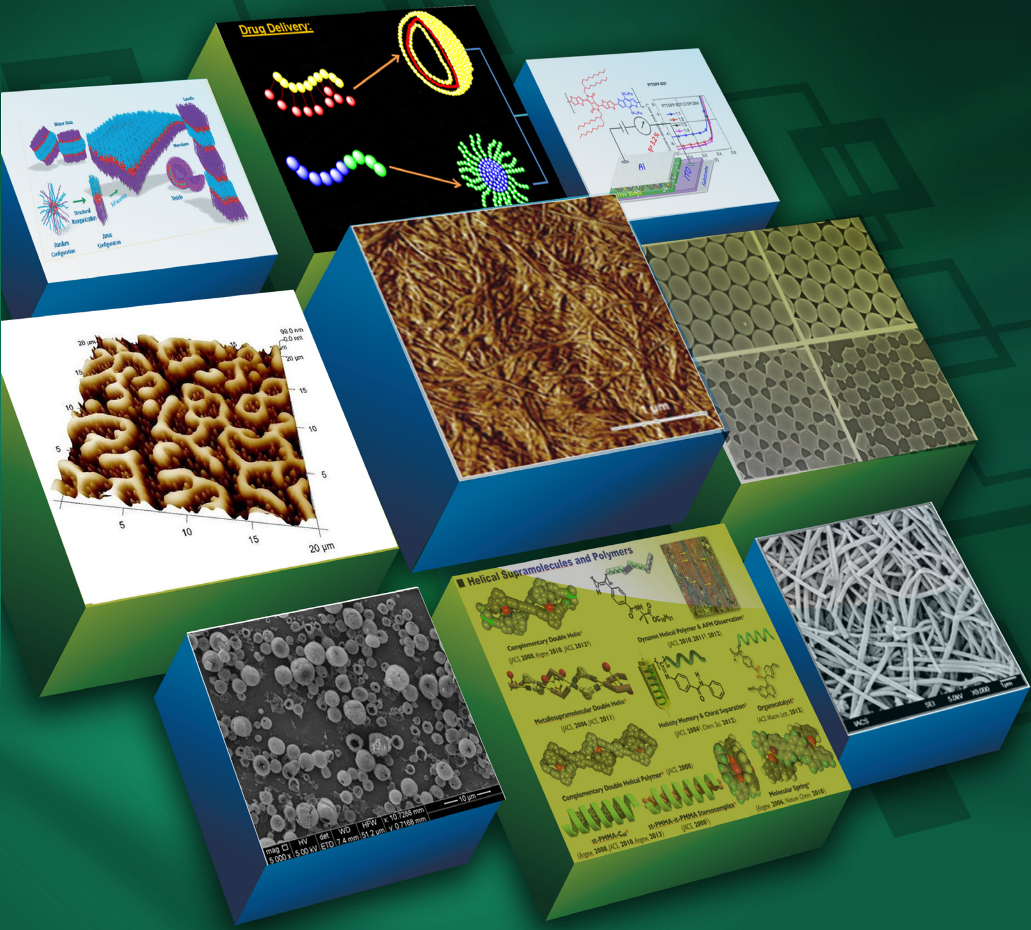
3rd FAPS Polymer Congress and MACRO-2013



May 15-18, 2013
Indian Institute of Science, Bangalore

3rd FAPS Polymer Congress and MACRO-2013

May 15-18, 2013

Abstracts

Indian Institute of Science, Bangalore

Message

We are delighted that the Third Federation of Asian Polymer Societies (FAPS) Polymer Congress is being held in India at Bangalore from May 15 to 18, 2013 and is being hosted by the Indian Institute of Science (IISc) with Prof. S. Ramakrishnan as the General Secretary. This Congress is being jointly hosted along with the Twelfth National Meeting of the Society of Polymer Science (India) (SPS-I), which is one of the Founder Members of the FAPS. SPS (I) is sponsoring this Congress along with the Polymer Processing Academy.

