization of SWCNTs and graphene for different extent of time, optimized the time of functionalization and finally studied the dispersion behavior of the functionalized sample so that it can act as an efficient additive for the preparation of fluorosilicone nanocomposites.A comparitive study of the effect of these functionalized nanofillers on the dynamic mechanical, thermal and electrical properties of fluorosilicone polymers were investigated. To the polymer pristine nanofillers, –COOH functionalised SWCNT and Graphene were added individually as well as in combination as hybrid fillers in varying weight percentage and ultrasonicated in diethyl ether solvent. The dispersion conditions of the solvent in nanofillers were optimised via Zeta potential measurements. Good dispersion of nanofillers and fluorosilicone polymer was obtained which is attributed to the effective hydrogen bonding between the polar groups of nanofillers and fluorosilicon polymer. Nanofiller loaded fluorosilicone copolymer is room temperature curable via platinum catalysed hydrosilylation mechanism using cyclic siloxane having active hydride functionalities .Viscoelastic and solvent resistant properties of the filler loaded systems (of the order of less than 0.1 wt%) were compared with bare fluorosilicone copolymer to prove that the nano filler loaded system retained viscoelastic characteristics even after long term exposure to solvents. Electrical conductivity and thermal stability of the composites were studied and compared with the neat copolymer. The studies revealed that very low loadings of nanofillers confer both long term and short term viscoelastic characteristics to copolymeric fluorinated siloxane systems.

Green synthesis of Ag nanoparticles using polysaccharide from Pleurotus ostreatus cultivar: its characterization and study of antibacterial property

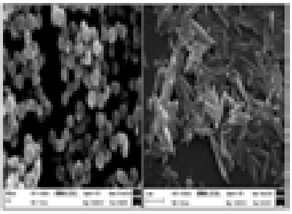
Kankan K. Maity[1] & Syed S. Islam[2*]
[1]Department of Chemistry, Haldia Government College, Debhog, Haldia, India,
[2]Department of Chemistry and Chemical Technology, Vidyasagar University,
Midnapore 721102, West Bengal, India

A simple green route for the synthesis of silver nanoparticles in aqueous solution of polysaccharide, extracted from the mushroom, Pleurotus ostreatus cultivar, acting as both reducing and stabilizing agent, has been demonstrated in this work. The excellence of this method lies not only in its eco-friendliness but also in its simplicity. The advantages of this method are that there is no extra reducing and stabilizing agent is required. UV-Vis spectroscopy, HR-TEM and XRD were used to characterize these silver nanoparticles. The SPR band of UV-Vis spectrum at 415 nm confirmed the formation of silver nanoparticles. Transmission electron microscopic analysis showed an average size of Ag nanoparticles of 30 nm and its XRD and SAED pattern confirmed the FCC crystalline structure of metallic silver. Incorporation of Ag also increased the thermal stability of the polysaccharide. These Ag nanoparticles showed excellent antibacterial activity against both Gram positive and Gram negative bacteria.

Synthesis of Copper particles using different Poloxamers: Pluronics F-127 & F-68

Dipanwita Maity[1], Sutanuka Pattanayak[2], Mukut Chakraborty[2] ,
Dipankar Chattopadhyay[1]*
[1]Department of Polymer Sc. & Tech., University of Calcutta, 92, A.P.C Roy Road, Kol-9
[2]Department of Chemistry, West Bengal State University, Barasat, Kol-126
*dipankar.chattopadhyay@gmail.com

Poloxamers are nonionic triblock copolymers composed of a central hydrophobic chain of polyoxypropylene (poly(propylene oxide)) flanked by two hydrophilic chains of polyoxyethylene (poly(ethylene oxide)). The word "poloxamer" was coined by the inventor, Irving Schmolka, who received the patent for these materials in 1973. Poloxamers are also known by the trade names Synperonics, Pluronics, and Kolliphor. We have chosen Pluronic F-127 and F-68 as our reaction media. In this study, synthesized Copper particles have different sizes and shapes upon changing the poloxamers. The whole reaction was done on oil bath at a constant temperature of 80°C. Formation of copper particles was identified by 630 nm broad-peak in UV-Vis spectrophotometer. The polymer capped copper particles were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FTIR). Size and shape of particles were observed by Scanning electron microscopic (SEM) technique. Reactions are environmentally benign as they are carried out in aqueous medium. Copper sulphate (CuSO4) is used as the metal precursor and the existence of reducing property of the pluronics is proved by the formation of Cu^0 particles from Cu^{2+} ions.



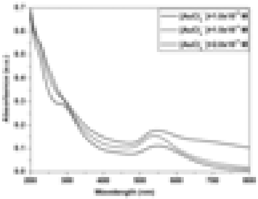
F-127 and F-68 capped Cu particles

References:
[1] Ruiz et al . Nanoscale Research Letters2011, 6 :343
[2] Il-Wun Shim,* Won-Tae Noh, Jiwoon Kwon, Jung Young Cho, Kyung-Soo Kim, and Dong Hee Kang. Bull. Korean Chem. Soc. 2002 , Vol. 23, No. 4
[3] Gupta et al. Journal Of Nanostructure in Chemistry 2013, 3 :41
[4] B.A. Rozenberg, R. Tenne. Prog. Polym. Sci. 33 (2008) 40 – 112.

Biosynthesis of Gold nanoparticles using natural Lac resin and study of its Fluorescence property

Sutanuka Pattanayak[1], Md. Masud Rahaman Mollick[2],
Sharmila Chakraborty[3] & Mukut Chakraborty[1]*
[1]Department of Chemistry, West Bengal State University, Barasat, Kol-126
[2]Department of Polymer Sc. & Tech.,University Of Calcutta, 92, A.P.C.Roy Road, Kol-9
[3]Department of Microbiology, Sammilani Mahavidhyalaya, Kol-94
*mukutchem@yahoo.co.in

The use of natural ingredients in noble metal reduction and nanoparticles synthesis has become more promising in comparison to chemical synthetic pathways. A typical plant extract containing such reducing properties combined with pronounced fluorescence property has been segregated and identified in natural Lac resin which was collected from rural West Bengal. The main compounds which are responsible for the fluorescence and reducing property of Lac are Laccaic acids. This pluralism is due to the presence of a number of different laccaic acids A, B, C and D. These are commonly known as lac dyes and the aqueous solution has a very intense red colour. The UV-Vis study gives a peak (λ_{max}) at 361 nm. We have synthesized gold nanoparticles using this Lac extract in water medium, the green solvent at room temperature and also tried to identify the exact binding sites of the reductant. Synthesis of nanoparticles was established by UV-Vis spectroscopy and fluorescence study was done simultaneously with the same nanoparticles solution. To locate the binding sites of reductants and to calculate the binding constant, the Lac extract/auric chloride reaction was carried out using spectrophotometric and fluorometric studies at different times as the reaction proceeded. Other characterizations such as SEM, TEM, XRD and FTIR studies of the synthesized nanoparticles were also done.



UV-Vis spectra of AuNPs

References:

[1] Mostafa M.H. Khalil*, Eman H. Ismail, Fatma El-Magdoub. Arabian Journal of Chemistry 2012,5,431–437

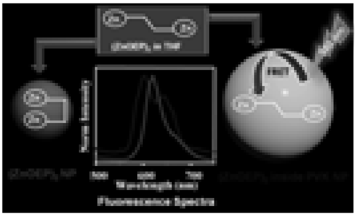
[2] K. George thomas*,and prashant v. Kamat*. Acc. Chem. Res. 2003,36,888-898

[3] Ulrike Haas, Christoph Thalacker, Jo¨ rg Adams,* Ju¨ rgen Fuhrmann, Silke Riethmu¨ ller, Uwe Beginn, Ulrich Ziener, Martin Mo¨ ller,*Rainer Dobrawa and Frank Wu¨ rthner*. J. Mater. Chem. , 2003,13,767–772

Porphyrin Doped Luminescent Semiconducting Polymer Nanoparticles

Sadananda Mandal, Rajesh Bera, Bodhisatwa Mondal and Amitava Patra*
Department of Materials science,
Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032
*msap@iacs.res.in

Porphyrin doped conjugated polymer nanoparticles have attracted considerable attention because of their multifunctional activities in medical imaging, biosensing, drug delivery, photonics, and biophotonics owing to their tunable optical properties, facile synthesis, minor toxicity, and enhanced biocompatibility. Here, the conformational variation of bis (zinc octaethylporphyrin), $(ZnOEP)_2$ and aggregation behaviour of zinc octaethylporphyrin, ZnOEP in poly (9-vinylcarbazole) (PVK nanoparticles have been demonstrated. Steady state and time resolved spectroscopic investigation reveals that the bis porphyrin exhibits anti-conformation inside PVK nanoparticle and syn conformation in polymer nanoparticle form. ZnOEP became self-aggregated as J-type supramolecular organization when the molecules are encapsulated in PVK nanoparticles. Fluorescence quenching and shortening of decay time of PVK nanoparticles, unambiguously confirm the photoinduced energy transfer (above 90%) from PVK host to the porphyrin guest which opens up the further prospect of application in light harvesting system.



References:

[1] Mandal, S.; Bhattacharyya, S.; Borovkov, V.V.; Patra, A. J. Phys. Chem. C **2011**, 115, 24029-24036.

[2] Mandal, S.; Bhattacharyya, S.; Borovkov, V.V.; Patra, A. J. Phys. Chem. C **2012**, 116, 11401-11407.