The scientific programme covering diverse areas of polymer science appears very exciting. We also observe that there are many distinguished speakers from overseas who have travelled long distances to share their perspectives. Thus, the Conference provides an excellent platform for interaction between established practitioners of science and young students and faculties, at the beginning of their research career. We compliment the organizers of the Conference for putting together an excellent scientific programme.

The domain of polymer science, like many other branches of science, is in a great state of flux. The character of the discipline is rapidly changing both in industry and academia. Polymer Science should now be considered as an enabling discipline, which creates value to either biology or material science. Consequently, areas such as functional polymers, bio-inspired polymers, and organic polymer hybrids with inorganic materials are assuming greater importance. From an era, when polymers touched our life visibly in every walk of life, polymers are increasingly becoming invisible to us. In the future, polymers will continue to be important in many critical applications, such as, in energy conversion, human health and wellness, water conservation, environmental remediation, and communication, information and entertainment technologies. Consequently, polymer scientists will be increasingly called upon to work with scientists from many other disciplines to create new solutions to meet the needs of the people and the planet.

Polymer Science as a discipline is less than a hundred years old. In this short span *it has traversed a considerable distance and has become a ubiquitous part of our everyday life. However, the future appears even brighter, as the world searches for solutions to some of the most complex problems faced by mankind. This conference, we hope, will add to the knowledge base in this rapidly evolving area.*

We extend a warm welcome to all delegates and wish the 3rd FAPS Polymer Congress and Macro 2013 all the success.

S. Sivaram

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

Professor Ashok Misra,
Chairman, Intellectual Ventures India, Bangalore,
President, Polymer Processing Academy
Council Member, Federation of Asian
Polymer Societies

Preface

It is my pleasure and honor to welcome all the delegates to the 3rd Polymer Congress of the Federation of Asian Polymer Societies (FAPS) and MACRO-2013, which is the biannual national meeting of the Society of Polymer Science-India (SPSI). The Indian Institute of Science is privileged to be able to host this event and my colleagues at the Institute join me in welcoming each one of you to this event.

The Indian Institute of Science is one of the first institutes to be set-up as a public-private partnership initiatives; it was established utilizing a financial grant from J N Tata, founder of the TATA group of companies, and a land-grant from the then Maharaja of Mysore, Shri Krishnaraja Wodeyar IV. The institute of was opened in 1909 with just two departments, one of which was General and Applied Chemistry; this clearly indicated the level of importance and relevance that chemistry was accorded even in the early part of the last century. Today, the institute houses over 40 departments ranging from Aerospace Engineering to Nanoscience and Engineering, and from Ocean and Atmospheric Sciences to Neuroscience. Although, the institute was initially started as a postgraduate institution granting only advanced degrees, two years ago, after celebrating its centenary, the institute pioneered a 4-year undergraduate (BS) program, in an effort to embed young bright minds, just out of high school, into a research environment. The institute takes great pride that a large number of the pioneers of Indian Science have either been educated here or have taught here before taking up leadership positions elsewhere in the country to initiate and foster the growth of various key disciplines, such as atomic energy, defense and space research. Apart from these academic attributes, the institute is also housed in 400 acres of what appears to be an oasis within the rapidly developing concretized city of Bangalore; so do take time to walk around or cycle within our campus and enjoy its serene natural beauty.