[3] Mandal S.; Nayak, S.K.; Mallampalli S. ; Patra, A. ACS Appl. Mater. Interfaces **2014**, 6, 130-136.

[4] Mandal, S.; Kundu, S.; Bhattacharyya, S.; Patra, A.J. Mater. Chem. C **2014**, 2, 8691-8699.

Energy transfer from Carbon dots to π-Conjugated luminescent polymer nanoparticles: Crystallinity matters!

Monoj Kumar barman, Santanu Bhattacharyya, and Amitava Patra*
Department of Materials Science,
Indian Association for the Cultivation of Science, Kolkata, 700 032, India

Fluorescent Carbon nanodots constitute a fascinating class of recently discovered nanocarbons for their use in energy conversion/storage, bioimaging, drug delivery, sensors, diagnostics, and composites.[1] Herein, polyethylenimine branched (BPEI) functionalized carbon dots[2] (C-dots) are synthesized by changing the synthesis time using microwave pyrolysis method. The photoluminescence intensity and average decay time of C-dots are found to be increased with increasing the crystallinity of C-dots. C-dot-MEH-PPV polymer nanoparticles composites are formed by electrostatic interaction between these particles. The intensity of C-dots quenches dramatically with increasing the concentration of MEH-PPV (Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) nanoparticles (PNPs) and the intensity of PNPs increases gradually under excitation at 370 nm. This phenomenon may be due to energy transfer from C-dots to PNPs because there is a good spectral overlap between the emission spectra of C-dots and the absorption spectra of PNPs. The drastic photoluminescence quenching and the shortening of decay time of C-dots in composites confirm the efficient resonance energy transfer from C-dots to polymer nanoparticles.[3] The energy transfer efficiency (66% to 89%) and rate of energy transfer is found to be depended strongly on the crystallinity.[4] These C-dots-polymer composites would open up a way for developing new challenging materials for potential applications in photonics and optoelectronics.

References:

[1] Baker, S. N.; Baker, G. A.; Angewandte Chemie, International Edition. **2010**, *49*, 6726-6744, S6726/6721-S6726/6725.
[2] Dong, Y.; Wang, R.; Li, H.; Shao, J.; Chi, Y.; Lin, X.; Chen, G.; Carbon. **2012**, *50*, 2810-2815.
[3] Bhattacharyya, S.; Paramanik, B.; Patra, A.;. Journal of Physical Chemistry C. **2011**, *115*, 20832-20839.
[4] Barman, M. K.; Bhattacharyya. S.; Patra, A.; Phys. Chem. Chem. Phys. **2013**, *15*, 16834-16840.

Effect of Dispersing Agents on Synthesis and Application of Nano Titanium Oxide for Antimicrobial Property

Neha Mehra[1], Ravindra. V. Adivarekar[2]
[1] Department of Fabric & Apparel Science, Lady Irwin College,
Sikandra Road, Mandi House, New Delhi - 110001
[2] Department of Fibres & Textile Processing Technology,
Institute of Chemical Technology, N P Marg, Matunga, Mumbai – 400 019, India

With the growing demand for comfortable, clean and hygienic textile goods, an urgent need for production of antimicrobial textiles has arisen. In this work, synthesis of nano titanium oxide has been done by sol gel method and the effect of dispersing agents with varying ionic character on the particle size of the synthesised nano particles in terms of crystallinity and particle size was studied. Also, they were applied on cotton substrate and tested for their antimicrobial activity. The effect of the application of nano titanium oxide on the physical properties of the substrate, such as tensile strength, bending length, crease recovery angle has been analysed.

Thermal and pH Responsive Polymer-Coated Magnetic Nanoparticles for Targeted Delivery of Anti-Cancer Drug

Sujan Dutta[a], Banalata Sahoo[a], K. Sanjana P. Devi[b], Rakesh Banerjee[a],
Tapas K. Maiti[b], Panchanan Pramanik[a], Dibakar Dhara[a*]
[a]Department of Chemistry,
[b]Department of Biotechnology,
Indian Institute of Technology Kharagpur, West Bengal, India
*Email: dibakar@chem.iitkgp.ernet.in

Targeted and efficient delivery of therapeutics to tumor cells is one of the key issues in cancer therapy. In the present work, we report temperature and pH dual responsive core–shell nanoparticles comprising shell coated with smart polymer on magnetic nanoparticles as an anti-cancer drug carrier and cancer cell-specific targeting agent. Magnetite nanoparticles, prepared by simple co-precipitation method,were surface modified by introducing amine groups using 3-aminopropyltriethoxysilane. Various dual-responsive di/tri blockcopolymers consisting ofpoly(N-isopropylacrylamide), poly(acrylic acid) and poly(ethylene glycol) were synthesized by RAFT polymerization. The polymers were then attached to the amine-functionalized nanoparticles via EDC/NHS method. Further, to accomplish cancer-specific targeting properties, folic acid was tethered to the surface of the nanoparticles. The nanoparticles were characterized by XRD, TEM, SAED, FESEM, EDX, TGA, zeta potential, VSM measurements, and FTIR, UV-Vis spectral analysis. Doxorubicin (DOX) was loaded into the nanoparticles and its release behavior was subsequently studied as a function of temperature and pH. Result showed a sustained release of DOX preferentially at the desired lysosomal pH and temperature condition. The biological activity of the DOX-loaded MNPs was studied by MTT assay, fluorescence microscopy, and apoptosis. Intracellular-uptake studies revealed preferential uptake of these nanoparticles into cancer cells (HeLa cells) compared to normal fibroblast cells (L929 cells). The in-vitro apoptosis study revealed that the DOX-loaded nanoparticles caused significant death to the HeLa cells. These nanoparticles were capable of target specific release of the loaded drug in response to pH and temperature, and hence may serve as a potential drug carrier for in-vivo applications.

References:

[1] B. Sahoo; K. S. P. Devi ; R. Banerjee ; T. K. Maiti ; P. Pramanik ; D. Dhara. *ACS Applied Materials and Interfaces 2013, 5, 3884–3893*
[2] Dutta, S.; Dhara, D. *Communicated*

Simulation and modeling on Effective Thermal Conductivity of nano-AlN particle filled HDPE Polymer Composites

P. Rajeshwari[1*] and T. K. Dey[1]
[1*]Thermo-physical Measurement Laboratory, Cryogenic Engineering Centre,
Indian Institute of Technology, Kharagpur, West-Bengal
[1]rajeshwari.iitkgp@gmail.com*

With miniaturization of microelectronics and associated increase in power densities, thermal management has become a critical issue to achieve sustained device performance and their lifetime [1]. Polymer filled with appropriate fillers having improved thermal conductivity offers possibilities of its applications as heat sinks in electronic packaging .The thermal properties of particles filled polymers is a complex function of their geometry, thermal conductivity of different phases, distribution in the matrix and contact between the particles [1,2]. In the present article, Simulation and modeling approach were employed to investigate the effective thermal conductivity of high density polyethylene filled nano - aluminum nitride particles (HDPE / nano-AlN polymer composites) with and without loading the nano-AlN with HDPE polymer matrix. A transient plane source method is used to measure the experimental effective thermal conductivity of the HDPE / nano-AlN composites consisting of 0-20vol.% loading. In the modeling approach, COMSOL is used to calculate the effective thermal conductivity of the composite by using the results of the thermal analysis. Three-dimensional models are used to simulate the microstructure of composite materials for various vol.% loading of thermal conductivities of nano-AlN filler to HDPE matrix material. The spheres in a cube array model has been used to simulate nano-AlN particle filled composite. The obtained results showed an enhanced effective thermal conductivity over a wide range of filler loading 0-20 vol.% HDPE / nano-AlN composites. For various concentrations of HDPE / nano-AlN composites, the experimentally measured thermal conductivity values are well compared with the obtained effective thermal conductivity using simulation models. At lower filler concentration, up to 6 vol.% of nano-AlN , simulation model predict well with the experimentally measures effective thermal conductivity of the prepared composites. However, for higher filler loading (> 6vol.%) there is an exponential increase in effective thermal conductivity value.

References:

[1] Dey, T.K.; Tripathi, M. Thermochimica Acta . **2010**, 502, 35 – 42.

[2] Goyal, R.K.; Tiwari, A.N.; Mulik, U.P.; Negi, Y. S. Compos. Sci. Technol. **2007**, 67, 1802 – 1812.

Candida Antarctica lipase B immobilization on poly (glycidyl methacrylate) grafted magnetic nanoparticles

Ravindra Ghorpade*, Asmita Thorave, Nayaku Chavan and Surendra Ponrathnam
Polymer Science and Engineering Division,
CSIR – National Chemical Laboratory, Pune, Maharashtra, India
*rv.ghorpade@ncl.res.in

First time biocompatible reactive polymer, poly(glycidyl methacrylate) [poly(GMA)], grafted from magnetic nanoparticles by AGET/ATRP method, has been utilized to immobilize Candida Antarctica B enzyme. Epoxy functionality of poly(GMA) grafted on magnetic nanoparticles used for covalent attachment of enzymes. Enzyme immobilized polymer grafted magnetic nanoparticles were characterized by TGA, FTIR, TEM and VSM magnetometer. Reactive functional groups assist the formation of a permanent covalent bond between the polymer and the enzyme without affecting its tertiary structure. Resulting from the increased functionality, the immobilization amount of the enzyme on the magnetic nanoparticle surface has been greatly improved. Furthermore, the enzyme immobilized magnetic nanoparticles have higher optimum temperature compared with those of free lipase and exhibited better thermal stability as well as exhibited excellent repeatability. Immobilized enzymes used to catalyze a ring opening polymerization of ε-caprolatone. Process offers opportunities to reduce the reaction time and easy separation of the product and catalyst.