A couple of years ago during the FAPS Council meeting in China, when it was confirmed that India will host the 3rd FAPS Polymer Congress, and I was asked to organize it at the Indian Institute of Science, Bangalore, it was with some trepidation that I accepted. However, the task of organizing this meeting was made a lot easier because of the outstanding commitment and support of the institute administration, my young colleagues and students, all of whom spent enormous amounts of their time in helping me organize this event. The academic program *for the eight thematic sessions was ably put together with the help of my colleagues from various institutes within the country and abroad; I am deeply grateful for their unwavering commitment to the task, which was key enabler to bring together a program that exemplifies the beauty and range of polymer science, as practiced today. Finally, and most importantly, several industries generously came forward to sponsor this event as did our governmental agencies; we are indeed very grateful to all of them for their support without which an event such this would be difficult to conduct. I do hope you enjoy the academic deliberations during the three and half day meeting and wish you all a very pleasant stay in Bangalore.*

Ramakrishnan

S. Ramakrishnan
General Secretary, FAPS-MACRO 2013
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Plenary

Synthesis, Structure and Functions of Biomimetic Helical Polymers and Oligomers

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

Unique macromolecules and oligomers that fold into a preferred-handed single- or double-stranded helical conformation induced by chiral substituents covalently bonded to the main-chains or external chiral stimuli followed by memory of the helical chirality are presented.[1] The direct observations of helical structures of artificial helical polymers 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]

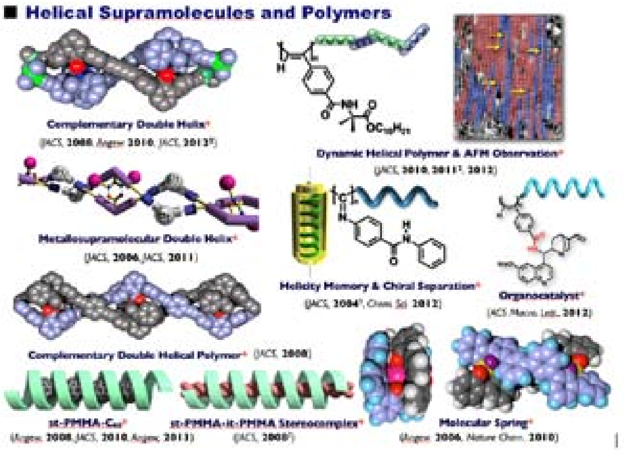


Figure Structures of single- and double-stranded helical polymers and oligomers with specific functions.

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

Shifting Paradigms in Polymer Crystallization

M. Muthukumar*
Polymer Science and Engineering Department
University of Massachusetts
Amherst, MA 01003 USA
e-mail: muthu@polysci.umass.edu

The topological connectivity of polymer chains spontaneously imposes entropic frustrations in their ordering into crystalline states. With a combination of analytical arguments and molecular modeling, buttressed with experimental facts, we have revisited the long-standing problem of polymer crystallization and evaluated the significant role played by conformational entropy of polymer chains. We will focus on (i) the onset of nucleation during the primordial stage of crystallization, (ii) spontaneous selection of finite lamellar thickness in equilibrium, (iii) lamellar growth kinetics, and (iv) spontaneous chiral symmetry breaking in spherulites. The basic concepts of polymer crystallization are applicable also to directional self-assemblies in biological systems, such as amyloids, bacterial walls, and viruses, and the analogies will be briefly mentioned.

Lithography: The Challenge of Forming Precise Structures on the Length Scale of Macromolecules

Christine Ouyang, Yeon Sook Cho, Marie Krysak, Christopher K. Ober*
Materials Science & Engineering, Cornell University, Bard Hall, Ithaca, NY, USA.
* cko3@cornell.edu

One of the great challenges given by advances in microelectronics is the ongoing need to reduce the critical dimensions of semiconductor devices. To make this possible, photolithography has evolved dramatically to the point that it now produces patterns on the length scale of the macromolecules used in photoresists. The result is a host of new approaches to the patterning of polymer systems and the need for precise characterization of their processing and properties. Block copolymers offer a means to resolve this impasse by removing part of the polymer chain to make small patterns, but like any other resist system they have distinct limitations. We have been investigating several block copolymers that have in common a functional, polar block and a readily scissionable block due to their potential for patterning by both bottom-up self-assembly and top-down lithography. A polar block such as poly(4-hydroxystyrene) is capable of exploiting all the photoresist chemistry of advanced photoresists. We have recently shown we can control the self-assembly process by solvent vapor annealing, and by choice of solvent [1]. In addition to self-assembly, approaches using molecular glass and nanoparticle photoresists will also be described [2]. The systems have the advantage that they may be used to produce arbitrarily shaped patterns in contrast to self-assembled materials and show prospects of sub-20 nm structure formation. New tools for thermal processing such as laser spike annealing enable thermal excursions above 500 °C in microsecond time regions and will be discussed [3].

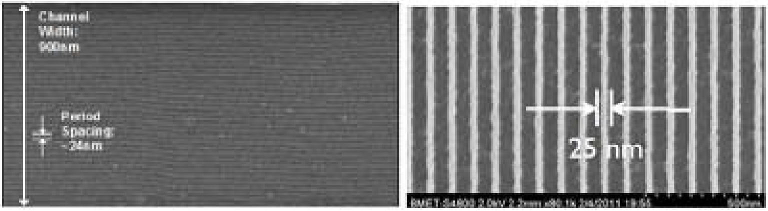


Fig. 1: Small scale features made by (left) self-assembly of block copolymers and (right) direct patterning of nanoparticle photoresists.

References

[1] Bosworth, J.K.; Sha, J.; Black, C.T.; Ober, C.K. ACS Nano, 3(7), (2009) 1761.
[2] Shiu, K.; Curtis, M. D.; Huffmann, J. C. J. Am. Chem. Soc. 118, (1988) 2014.
[3] Trikeriotis, M.; Krysak, M.; Chung, Y.S.; Ouyang, C.; Cardineau, B.; Brainard, R.; Ober, C.K.; Giannelis E.P.; Cho, K. Journal of Photopolymer Science and Technology, 25(5), (2012) 583.
[4] Jung, B.; Sha, J.; Paredes, F.; Chandhok, M.; Younkin, T.; Wiesner, U.; Ober, C.K.; Thompson, M., ACS Nano, 6(7), (2012) 5830-5836.

LbL Assemblies Using Weak Interaction and Their Application

Mitsuru Akashi*
Department of Applied Chemistry, Graduate School of Engineering, Osaka University
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
E-mail: akashi@chem.eng.osaka-u.ac.jp

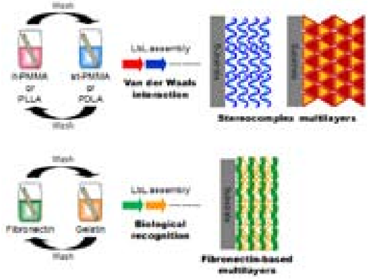


Figure 1. Schematic illustration of the LbL assemblies using van der Waals interactions and biological recognition [7].

The design and control of substrate surfaces with nanometer- or micrometer-sized polymer films are of considerable interest for both fundamental and applied studies in the biomedical field because of the required surface properties. The layer-by-layer (LbL) technique was discovered in 1991 by Decher and co-workers for the fabrication of polymer multilayers constructed mainly through electrostatic interaction [1]. We have extended the scope and applicability of this LbL assembly by introducing molecularly regular conformations of polymers or proteins by employing for the first time weak interactions, such as der Waals interactions [2] and biological recognition [3] (Figure 1). Since these weak interactions are the sum of the attractive or repulsive forces between parts of the same molecule, they allow macromolecules to be easily arranged into the most stable conformation in LbL film. We have achieved stereocomplex LbL formations of stereoregular polymers and their application for stereospecific template polymerization and nanomaterials using methacrylic acid (MAA) and methyl methacrylate (MAA) [4,5]. We have also reported for the first time extracellular matrix (ECM) multilayers focused on fibronectin (FN) using biologically specific recognition. By using the ECM multilayers, three-dimensional (3D) cellular multilayers could be developed to apply for tissue engineering and pharmaceutical application [6].