References:

[1] Chen, B.; Hu, J.; Miller, E.; Xie, W.; Cai, M.; Gross, R. A. Biomacromolecules **2008**, 9, 463–471.
[2] Bruice, T. C.; Bruice, P. Y. J. Am. Chem. Soc. **2005**,127, 12478-12479.
[3] Mei, Y.; Kumar, A.; Gross; R. A. Macromolecules **2003**, 36, 5530-5536.

Drug polarity approach towards effective drug loading with hyperhydrophilic gold imprisoned polymer matrix: Adsorption isotherm and kinetics evaluation

Sachin Mane
Polymer Science & Engineering Division,
CSIR-National Chemical Laboratory, Pune, India

Hyperhydrophilic polymer was synthesized and imprisoned with gold by simple aqueous reduction method for drug loading application perspectives in acidic buffer. Although surface area, particle size, reactivity, scanning electron microscopy and energy dispersive x-ray analysis of base and MSP was performed. Owing to high polarity and compatibility with hydrophilic polymer, pantoprazole sodium reveals exponential adsorption inversely drug loading is gradual for chloroquine. Notably pantoprazole sodium loaded 72% and chloroquine 26% in initial 2 h whereas raised to 91% pantoprazole sodium and 62% chloroquine in 24 h at pH 3. It is worth noting that initial 2 h is exponential adsorption period for pantoprazole sodium whereas exponential adsorption begins after 12 h for chloroquine. Monolayer drug adsorption was obtained since Langmuir adsorption isotherm followed by both drug. Pseudo first and second order kinetics was also evaluated to perceive adsorption mechanism and equilibrium capacity respectively. Furthermore, pseudo second order kinetics reveals linear increase in adsorption.

Facile Synthesis of Graphene Oxide from Tattered Graphite for Device Applications

Gaurav Kumar[1], Saba Khan[1], Samya Naqvi[1], Neha Gupta[1], Niharika Saxena[1], Neeraj Chaudhary[1], Pramod Kumar[2],[*] Rachana Kumar[1**] and Suresh Chand[1]
[1]Physics of Energy Harvesting Division, Organic and Hybrid Solar Cells Group,
National Physical Laboratory, New Delhi, India
2Department of Applied Sciences, Indian Institute of Information Technology,
Allahabad, Uttar Pradesh, India
*pramod.phy@gmail.com; rachanak@nplindia.org***

Facile synthesis of graphene oxide (GO) is of high importance for the preparation of graphene sheets. Graphene oxide is prepared from graphite by several methods. In the present work, we introduce a milder method of GO synthesis from tattered graphite. For the preparation of tattered graphite, micron sized graphite is refluxed in conc. Nitric acid for 24 hours.[1] The resultant material is filtered and washed several times with deionized water to remove all acid impurities and dried in oven at 80 °C. Further, potassium permanganate and tattered graphite (3:1 ratio) are milled together until homogeneous. Then transferred to a beaker (in ice-bath) and conc. sulfuric acid (98 %,) is added drop-wise with continuously stirring. The stirring is continued till a large volumetric expansion is observed. Deionized water is added, with rapid stirring followed by heating at 90 °C for ~ 1 hour and black colored suspension is formed. The suspension is centrifuged to remove the acid supernatant followed by washing with water : methanol mixture till neutral pH to remove the impurities of acid and salt. Black GO is dried and collected and characterized by FTIR, UV-vis absorption spectroscopy, Raman spectroscopy, and XRD. $I_{(D)}/I_{(G)}$ ratio from Raman spectra suggests 47.3 Å cluster diameter and from XRD the crystallite size is calculated to be 46.1 Å, corroborating the Raman results. Finally GO is used as hole transport layer in organic photovoltaic device and compared with conventional PEDOT:PSS, which will be included in full paper.

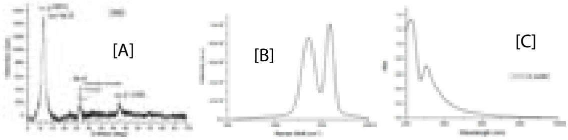


Figure 1. [A] XRD [B] Raman spectra and [C] UV-vis spectra (in water) of GO.

Acknowledgements: CSIR TAPSUN and DST for funding, Mr. Ramil Bharadwaj and Dr. G. D. Sharma for technical support.

References:

[1] W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, **80**, 1339–1340.
[2] B. C. Brodie, Ann. Chim. Phys., 1860, **59**, 466–472.
[3] R. Kumar, P. Kumar, S. Naqvi, N. Gupta, N. Saxena, J. Gaur, J. K. Maurya, S. Chand, New J Chem. 2014, **38**, 4922.

Development of self-healing character of commercial rubbers

Amit Das[1,2]*, Aladdin Sallat[1], Frank Böhme[1], Marcus Suckow[1], Sven Wießner[1], Klaus Werner Stöckelhuber[1], Jyrki Vuorinen[3], Brigitte Voit[1], G. Heinrich[1]
[1]Leibniz Institute of Polymer Research Dresden, Germany
[2]Tampere University of Technology, Tampere, Finland
[3]Technische Universität Dresden, Dresden, Germany
*das@ipfdd.de, amit.das@tut.fi

A cross-linked rubber is an elastic material where the macromolecular chains are linked together by covalent or non-covalent interactions. Formation of crosslinking network allows to stretch up the material by several hundred percent and it can come back to its original shape immediately after removing the stress. Simultaneously, it reduces the viscous properties of the materials in a considerable extent. On the other hand, the raw rubber being a visco-elastic material without any crosslinking may behave like liquid. That means it flows like liquid but rather slowly. Due this primitive viscoelastic nature an uncross-linked rubber sample always showing self-healing characteristics and it is the inherent properties of liquid. Here we simply treated a commercial rubber by an imidazole type of organic compound and processed the rubber at 100°C. Introduction of the imidazolium moieties onto the back bone of the rubber chains results to ionic character of the polymer. Owing to the ionic association[1,2], the materials thus obtained were found to behave like a cross-linked elastomer with unique self-healing characteristics. The materials retain its original properties when it is fully cut and allowed to self-repair[3].Ionic group induced network structure was confirmed by the study of rheometric and other mechanical characterization. The self- healing properties are also very strongly reflected in studies of fracture mechanical behaviors. The crack growth rate was found to be remarkably reduced with this developed materials as compared with sulphur cured standard rubbers as observed by tear fatigue analysis. This simple approach to convert a commercial rubber to self-healing cross-linked rubber could offer a unique opportunity where application of these materials would be easily realized in highly engineering materials like tyres where safety, performance and longer fatigue life time are very crucial factors.

References:

[1] Basu, D., Das, A., Stöckelhuber, K.W., Jehnichen, D., Formanek, P., Sarlin, E., Vuorinen, J.,Heinrich, G. Evidence for an in-situ developed polymer phase in ionic elastomers.Macromolecules **2014**,47, 3436-3450

[2] Eisenberg, A. Clustering of ions in organic polymers - a theoretical approach. Macromolecules, **1970**, 3, 147-154

[3] Cordier, P., Tournilhac, F., Ziakovic, C.S. and Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature**2008**, 451, 977-980

A Constitutive Law of Rubber Elasticity: From Molecule to Rubber Components

G. Heinrich1,2

[1] Leibniz-Institut für Polymerforschung Dresden e. V. (DE)

[2] Technische Universität Dresden, Institut für Werkstoffwissenschaft (DE)

The presentation introduces into the rigorous (non-Gibbsian) molecular-statistical scenario for developing a theory of polymer networks with fixed topological constraints like permanent crosslinks and trapped entanglements (S. F. Edwards et al.). The specific features of mean-field approximations in the frame of the ‚Merseburg'-model of tube-like constraints of network chain conformations in stretched rubbers will be explained (Heinrich, Straube et al.). Extensions of the model include the presence of reinforcing fillers and the effects of limited network chain extension (Vilgis, Heinrich). The so derived materials law of rubber elasticity is suitable for implementation into a finite element code (Kaliske, Heinrich). This model is considered presently as one of the most powerful constitutive models for rubbers (Verron et al.). Further extensions of the model include specific details of nature and morphology of fillers and led to the combined micro-mechanical polymer network & filler-flocculation model (Klüppel et al.) which is here shortly termed as the ‚Merseburg-Hannover'-model of rubber elasticity.

Several examples show applications with respect to large scale and FE directed modelling of rubber parts like motor mounts, sealings, etc. (Kaliske et al; Freund, Ihlemann, Lorenz, Juhre, Klüppel). Very recent applications are related to quantitative evaluation of crack propagation in rubber parts using J-integral concept (Lombardi et al.).

The presented approach to solely physically based rubber material laws and their subsequent treatment and application can be considered as the only multi-scale approach that comprises consequently the route from statistical polymer mechanics via continuum mechanics to FE modeling, or in other words, from polymer network molecules to rubber parts.

An outlook discusses the present efforts to incorporate into the prevailing concept the time dependent viscoelasticity of rubber materials.

References:

[1] R. T. Deam and S. F. Edwards, Phil. Trans. R. Soc. Lond. A280 1296, 317-353 (1976)

[2] G. Heinrich, E. Straube: Acta Polymerica **34**, 589-594 (1983); **35**, 115-119 (1984)

[3] G. Heinrich, E. Straube: Polymer Bulletin **17**, 247-253 (1987)

[4] G. Heinrich, E. Straube, G. Helmis: Advances in Polymer Science **85**, 33-87 (1988)

[5] G. Heinrich, T. Vilgis: Macromolecules **26**, 1109-1119 (1993)

[6] G. Heinrich, M. Kaliske: Computational and Theoretical Polymer Science **7**, 227-241 (1998)

[7] M. Kaliske, G. Heinrich: Rubber Chemistry and Technology **72**, 602-632 (1999)

[8] G. Marckmann, E. Verron, Comparison of Hyperelastic Models for Rubber-like Materials, Rubber

[9] Chemistry and Technology **79**, 835-857 (2006)

[10] M. Klüppel: Advances in Polymer Science **164**, 1-86 (2003)

[11] M. Freund, J. Ihlemann, H. Lorenz, D. Juhre, M. Klüppel: Kautschuk Gummi Kunststoffe **64**, 50-55 (2011)

[12] H. Lorenz, M. Klüppel, G. Heinrich: ZAMM - Journal of Applied Mathematics and Mechanics **92,** 608– 631 (2012)

[13] R. Lombardi, K. Schneider, Ch. Kipscholl, S. Cotugno, P. Straffi, G. Mensitieri, G. Heinrich, Proceedings Rubber Con 2014 "Advanced Engineering & Materials Developments", Manchester (UK), 14-15 May 2014

Effect of nanoparticles on photo-oxidative degradation of rubber nanocomposites

Navinchandra G. Shimpi
Department of Chemistry, University of Mumbai, Santacruz (E) Mumbai
Email: navin_shimpi@rediffmail.com

Photo-oxidative degradation (weathering study) of rubber nanocomposites was studied under accelerated UV (≥ 290 nm) irradiation at different time intervals with changes in mechanical, thermal and physical properties before and after UV exposure. Prolonged exposure to UV leads to a progressive decrease in mechanical, thermal and physical properties along with a change in behavior of filler-matrix interaction, which was due to decrease in cross-linkage density with increase in the mobility of rubber chains. The increases in carbonyl (>CO), hydroxyl (-OH) functional groups after degradation of rubber nanocomposites at different time intervals were studied using FT-IR. Moreover, the change in morphological behavior of viton rubber composites before and after degradation was studied using SEM. Overall, the study shows that the rubber nanocomposites were affected more upon irradiation compared to pristine rubber (except silicone: nPS composites) and it was more prominent at higher wt % loading and higher time interval of UV exposure. In case of silicone: nPS composites, the rate of decrease in properties is more prominent for pristine silicone rubber as compared to nPS filled silicone rubber. This concludes that nPS enhances the stability of silicone rubber up to 1.5 wt % loading of nPS due to uniform dispersion and good compatibility followed by decrease in stability due to agglomeration of nPS in silicone matrix.

Keywords: Nanoparticles, nanocomposites, photo-oxidative degradation and morphology

Theory of Kinetics of Gel Swelling

Swati Sen and Arindam Kundagrami
IISER Kolkata, Mohanpur, West Bengal, India, 741246

Swelling of polymer gels is an important kinetic phenomenon, more so in the case of charged gels (polyelectrolyte gels) as the volume of the gel may change by several orders of magnitude. Although the equilibrium properties of a polyelectrolyte gel before or after the swelling is well studied, there is still need for a good understanding of the kinetics of the swelling. The main aim of our work is to apply the concept of charge regularization (adjustment of the degree of ionization of the polymer), and determine the effect of counterion pressure in the swelling kinetics. In the process we calculate the location of the gel-solvent interface over a period of time. We further calculate the osmotic stress and degree of ionization at all points inside the gel at different times during swelling. In this talk, we will present a few preliminary results.

Silicone-A Macromolecular Wonder

Dr. Anubhav Saxena
[1]Momentive Performance Materials (India) Pvt. Ltd.,
Survey No. 9, Electronic City (West), Hosur Road, Bangalore 560100
anubhav.saxena@momentive.com

Silicones are a class of inorganic polymers that contains –Si-O-Si- bond into their backbone. Depending upon the molecular weight of the polymer, these materials can be readily available in three different forms including liquid, gum and solid. These materials continue to attract a growing academic / industrial attention due to their attractive optical, thermal, insulating and surface properties.[1] New applications of these materials are being considered in new markets such as in Agriculture, Oil & Gas, Electronics, Personal Care, and Healthcare etc.[2-4] Elucidation of structure-properties relationships which in turn determines the final performance in many different applications is one of the very important yet challenging aspects in silicone chemistry. In this presentation we will describe microstructural characterization experiments on various model and commercial silicones. Some interpretation on the key material properties of the silicones will also be presented based on our characterization data.

References:

[1] Mark, J. E. *Acc. Chem. Res.*, **2004**, *37*, 946–953.

[2] Saxena, A.; Dasgupta, D.; Bhat, S.; Tiwari S., Samantara L.; Wrobel, D. *Journal of Applied Polymer Science* **2014**, 131, *40125.*

[3] Joshi, V.; Srividhya, M.; Dubey M.; Ghosh, A. K.; Saxena, A. *Journal of Applied Polymer Science* **2013**, 130, *92–99.*

[4] Saxena A., Markanday M, Sarkar A, Yadav V. K., and Brar A. S. *Macromolecules* **2011**, 44, 6480–6487.

Resinous Mass Isolated from the Latex of *Euphorbia caducifolia* Haines as Potential Green Tackifier for Natural Rubber Compounds

Sanjay K. Bhattacharyya, Rabindra Mukhopadhyay,
Abhijit Bandyopadhyay[1*]
Harishankar Singhania Elastomer & Tyre Research Institute, JK Tyre, Rajasthan, India
[1]Department of Polymer Science & Technology,
University of Calcutta, 92, A.P.C. Road, Kolkata- 700009, India
**abpoly@caluniv.ac.in*

A resinous mass was isolated from the latex of Euphorbia caducifolia Haines and was characterized. The tree is abundant in the district of Rajasthan in India. The total solid content of the latex was found to be 27% out of which nearly 70% was soluble in toluene. Both the fractions were found to tacky however, the soluble fraction was slightly more tacky than the insoluble fraction due to high metal content. Analysis showed that both the fractions were mainly composed of various terpenes and terpenoids. Nearly 83% of the soluble fraction contained monoterpenes and terpenoids, 8.3% as triterpenes and terpenoids and the rest as polyterpenes i.e. natural rubber. Both the fractions exhibited low melting envelops similar to conventional tackifiers and produced insignificant volatile loss within processing window (80-150^0 C). Application of both soluble and insoluble fractions into gum natural rubber compound as substitute to PF and CI resins showed nearly equivalent tack properties with CI but slightly inferior to PF resins at 3 and 5 parts loading respectively. However, the green additives were instrumental in raising the cure rate, especially the soluble mass and improving the post-ageing retention of mechanical properties of the compounds compared to conventional tackifiers.

Interrelationships of Morphology, Thermal and Mechanical Properties in Uncross-linked and Dynamically Cross-linked PP/EOC and PP/EPDM Blends

Kinsuk Naskar*
Rubber Technology Centre, Indian Institute of Technology,Kharagpur, Kharagpur, India
**knaskar@rtc.iitkgp.ernet.in*

Thermoplastic elastomers (TPEs) are one of the fastest growing polymeric materials which combine the elastic and mechanical properties of cross-linked rubbers with the melt processability of thermoplastics at elevated temperatures. TPEs find lot of applications in automotives, building and constructions, wires and cables, soft touch etc. The most important advantage of a TPE is its ability to reuse and recycle the production scrap and waste. Thermoplastic vulcanizates (TPVs) or dynamic vulcanizates are a special class of TPEs, produced by simultaneously mixing and cross-linking a rubber with a thermoplastic at elevated temperature. As a result a typical morphology is formed, where the cross-linked rubber particles are finely dispersed in a continuous matrix of thermoplastic. The size of the dispersed rubber particles and their distribution in the matrix primarily govern the performance of TPVs.

Thermoplastic vulcanizates (TPVs) based on polypropylene (PP) with ethylene octene copolymer (EOC) and ethylene propylene diene rubber (EPDM) have been developed by co-agent assisted dicumyl peroxide cross-linking system. The study was pursued to explore the influence of two dissimilar polyolefin polymers (EOC and EPDM) having different molecular architectures on the state and mode of dispersion of the blend components and their effects with special reference to morphological, thermal and mechanical characteristics. The effects of dynamic cross-linking of the PP/EOC and PP/EPDM have been compared by varying the concentration of cross-linking agent and ratio of blend components. The results suggested that the uncross-linked and dynamically cross-linked blends of PP/EOC exhibit superior mechanical properties over PP/EPDM blends. From the hysteresis experiments it was found that PP/EOC blends also perform better fatigue properties over PP/EPDM based blends. It was demonstrated that, the origin of the improved mechanical properties of EOC based blends is due to the combined effect of the unique molecular architecture with the presence of smaller crystals and better interfacial interaction of EOC phase with PP as supported by the results of thermal and fatigue analyses.