Nanometer-Sized ECM films for 3D-Human Tissue Models

We have developed a simple and unique bottom-up approach, hierarchical cell manipulation technique, using nanometer-sized LbL films consisting of fibronectin and gelatin (FN-G) as a nano-ECM [3]. The FN-G nanofilms were prepared directly on the cell surface, and we discovered that at least 6 nm thick FN-G films acted as a stable adhesive surface for adhesion of the second cell layer. The multilayered constructs like a blood vessel wall structure indicated almost the same drug response as in vivo natural blood vessel, suggesting the possibility to use as an in vitro blood vessel model to analyze drug response [6b]. Recently, we also developed a rapid bottom-up approach, cell-accumulation technique, by a single cell coating using FN-G nanofilms, because the fabrication of two-layers (2L) was limitation through the above technique due to the time required for stable cell adhesion [6a]. This rapid approach easily provided approximately ten to twenty-layered (over 100 μm) 3D-tissues after only one day of incubation. Moreover, fully and homogeneously vascularized tissues of 1 cm width and 100 μm height were obtained by a sandwich culture of the endothelial cells. These hierarchical cell manipulations will be promising to achieve one of the dreams of biomedical field, in vitro creation of artificial 3D-tissue models [8].

References

[1] Decher, G. Science 1997, 277, 1232.
[2] a) Serizawa, T., Hamada, K., Kitayama, T., Fujimoto, N., Hatada, K., Akashi, M. J. Am. Chem. Soc. 2000, 122, 1891; b) Serizawa, T., Yamashita, H., Fujiwara, T., Kimura, Y., Akashi, M. Macromolecules 2001, 34, 1996.
[3] Matsusaki, M., Kadowaki, K., Nakahara, Y., Akashi, M. Angew. Chem. Int. Ed. 2007, 46, 4689.
[4] a) Serizawa, T., Hamada, K., Akashi, M. Nature 2004, 429, 52; b) Akagi, T., Fujiwara, T., Akashi, M. Angew. Chem. Int. Ed. 2012, 51, 5493.
[5] a) Kida, T., Mouri, M., Akashi, M. Angew. Chem. Int. Ed. 2006, 45, 7534; b) Kondo, K., Kida, T., Ogawa, Y., Arikawa, Y., Akashi, M. J. Am. Chem. Soc. 2010, 132, 8236.
[6] a) Nishiguchi, A., Yoshida, H., Matsusaki, M., Akashi, M. Adv. Mater. 2011, 23, 3506; b) Matsusaki, M., Amemori, S., Kadowaki, K., Akashi, M. Angew. Chem. Int. Ed. 2011, 50, 7557; c) Matsusaki, M., Sakaue, K., Kadowaki, K., Akashi, M. Adv. Healthcare Mater. 2013, 2, 534; d) Chetprayoon, P., Kadowaki, K., Matsusaki, M., Akashi, M. Acta Biomaterialia, 2012, 9, 4698.
[7] Matsusaki, M., Ajiro, H., Kida, T., Serizawa, T., Akashi, M. Adv. Mater. 2012, 24, 454;
[8] Matsusaki, M. Bull. Chem. Soc. Jpn. 2012, 85, 401.

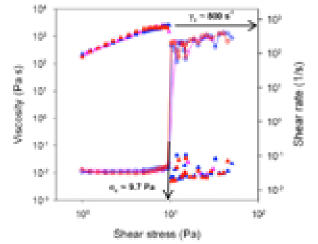
Smart Polymer Hydrogels: Thermodynamics and Rheology

Ashish Lele*[,a], Shyni Varghese[b], M. V. Badiger[a], R A Mashelkar[a], Prakash Wadgaonkar[a], Aarti Shedge[c],
Indravadan Parmar[a]
[a]Polymer Science and Engineering Division, National Chemical Laboratory, Pune – 411 008 INDIA
[b]Department of Bioengineering, University of California at San Diego, La Jolla CA 92093-0412, USA.
[c]Polymeres, Colloids, Interfaces, UMR University du Maine-CNRS 6120, Le Mans, France.
*ak.lele@ncl.res.in

Smart polymer hydrogels are macromolecular networks that respond to external stimuli. The hydrogel networks, which contain osmotically absorbed water, can have infinite (permanent) or finite (transient) lifetime. Gels of the former category are covalently crosslinked and undergo reversible first order volume phase transition in response to stimuli. Gels of the latter category are physically crosslinked and show a sol-gel transition i.e., their rheology changes from being liquid-like to solid-like when subjected to stimuli. Over the last ten years, we have investigated the thermodynamics and rheology of both types of hydrogels with the objective of understanding the underlying molecular mechanisms for their stimuli response.

In the first part of my talk, I will review our earlier work where we have shown that a fine balance of hydrophobic interactions and hydrogen bonding interactions is necessary to effect a first order thermodynamic volume transition in thermoreversible permanent hydrogels [1] {Figure 1(a)}, and that modulating these interactions can enable tailoring the transition temperature of such hydrogels [2]. More recently, we have investigated the rheology of a unique class of transient hydrogels that show an abrupt and large gelation when subjected to a small change in shear stress or temperature [3] {Figure 1(b)}. I will discuss interesting features of the rheological data and deduct mechanistic insights about the sol-gel transition.

Figure 1(a), top: First order volume phase transition of a covalently crosslinked copolymer gel showing swollen state (right, 10°C), collapsed state (left, 12°C) and biphasic state (centre, 11°C).
Figure 1(b), right: Abrupt shear thickening of a semi-dilute solution of associating polymer caused by sol-gel transition at a critical shear stress.



References
[1] Lele, A. K.; Badiger, M. V.; Hirve, M. M.; Mashelkar, R. A. Chem. Eng. Sci., 50 (1995) 3535.
[2] Badiger, M. V.; Lele, A. K.; Bhalerao, V. S.; Varghese, S.; Mashelkar, R. A. J. Chem. Phys., 109 (1998) 1175.
[3] Lele, A. K.; Shedge A. S.; Badiger, M. V.; Wadgaonkar, P. P.; Chasseneiux, C. Macromolecules, 43 (2010) 10055.

Stimuli-Responsive Polymer Films Comprising Molecular and Supramolecular Fluorescence Emitters

Soo Young Park*
Center for Supramolecular Optoelectronic Materials and WCU Hybrid Materials Program, Department of Materials Science and Engineering, Seoul National University, Seoul, 151-744, Korea,
E-mail:parksy@snu.ac.kr

During last decade, we have explored the unique photophysical properties of α-cyanostilbene compounds which significantly differ from those of stilbene or azobenzene chromophores.[1] It was found that α-cyanostilbene moiety is an outstanding supramolecular self-assembly motif to give characteristic nanostructures of various dimensionality when dispersed in a polymer matrix. Most peculiarly, self-assembly of these molecular motif is accompanied by the significant fluorescence modulation. By appropriate molecular design and synthesis, we could demonstrate supramolecular and/or macromolecular systems which can respond to various external stimuli like UV, thermal, chemical, and mechanical signals.[2] Moreover, photochromic fluorescence switching and patterning using different classes of fluorescent/phosphorescent molecular system (ESIPT dyes[3] and Ir(III) complexes[4] dispersed in polymer film, and infinitely coordinated polymer film[5]) will also be introduced in this presentation.

References

[1] An, B.; Gierschner, J; Park, S. Y. Accounts Chem. Res., 45(2012)544.
[2] Yoon, S. J.; Chung, J. W.; Gierschner, J.; Kim, K. S; Choi, M. G.; Kim, D.; Park, S. Y. J. Am. Chem. Soc., 132(2010)13675.
[3] Kwon, J. E.; Park, S. Y. Adv. Mater., 23(2011) 3615.
[4] You, Y.; Park, S. Y. Dalton Trans. (2009) 1267.
[5] You, Y; Yang, H; Chung, J. W.; Kim, J. H.; Jung, Y.; Park, S. Y. Angew. Chem. Int. Ed., 49(2010)3757.