Keywords: polymer blends, elastomers, dynamic cross-linking, peroxide, morphology

References:

[1] Naskar, K.; Noordermeer, J. W. M.; Rubber Chemistry and Technology, **2003**, 76, 1001–1015.

[2] Naskar, K.; Gohs, U.; Wagenknecht, U.; Heinrich, G.; Express Polymer Letters, **2009**, 3, 677–683.

[3] Babu, R. R.; Singha, N. K.; Naskar, K.; Express Polymer Letters, **2010**, 4, 197–209.

[4] Babu, R. R.; Gohs, U.; Naskar, K.; Mondal, M.; Wagenknecht, U.; Heinrich, G.; Macromolecular Materials and Engineering, **2012**, 297, 659–669.

[5] Babu, R. R.; Naskar, K.; Advances in Polymer Science, **2011**, 239, 219–247.

Liquid Silicone Rubber (LSR)-A Performance Elastomer

Debarshi Dasgupta[1], Shreedhar Bhat[1], Sandip Tiwari[1],
Laxmi Samantara[1], Dieter Wrobel[2], and Anubhav Saxena[1]*
[1]Global Research & Development Centre; Momentive Performance Materials, Bangalore
[2]Research & Development Centre Momentive Performance Materials GmbH,
Building R20; 51368 Leverkusen, Germany
**Anubhav.Saxena@momentive.com*

Elastomers are unique class of engineering materials exhibiting high reversible deformation under mechanical stress with distinctly low elastic modulus. Such property arises due to the extremely low inter-chain interactions and the presence of certain degree of crosslink structure which prevents sliding of chains against their immediate neighbors causing plastic flow.[1-2] Liquid Silicone Rubber (LSR) is a prime candidate in performance elastomer offering wide operating temperature window, excellent weather- ability, ultralow temperature toughness, high biocompatibility and higher optical transparency[3] in comparison to synthetic organic elastomers. By composition, LSR is nanocomposite of reinforcement silica fillers compounded into reactive Poly (dimethyl siloxane) (PDMS) resin blends which will be cured to yield elastomeric structure. The presentation will highlight the generic chemistry involved in LSR processing and at the same time also explores the morphological aspect[4] of silica nanofillers in controlling the mechanical properties of the elastomer.

References:

[1] Treloar, L. R. G. The physics of Rubber Elasticity. 3rd ed. Oxford; clarendon Press; **1975**

[2] Mark J. E.; Erman, B. Rubber-like Elasticity: A Molecular Primer 2nd Ed. Cambridge University Press **2007**

[3] Mark, J. E. Acc. Chem. Res. **2004,** 37, 946.

[4] Saxena, A.; Dasgupta, D.; Bhat, S.; Tiwari, S.; Samantara, L.; Wrobel, D. *J Appl. Polym.. Sci.* **2014**, 131(7), 40125

Wetting effects of D_2O on polyurethane hard blocks: a SANS analysis

Chandan Sharma[1*], Nilanjon Naskar[1], Vinod K. Aswal[2], and G. Harikirshnan[1]
[1]Chemical Engineering Department, IIT Kharagpur, Kharagpur, India
[2]Solid State Physics Division, BARC, Mumbai, India
*mch@iitkgp.ac.in

Polyurethanes are versatile polymers with wide range of applications such as coatings, thermal insulation, foams etc. Thermodynamically driven block segmentation during synthesis is a key factor in deciding the thermo-mechanical properties of all classes of polyurethanes. Small angle neutron scattering is a widely used tool to characterize the nanoscopic segmented morphology. Contrast variation is a technique which is used to simplify complex structure using neutrons. In polyurethane systems, D_2O wetting method is widely used to make the hard domains prominent. The effect of D_2O wetting on the size and shape of hard domains was investigated using SANS on various types of PU's. SANS analysis shows an increase in core radius and volume fraction of hard domains. This can be due to urea domain swelling on D_2O wetting. Hence, this study indicates the likelihood of anomalies that could occur in size and shape estimation of polyurethanes as characterized by SANS.

References:

[1] Mang, J.T.; Hjelm, R.P.; Orler, E.B.; Wrobleski, D.A. Macromolecules **2008**, 41, 4358 – 4370.

[2] Stuhrmann, H.B. Journal of Physics: Conference series **2012**, 351, 012002.

[3] Sun, Y.S.; Jeng, U.S.; Huang, Y.S.; Liang, K.S.; Lin, T.L.; Tsao, C.S. Physica B: Condensed matter **2006**, 385, 650-652.

Thermoplastic polyurethane coatings for Aerostat: influence of polyurethane chemistry and additives on weathering properties

Upashana Chatterjee[1], Mangala Joshi[1]*, Bhupendra S Butola[1], Vikas Thakare[2], Gaurav Singh[2] and Mahesh Kumar Verma[2]
[1]Department of Textile Technology, IIT Delhi, New Delhi
[2]Aerial Delivery Research and Development Establishment, DRDO, Agra
*mangala@textile.iitd.ac.in

'Aerostat' is an advanced inflatable coated textile structure having an aerodynamic shape which can be raised to desirable altitude for prolonged duration. Unlike fixed-wing aircraft or helicopters, aerostats are based on 'lighter-than-air (LTA)' technology, typically using helium gas to stay aloft and tethered using a mooring system operated from a fixed location. A typical aerostat envelope structure consists of a strength layer generally of woven textiles and a protective layer of polymer to serve the purpose of gas barrier and thus maintain the structure in inflated condition. In such case, the lifetime of the ultimate inflatable Aerostat structure is primarily determined by the protective properties of the polymeric coating against harsh atmospheric weathering stresses, most commonly UV radiation. But the use of conventional polymeric coatings (PVC, Acrylic etc.) in these applications gets very limited because of their poor weathering resistance [1]. As an alternative material for the protective layer of the aerostat, thermoplastic polyurethane (TPU) has recently attracted more and more interests [2, 3]. In this work, the influence of isocyanate (aromatic and aliphatic) and polyol (ester and ether) types of TPU, individually as well as in combination with different UV protective additives (UVA, HALS, AO), have been studied against xenon arc artificial weathering for different exposure time. Helium gas barrier properties of the different TPU coatings have been tested as per ASTM D-1434. As a measure of degradation behavior, change in surface morphologies and other physical properties of TPU films with exposure time have also been evaluated through microscopic technique, spectroscopic technique and uniaxial tensile test.

Acknowledgement:
Financial support is acknowledged from Aerial Delivery Research and Development Establishment (ADRDE), Defense Research and Development Organization (DRDO), India

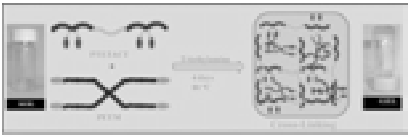
References:

[1] Guillet, J. Pure Appl Chem. 1972, 30,135 –144.
[2] Chattopadhyay, D.; Raju, K. Prog Polym Sci. 2007, 32, 352 – 418.
[3] Boubakri, A.; Guermazi, N., Elleuch, K.; Ayedi, H. Material, Mater Sci Eng: A 2010, 527, 1649 – 1654.

Unique Dual Responsive Gel byThiol- Alkyne Click Chemistry

Pawan Kumar, Mutyala Naidu Ganivada and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

In this study, we describe the application of thiol-alkyne chemistry for the development of one of the unique 3 D gel networks. Poly(ethylene glycol) functionalized with tetra-acetylene (PTETACT) and pentaerythritol (3-mercaptopropionic acid) (PETM) are cross-linked by a thiol-alkyne reaction with a tetra-functional thiol to create robust, tunable networks. A new class of unique gels is produced by gelations in various organic solvents as well as water. The newly developed gel shows maximum swelling in dichloromethane (DCM) followed by chloroform, dimethylformamide (DMF), dimethylsuphoxide (DMSO), and water. Interestingly, swelling of the gel never occurs with toluene and hexane. Microscopic pore formation of the gels is confirmed by Scanning Electron Microscope (SEM) studies. This is the first report of creating 3 D gel networks by thiol-alkyne reaction in the presence of triethylamine under moderate temperature.



Keywords: organogel, hydrogel, click chemistry, thiol-alkyne, rheology, PEG

References:

[1] Webber, R. E.; Creton, C. *Macromolecules***2007**, *40*, 2919-2927.

[2] Ganivada, M. N.; Nerella, V.R.;Dinda, H.; Kumar, P.; Sarma, J. D. and Shunmugam, R. *Macromolecules*, **2014,** 47, 2703-2711.

[3] Ganivada, M. N.; Kumar, P. and Shunmugam, R.; Submitted 2014.

Influence of Network Structure on the Viscoelastic Properties of Dynamically Vulcanized Rubber/Plastic Blends: An Alternative Approach to Understand the Microstructure Evolution

Pranab Dey[1], Kinsuk Naskar[1], Biswaranjan Dash[2], Sujith Nair[2],
Unnikrishnan G[2], Golok B. Nando[1]*
[1]Rubber Technology Centre, Indian Institute of Technology Kharagpur, India
[2]CEAT Limited, Gujarat, India
goloknando@gmail.com

The formation of finely dispersed micron-sized cross-linked rubber agglomerates in the thermoplastic matrix during dynamic vulcanization is now a well accepted theory to explicate the final properties of thermoplastic vulcanizates (TPVs). Based on our previous results, we have investigated further the most influential and essential parameters which controls the ultimate properties of the TPVs. Three TPVs based on poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer (S-EB-S) and solution polymerized styrene butadiene rubber (S-SBR) have been prepared containing different proportions of rubber fraction. Thereafter, advanced microscopic techniques *viz.* TEM, FESEM and AFM have been used for the microstructure analysis. The dynamic experiments have then been performed to correlate the morphological observations with viscoelastic properties. The experimental results and the morphological images confirm that the network structure formation during dynamic vulcanization and its integrity is the most influential parameter to cause the utmost properties for the TPVs. The finely dispersed cross-linked rubber particles obtained during dynamic vulcanization are actually the disintegrated and agglomerated rubber nano-particles having average particle size between 80 and 85 nm. It has also been confirmed that the integrated rubber network structure has an inverse relationship with the proportion of rubber fraction present in the TPVs. Mechanical properties, melt rheology and dynamic viscoelastic measurements also support the network structure disruption and disintegration observed in the morphological images and thus, nullifies the supremacy of dispersed phase morphology theory behind the superior properties obtained from the TPVs. This work elucidates the necessity and importance of integrated network structure formation over the morphology evolution during dynamic vulcanization and leads to a new avenue to understand morphology-mechanical-rheological-viscoelastic property correlation in TPVs.

References:

[1] van Duin, M. Macromol. Symp. **2006**, 233, 11 – 16.
[2] Bousmina, M.; Muller, R. Rheol. Acta **1996**, 35, 369 – 381.
[3] Abdou-Sabet, S.; Puydak, R. C.; Rader, C. P. Rubber Chem. Technol. **1996**, 69, 476 – 496.
[4] Antunes, C. F.; Machado, A. V.; van Duin, M. Eur. Polym. J. **2011**, 47, 1447 – 1459.

Novel organo-modifiedkaolinsas reinforcing fillersfor rubber industry

Sreelekshmi R. V.[1] , and Menon A. R. R.[1]*
[1]CSIR-NIIST, T.V.M-19, Kerala, India
*drarrmenon@gmail.com

Rubber / Clay nanocomposites (RCNs) constitutean area of active research due to theirpotential industrial applications. Organo-modified nanofillers enhance the mechanical properties of the nanocompositesexceptionally(1, 2). The main challenge in preparing RCNs using nanoclays is that the clays are hydrophilic in nature whereasmany of the polymers arehydrophobic which makes them incompatible leading to reducedphysico-mechanical properties. Modification of claysusing organic surfactants improves their compatibility with rubber matrix. Organomodified clay–rubber nanocomposites are reported to show 'exceptional improvements' in physico-mechanical properties at very low dosages of the modified clay, enabling various industrial applications. Many of the organo-modifiersreported for clays are rather expensive since these are based onpetrochemical sources that are depleting day-by-day.

Phosphorylated Cashew Nut Shell Liquid prepolymer (PCNSL) – a derivative of CNSL (alow cost renewable natural resource) has been reported as a multifunctional additive for rubbers. PCNSL is amphiphyllic in nature with a hydrophilic phosphate group and a hydrophobichydrocarbon side chain making it an ideal candidate as a compatibilizer between polar and nonpolar polymers or additives.However its use as an organomodifier for inorganic fillers has not been reported.

Rubbervulcanizates containing very low dosages of PCNSL modified kaolin showed improved physico-mechanical properties compared to unmodified kaolin and commercially available precipitated silica used in the rubber industry.It shows promising future in the design and development of cost effective industrial rubber products such as foot-wears or sidewall of automobiletyres.

References:

[1] Ismail, N. I.N; Ansarifar M. A.;Song, M.; J. Appl.Polym. Sci. **2014**, 131, 41061.

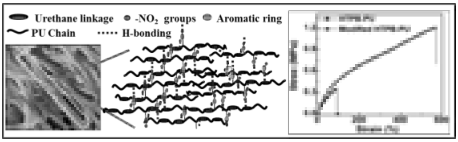
[2] Chaoqun Li, Zhiwei Jiang, Tao Tang J. Appl.Polym. Sci**. 2014**, 131, 40618.

[3] Sukumar,R.; Menon,A.R.R.; J. Appl. Polym. Sci. **2007**, 107, 3476-83.

Simultaneous improvement of tensile strength and elongation: An unprecedented observation in case of HTPB polyurethanes

MalkappaKuruma and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad 500 046
E-mail: tusharjana@uohyd.ac.in

Chemical modifications of hydroxyl-terminated polybutadiene (HTPB) with hydrogen bond forming functionalities were used as tactics to improve both tensile strength and elongation of polyurethanes (PUs) simultaneously. PUs were prepared using various diisocyanates with modified HTPB in which dinitrobenzene (DNB) groups are attached to terminal carbon atoms. The spectroscopic studies revealed the presence of an additional hydrogen-bonding network between DNB and the urethane backbone, which resulted into supramolecular cross-linking and was found to be responsible for significant improvement in mechanical properties of HTPB-DNB-PUs. Also, substantial improvement of elongation at break was observed in the case of HTPB-DNB-PUs,Smallangle X-ray scattering (SAXS) and thermodynamically studies indicated a strong segmental mixing between the hard and soft segments of HTPB-DNB-PUs. Growth of partial crystalline character in HTPB-DNB-PUs was believed to be responsible for "fibrous-assembly" morphology. In summary, modification of HTPB induced extra cross-linking through supramolecular hydrogen bonding which in turn concurrently enhanced both strength and elongation of Pus.



References:

[1] Shankar R. M.; Roy T.; Jana T. Journal of Applied Polymer Science, **2009,** 114, 732-741
[2] Malkappa K.; Jana T. Ind. Eng. Chem. Res. **2013,** 52, 12887−12896
[3] Chung, H.; Washburn, N. R. ACS Appl. Mater. Interfaces.**2012,** 4, 2840-2846
[4] Lu, Y.; Larock, R. C. Biomacromolecules.**2008,** 9, 3332-3340
[5] Harris, D. J.; Assink, R. A.; Celina, M. Macromolecules.**2001,** 34, 6695-6700
[6] Luciene, D.V.; Thiago, C.; Milton, F. D.; Marta K. T.; Luis, C. R. Mater.Res. **2011,** 14, 372-375

Room Temperature grafting of Cardanol, a waste from the Cashew Industry on to Styrene Butadiene Rubber in the Latex Stage

Vinay Krishna Gupta[1], Denial Mahata[2], Dipakranjan Mal[1] and Golok B Nando[2*]
[1]Department of Chemistry, Indian Institute of Technology Kharagpur, India 721302
[2]Rubber Technology Centre, Indian Institute of Technology Kharagpur, India 721302
*golokb@rtc.iitkgp.ernet.in

Cardanol, an agricultural by-product of the cashew industry, is a cheap and abundantly available renewable resource. The multifunctional activity of cardanol in the rubber and polymer industries has been well-established in recent years. Cardanol, a naturally occurring meta-pentadecenyl alkyl chain substituted phenol, is used as multifunctional additives (MFA) in rubbers. It is expected that grafting of cardanol onto styrene butadiene rubber (SBR) will develop the multifunctional characteristic of rubbers. The present study deals with the grafting of cardanol onto SBR in the latex stage using benzyltrimethylammonium chloride and potassium persulfate as free radical initiator. The grafting parameters have been optimized for maximum yield in terms of percent grafting and grafting efficiency by the Taguchi method. Four control parameters, i.e., initiator concentration, cardanol concentration, reaction temperature, and reaction time, are varied at three different levels. The grafted rubber was characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy and thermal analysis. IR spectrum of cardanol exhibited characteristic peak of cardanol for phenolic -OH. Also the percent of grafting (PG) and grafting efficiency (GE) of cardanol onto SBR were determined by residual weight method. Differential scanning calorimetry analysis of the grafted SBR showed a lower glass transition temperature than that of raw SBR which indicate the plasticization effect of cardanol. The thermogravimetric analysis showed the higher thermo-oxidative stability of cardanol grafted SBR. The analysis of variance method is used to evaluate the percentage contributions of the different control factors on the percent grafting and grafting efficiency.

Keywords: Cashew nut shell liquid (CNSL), Cardanol, Styrene Butadiene Rubber, Latex, Grafting efficiency (GE)

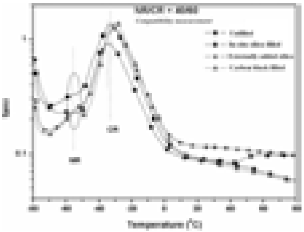
Reference

[1] Bhunia, H.P.; Basak, A.; Chaki T. K.; Nando, G. B. Eur. Polym. J. 2000, 36, 1157-1165.
[2] Vikram, T.; Nando, G. B. J. Appl. Polym. Sci. 2007, 105, 1280-1288.
[3] Mohapatra, S.; Nando, G. Ind. Eng. Chem. Res. 2013, 52, 5951-5957.