Pre-Banquet Lecture

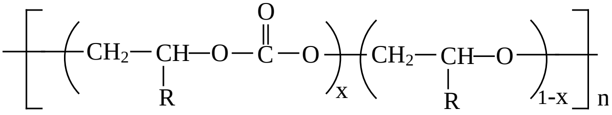
Surendra U. Kulkarni
Research Director & Site Head
SABIC Technology Center, Bangalore

Key Note

Functionalization of CO_2 Based Copolymer

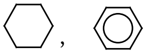
Yusheng Qin, Xianhong Wang*, Fosong Wang
Key lab of Polymer Ecomaterials, Changchun Institute of Applied Chemsitry,
Chinese Academy of Sciences, Changchun 130022, China
Email: xhwang@ciac.jl.cn

Since the pioneering work of Prof. Inoue in 1969[1], fixation of CO_2 into polymer is becoming increasingly attractive worldwide, even many industry activities have been reported[2]. These polymers have the following structure:



$$\left[\left(CH_2-\underset{R}{CH}-O-\overset{O}{\overset{\|}{C}}-O \right)_x \left(CH_2-\underset{R}{CH}-O \right)_{1-x} \right]_n$$

R=H, CH_3,



Where x is above 0.95, n is an integer generally above 10.

Catalyst design, especially for high selectivity and high activity catalyst, is always considered as key issue, however, if CO2 tries to be practical monomer for polymer industry, harsh challenges exist, which may even finally inverse the tendency and prohibit the dream to come into true. The obvious challenges are: 1) Most active catalysts contain toxic heavy metals, which is not suitable for the strict standard related to biodegradable polymers. 2) Most CO_2 based copolymers are hydrophobic having weak polarity, exhibiting low impact strength and narrow application temperature window, modification of CO_2 based copolymers are difficult, or leading to high cost. In this talk, we would like to show our continuing effort to make CO_2 an economically viable raw material for polymer industry, focusing on functionalization of CO_2 and propylene oxide copolymer, especially on hydrophilic CO_2 based copolymer, while another possibility using CO_2 based polyesterether polyol for polyurethane as new toughening agent will also be discussed.

References

[1] S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci. Part B : Polym. Lett.* **1969**, *7*, 287-292.

[2] Y. S. Qin and X. H. Wang, *Biotech. J.* **2010**, *5*, 1164-1180; S. Klaus, M. W. Lehenmeie, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460-1479; L. Gu, Y. G. Gao, Y. S. Qin, X. S. Chen, X. H. Wang, F. S. Wang, J. Poly. Sci., Polym. Chem., 2013, 51, 282-289.

Tailored polymeric structures

Invited Talk

A Single Component Inimer Containing Cross-linkable Polymer Coating for Dense Polymer Brush Growth

Padma Gopalan,* Daniel Sweat, Myungwoong Kim
[a]*Department of Materials Science and Engineering, University of Wisconsin-Madison, USA.*

We have developed a highly versatile universal approach to grow polymer brushes from a variety of substrates with high grafting density by using a single-component system. We describe a random copolymer which consists of an inimer, *p*-(2-bromoisobutyloylmethyl)-styrene (BiBMS), copolymerized with glycidyl methacrylate (GMA) synthesized by reversible addition–fragmentation chain-transfer (RAFT) polymerization. Thermal cross-linking created a mat that was stable during long exposure in organic solvent even with sonication or during Soxhlet extraction. The absolute bromine density was determined via X-ray photoelectron spectroscopy (XPS) to be 1.86 ± 0.12 Br atoms/nm^3. Surface-initiated ATRP (SI-ATRP) was used to grow PMMA brushes on the substrate which were characterized by ellipsometry, XPS, and atomic force microscopy (AFM with a grafting density of 0.80 ± 0.06 chains/nm^2. Through the self-assembly of block copolymers on top of the mat, nanopatterned brushes can be grown after selective removal of one domain from the block copolymers. The inimer containing cross-linkable copolymer can be viewed as a single component ultra-thin polymeric coating which can be applied to a range of substrates to grow high chain density polymer brushes by ATRP. The ease of synthesis, chemical tunability, homogeneity of composition, stability in organic solvents and applicability by simple spin-coating to a wide range of substrates makes this a versatile approach to create functionalized interfaces