Reinforcing efficiency of sol-gel derived in-situ silica for rubber blends

Bharat P. Kapgate and Chayan Das*
Department of Chemistry, Visvesvaraya National Institute of Technology,
Nagpur, India-440010
* *chayandas@hotmail.com*

Reinforcement effect of sol-gel derived nano silica on the properties of rubber blends composed of natural (NR) synthetic rubber has been investigated. Much better silica dispersion in the rubber blends is achieved following this technique in comparison to externally silica filled composites of similar composition. This leads to significant improvement in modulus, tensile strength and dynamic mechanical properties of all the in-situ silica filled composites relative to externally filled composites. Best mechanical properties are shown by the in-situ filled composite with at 40/60 blend ratio. This result is in agreement with the rheological properties, thermal properties and viscoelastic behaviors of this particular composite. Additionally, analysis of glass transition temperature (Tg) values reveals that compatibility of NR and CR is enhanced by incorporation of in-situ silica which in turn contributes in improving physical properties. This enhancement in the compatibility of rubber blends is attributed to the preferential accumulation of in-situ silica at the interphase of the two constituent rubbers. Ultimate properties of the composites are found to be governed by the blend composition, blend compatibility and state of filler dispersion, as well, in addition to filler content.



Enhancement in compatibility of NR/CR blends by the addition of in-situ silica

References:

[1] B. P. Kapgate, C. Das, A. Das, D. Basu, U. Reuter, G. Heinrich, *J. sol-gel Sci. Technol*. 2012, *63*, 501-509.
[2] B. P. Kapgate, C. Das, *RSC Adv*. (2014).
[3] A. Das, R. N. Mahaling, K. W. Stöckelhuber, G. Heinrich, *Compos. Sci. Technol*., 2011, **71**, 276-281.
[4] P. Sae-oui, C. Sirisinha, T. Wantana, K. Hatthapanit, *J. Appl. Polym. Sci*., 2007, **104**, 3478-3483.
[5] M. Messori, *In Situ Synthesis of Rubber Nanocomposites, In Recent Advances in Elastomeric Nanocomposites*. Springer Berlin Heidelberg, 2011, 57-85

Synthesis, Characterization, and Thermo-kinetic Studies under Non-isothermal Condition of Polyurethane Elastomer

Abhay K. Mahanta[1*] And Devendra D. Pathak[2*]
[1]Defence Research & Development Organization, SF Complex,
Jagdalpur-494001, Chhattisgarh, India
[2]Department of Applied Chemistry, Indian School of Mines,
Dhanbad-826004, Jharkhand, India
mahanta_ak@yahoo.co.in

A series of polyurethane elastomers, based on hydroxyl terminated polybutadiene (HTPB), toluene diisocyanate, 1, 4 - butanediol, and trimethylolpropane, with different stoichiometry were synthesized following one -step polymerization method in bulk. The polyurethane elastomers were characterized by one dimensional (^{1}H, ^{13}C, and DEPT-135 & 90), two dimensional (COSY, HMBC, and HMQC/HSQC) NMR spectroscopy, and FTIR using Attenuated Total Reflectance (ATR) technique. The elastomeric properties on dumb-bell shaped polyurethane specimens were measured by Instron Universal Testing Machine (UTM). The structure-properties relationships have been discussed in detail. The thermo-kinetics of the polyurethane elastomer under non-isothermal condition at heating rates of 4, 6, 8, 10, and 15 °C/min in the temperature range of 30-400 °C in an air atmosphere was investigated by Differential Scanning Calorimetry using integral approximation methods. The most probable kinetic model for thermo-oxidative degradation of polyurethane was found to be $f(\alpha) = 3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ by Coats and Redfern integral method. The activation energy (E) and pre-exponential factor (A) were in the range from 80 - 99 kJmol^{-1} and 6.54×10^7 - 2.64×10^{10} min^{-1} respectively. The kinetic triplets [E, A, and$f(\alpha)$] obtained from Coats and Redfern integral method were used for prediction of half-life and thermal lifetime profile of the polyurethane elastomer at different temperatures. The thermo-oxidative conversion of 50 % was considered as the point of failure suggesting end of thermal life of the polyurethane elastomer. It was found that the thermal life decreased significantly from 14 years to 1.2 years as the temperature increased from 25 °C to 45 °C. The study is a valuable guide for thermal processing, long term storage condition, and stability assessment of HTPB-based polyurethanes for various industrial applications.

References:

[1] Barral L.;Cano J.;Lopez J.;Bueno I.L.;Nogueira P.; Abad M.J.; and Ramirez C. Eup. Polym. J., **2000**,36,1231.
[2] Budrugeac P. Polym. Degradation and Stablity, **2000**, 67, 271.
[3] Panicker S. S. and Ninan K.N. Thermochimica Acta **1997**,290,191.
[4] Mahanta A.K. and Pathak D.D. In Polyurethane, InTech, http://dx.doi.org/10.5772/ 47995, 1st ed. Chapter, **2012**, 11,229.
[5] Gao Z.M.;Nakada M.; Amasaki I. Thermochimica Acta,**2001**,369,137.
[6] Reza E.K.; Hasan A.M. and Ali S. Iran. J. Chem. Chem. Eng., **2007**, 26(2), 119.

Synthesis and characterization of flexible/stretchable Polyetherimides containing aryl/alkyl side chains

Simi Annie Tharakan and M. Sarojadevi*
Department of Chemistry, Anna University, Chennai, India
msrde2000@yahoo.com

There have been many attempts to prepare process-able polyimides without sacrificing desired properties. To accomplish this goal, flexible bridging units as well as bulky groups are incorporated into the rigid polyimide backbone, or the attachment of bulky side groups has been widely used [1]. Polyimides containing ether linkages prepared through phenoxy derivatives via nitro displacements, especially General Electric's poly (ether imide) Ultem, have achieved great commercial success [2]. The majority of PEIs are non-crystalline and their glass transition temperatures (Tgs) ranges from 200 to 280^{0}C.

At the same time there is a continuing need for elastomers capable of withstanding elevated temperatures. In defense industry, specific needs are associated with aircraft fuel tank sealants and O-rings and gaskets in missile structures and engines. Silicone is the commonly used elastomeric material in these applications. However, there are performance limitations with these elastomers [3].

In 2007 D. H. Wang published the research work related to the effect of introducing multiple alkyl side chains on the thermal, mechanical and optical properties of aromatic polyetherimides [4]. The PEIs containing multiple alkyl side chains show much higher elongations but lower tensile strengths and moduli than the commercial Ultem_1000.

In my work I am trying to impart elastomeric properties in polyimides without sacrificing their excellent thermal and mechanical properties. Hence, it is proposed to prepare diamine monomers containing ether linkages in the backbone and pendant with long alkyl/aryl ether and characterize their structure by FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass spectra and elemental analysis. Polyetherimides will then be prepared with aromatic dianhydrides by the conventional two step process and characterized by spectral techniques to study the structure. The T_g and thermal stability will be studied by DSC/DMA and TGA respectively. The molecular weight will be determined with GPC. The mechanical properties of the thin films will be studied by UTM.

References

[1] Eastmond, C.; Paprotny, J. *J Mater Chem* (**1997**), 7,589.
[2] Williams, F. J.; Donahue, P. E. *J Org Chem* (**1977**), 42, 3414.
[3] *Thermaly Stable Eleatomers: A Review,* **by** Robert A**.** Rhein. China Lake, Calif., Naval Weapons Center, October (**1983). 38 pp. (NWC** TP **6372)**
[4] David H. Wang , Zhihao Shen , Stephen Z.D. Cheng , Frank W. Harris , *Polymer* 48 (**2007**) 2572-2584

Study OfTheRubber BehaviorUnder Cyclic Compression Loading

Rahul Jain[1], Himanshu Tripathi[1], Ritvik Gupta[2], Venkatesh L K [1], Kannan A[1]
[1] Applied Innovation EnSci – A Weir Group Company Bangalore, Karnataka, India
[2] Department of Mechanical Engineering,
Birla Institute of Technology and Science Goa, India

Rubber is the key component of the sleeves used for sealing in the gate valves. Sleeves are subjected to compressive stress due to the impact of the slurry on the gate . As a result, rubber experiences wear and fatigue. It is required to properly understand the behavior of the rubber under compressive loading. For this reason, atest rig was designed to conduct cyclic compression tests on rubber specimen to understand the loading behavior exhibited by rubber when subjected to a maximum compressive strain of 50% or higher.Load and the corresponding displacement was measured using load cell and displacement transducer respectivelyusing NI 9237 DAQ system connected to LabVIEW. Additionally, the strain rate was varied in a sinusoidal fashion using a cam and follower executing a Simple Harmonic Motion (SHM). This was done to simulate field condition in knife gate valve operation. When the gate comes down to stop the slurry flow through the valve, the strain rate experienced by the rubber is variable.

The rubber materials used for testing are of premium grade natural rubber (Polyisoprene). Two specimens used have hardness (Shore A) in the ranges 47-53 and 65-70.

Data obtained was processed to plot the variation of engineering stress experienced by rubber with the following: No. of cycles (for a fixed value of the displacement), strain rate. This test was done on both the specimens to compare the behavior exhibited by the two under identical test conditions. Both the specimens exhibited Mullins' effect. To effectively describe the behavior of stress softening observed in the first few cycles, a mathematical model was devised. Further study of variation of load with changing strain rate confirmed the effect of strain rate on the load experienced by the rubber.

References:
[1] J. Diani*, B. Fayolle, P. Gilormini, "A Review on Mullins' Effect"
[2] J. S. Bergstr¨om∗ and M. C. Boyce, "Constitutive modeling of the large strain time-dependent behavior of elastomers"
[3] C. M. Roland*, "mechanical behavior of rubber at high strain rates"

Investigation on cure,thermo-mechanical properties and chemical resistance behaviour of Bromobutyl rubber Bismaleimides based cure systems for Space use

Dhanya P*, S Ratheesh[1], Shashi Bhushan Singh[1], Ajith Kumar H[1],
Elizabeth John[1] and C.P Reghunadhan Nair[1]
*Cochin University of Science and Technology,
[1]Polymers and Special Chemicals Group
s_ratheesh@vssc.gov.in

The elastomeric materials are generally used as sealant over any other materials owing to their salient features like:light in weight, elastic recovery after stress, flexibility, extrusion resistance etc. There are many synthetic elastomers available which are used in making the elastomeric components as per functional requirement. Several new elastomeric formulations are being brought out yearly addressing the critical demands of aerospace industry. Bromobutyl rubber(BIIR) for example, by virtue of its inherent chemistry, has got low permeability to gases and good heat ageing properties, good weatherability, ozone resistance and resistance to corrosive environment involving acids, alkalies and polar solvents. The reactivity of butyl rubber afforded by the presence of allylic C-X bond in BIIR gives rise to unique cure reactions with several options.

In present study ,three different types of bismaleimides e.g. Bismaleimidodiphenylmethane (BMPM), 2, 2 - Bis4 -[(4maleimidophenoxy) phenyl]propane (BMIP) and Bis4-maleimidophenylether (BMIE) were used to study the effect of types of bismaleimide on BIIR crosslinking. The rheological and analytical studies were carried out to know the cure behavior of bismaleimides on BIIR compounds. The study on effect of these different cure systems on thermo mechanical properties and chemical resistance of BIIR compounds were carried out. The composition optimization to achieve required process ability and compatibility with liquid propellants used in liquid stages of rocket engines such as N_2O_4 and Monomethyl hydrazine(MMH) were also carried out. The crosslink density of three types of bismaleimides were calculated using the solvent (toluene and xylene)method. The swelling behaviour of different types of bismaleimide cured BIIR compound with Xylene is shown in figure1.

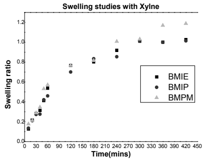


Fig-1

Reference

[1] Naba K. Dutta & D. K. Tripathy ,The Influence of Curing Systems on the Properties of Bromobutyl Rubber: Part 2

[2] Edith A. Turi, Thermal characterization of polymeric materials,vol2

Multi layered Natural rubber- woven Kevlar and UHMWHDPE fabric composites for soft body armor applications

Rupayan Roy[1], Abhijit Majumdar[1], Bhupendra Singh Butola[1]*
[1]Department of Textile Technolog, IIT Delhi
*bsbutola@textile.iitd.ac.in

In this work, the authors have investigated the impact performance of natural rubber (NR) coatedhigh strength, high modulus fabrics. The effect of different coating techniques were studied. Kevlar 149 and UHMWPE fabric were coated with different concentrations of NR solutions (20%, 30%).Samples were produced with different add on percentage. The NR solutions with 20 % and 30% solid content provided 4 and 6 % add-on on Kevlar fabric and 6 and 9% add-on on UHMWPE fabric. Multilayered fabric structures coated with NR were alsostudied. Compression mouldingwas used to prepare the layered fabric structures. The effects of coating with different add-on percentages on fabrics were studied. Different mechanical properties like, tensile strength, yarn pull out force, puncture resistance, peel resistance for double layered fabric system were studied. The pull out force increased by ~ 480% and 360% on Kevlar and UHMWPE fabrics coated with NR. The tensile strength of both the fabrics also increased by about 60%. A peel force of 2.3 and 2.6 kgf was obtained with two layered structures of Kevlar and UHMWPE respectively.

References:

[1] Das, D.; Datta, M.; Chavan, R. B.; Datta, S. K. Jour. Appl. Polym. Sci. **2005**, 98, 484–489.
[2] Kirkwood, K. M.; Kirkwood, J. E.; Lee, Y. S.; Egres, R. G.; Wagner, N. J.; Wetzel, E.D. Text. Res. Jour. **2004**, 74, 920-928.
[3] Srivastava, A.; Majumdar, A.; Butola, B. S. Mater. Sci. Engg. A. **2011**, 529, 224– 229.

Chemical Modification of Metallocene Based Polyolefinic Elastomers: Application as Compatibilizer

Anjan Biswas[1], Abhijit Bandyopadhyay[2], Nikhil K.Singha[3],
Anil K. Bhowmick[3]
[1]Govt. College of Engineering and Leather Technology, Govt. of West Bengal, Kol-98, India
[2]Department of Polymer Science and Technology, University of Calcutta,
92, A. P. C. Road, Kolkata- 700009, India
[3]Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India

Nylon 6 (PA_6) is a widely used engineering thermoplastic due to its excellent dimensional stability, light weight, chemical resistance, low cold brittleness temperature and excellent electrical properties. However, it has relatively low impact strength, which limits its applications. Although its toughness can be improved by the addition of plasticizers, research on other impact modifier continues.[1] Several studies of compatibilization of polyamide / elastomer blends involving the maleic anhydride grafted polyethylene–propylene–diene ternary rubber (EPDM-g-MA) have been reported.[2]

Metallocene-catalyzed poly(ethylene-co-octene) and poly(ethylene-co-butene) elastomers (designated as POE and PBE respectively) typically exhibit faster mixing and better dispersion compared to the conventional polyolefin elastomer EPDM when blended with polypropylene (PP).[3] Since the ratio of viscosity to elasticity in the case of POE / PBE is lower than that of EPDM, EPDM rubber often forms a spherical domain shape in the polymer matrix, whereas POE / PBE always forms an elliptic domain shape in the matrix.[4] Therefore, an attempt has been made in this investigation to substitute EPDM by rubbery grade of POE / PBE (i.e. POE_{16} / PBE_{16} respectively) to toughen PA_6.

Since, POE_{16} and PBE_{16} are completely non-polar in nature, they have been chemically modified via grafting of acrylic acid (AA) and sulfonation to impart polarity onto these elastomers. The effects of these polar AA modified or sulfonated POE_{16} / PBE_{16} in different concentrations in the PA_6/ (POE_{16}/PBE_{16}) blends of various compositions have been investigated in detail. Impact strength has also been reported in the case of the blend compositions containing high PA_6 for practical reasons. The physico-mechanical properties have been explained with the help of structural aspects of the blends, as investigated through X-ray diffraction, differential scanning Calorimetry, dynamic mechanical thermal analysis and scanning electron microscopy. Uncompatibilized blend of nylon 6/POE appears as physically immiscible blend, Better inter-phase dispersion aided by AA grafted POE supports efficient stress transfer among phases and causes almost two fold increase in impact resistance i.e. 108 J/m compared to 56 J/m only for the former.

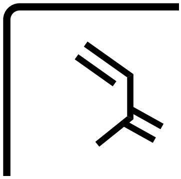
References

1. Krause, S. Macromol Chem Rapid Commun 1972, 17, 251–258.
2. Kunori, T.; Geir, P. H. J Macromol Sci Phys 1980, 18, 135–144.
3. Sperling, L.H. Plymeric Multicomponent Materials, Wiley: New York, 1998, Chap. 1.
4. Simanke, A. G.; Mauler, R. S. Polymer 1999, 40, 5489–5496.

Synthesis of Dual Stimuli-Responsive Disulfide Containing Hyperbranched Polymer by RAFT Polymerization and Formation of Core-Crosslinked Star Polymer Possessing Redox-Responsive Hyperbranched Core

Sunirmal Pal, Soma Mukherjee, Megan R. Hill, and Brent S. Sumerlin*
George & Josephine Butler Polymer Research Laboratory
Center for Macromolecular Science & Engineering, Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611-7200, USA.
sumerlin@chem.ufl.edu

Thermo- and redox-responsive degradable hyperbranched polymers, poly(*N*-isopropylacrylamide-*co*-*N,N´*-bis(acryloyl)cystamin) [P(NIPAM-*co*-BAC)], were prepared by statistical copolymerization of *N*-isopropylacrylamide and *N,N´*-bis(acryloyl)cystamine by reversible addition-fragmentation chain transfer (RAFT) polymerization. These hyperbranched polymers were further used for the synthesis of star copolymers, poly(*N*–isopropylacrylamide-*co*-*N,N´*-bis(acryloyl)cystamin)-*b*-poly(*N,N*-dimethylacrylamide) [P(NIPAM-*co*-BAC)-*b*-PDMA], *via* successive RAFT polymerization with various branching units in the core and with variable arm numbers. The effect of branching units on aggregation diameter and thermo-responsive behavior was investigated by dynamic light scattering (DLS) and UV–Vis spectroscopy. DLS results revealed that the aggregated size of branched polymer at the cloud point (CP) had a positive correlation with average repeat unit of branch. The redox response of the disulfide linkages in the hyperbranched polymers above and below the CP was observed by size-exclusion chromatography (SEC) and DLS. The linear polymer was found by reduction and different morphologies of polymers were observed by oxidation of linear polymers at above and below the CP. The formation of core-crosslinked star polymers above the CP was confirmed by transmission electron microscopy (TEM).



References:

[4] Bapat, A. P.; Ray, J. G.; Savin, D. A. Sumerlin, B. S. Macromolecules **2013**, *46*, 2188–2198.

[5] Vogt, A. P.; Sumerlin, B. S. Soft Matter **2009**, *5*, 2347–2351.

[6] Morimoto, N.; Qiu, X.-P.; Winnik, F¸oise M.; Akiyoshi, K. Macromolecules **2008**, *41*, 5985-5987.

Authors Index