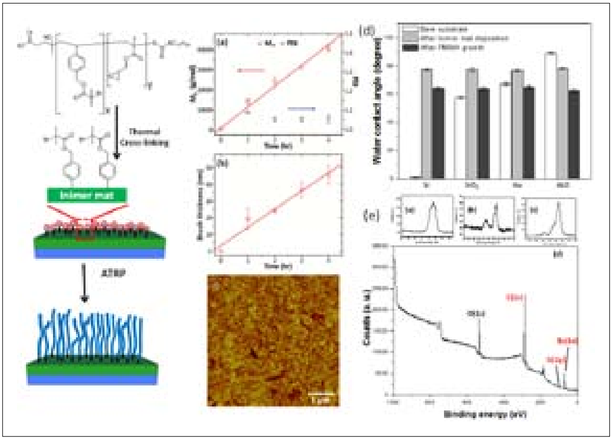


Figure 1. Schematic illustration of the process for the formation of the inimer mat and the brush growth along with the plots showing (a) M_n and PDI of the PMMA grown in solution as a function of polymerization time during SI-ATRP of MMA, (b) the linear increase in brush thickness as a function of time, and (c) AFM image of brushes grown from mat. Static water contact angles for various substrates before inimer mat formation, after cross-linking and after growth of PMMA brushes remain constant. XPS spectra of the inimer mat showing: (a) Br(3d), (b) Si(2p), (c) C(1s), (d) survey, scan allows quantification of initiator density.

References

[1] Sweat, D. P., Kim, M., Xiang, Y., Gopalan, P. *Langmuir* **2013 DOI:** 10.1021/la305060z

Synthesis and Self-assembling Peptide-Polymer Conjugates: Nanostructural Tailoring

Tapas K. Paira, Sanjib Banerjee, Anupam Saha and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032 INDIA
** E-mail: psutkm@iacs.res.in*

Peptides are nature's building blocks with precise chemical structures and diverse functionalities. Upon combining to polymers, forming peptide-polymer conjugates, hybridization of natural and synthetic building blocks may lead to materials with features down to the molecular level and contain inherent biocompatibility, self-assembly, physical and chemical properties and may lead to functional biomolecular materials with potential applications in various fields such catalyst, biocompatible implants and tissue engineering. I will discuss several recent developments of diverse synthetic routes of peptide-polymer conjugates in our laboratory. One of such conjugate containing poly(methacrylate)s and sequence-defined peptides is prepared by atom transfer radical polymerization (ATRP). A 'grafting from' ring-opening polymerization (ROP) techniques is used to prepare bio-compatible/biodegradable peptide-polyester hybrids. The synthesis of a new type of conjugate, poly(methyl methacrylate)-*b*-polytyrosine (PMMA-b-Ptyr) block copolymer using a combination of ATRP, "click" chemistry and ROP of tyrosine N-carboxyanhydride will be discussed. The successful synthesis of a new kind of amphiphile consisting of poly(ethylene glycol)-peptide-poly(ethylene glycol) (PEG-pep-PEG) hybrid having a hydrophobic fluorophore moiety using 'grafting to' technique will also be discussed. Finally, a convenient and green approach will be described for the synthesis of a L-lysine based zwitterionic polymer {poly-ε-L-lysinyl acrylamide) (PLAM)}, without using complex chemistries and tedious purification procedure in water as the reaction media. This is followed by discussing solution self-assembly of these as-synthesized peptide-polymer conjugates into materials with nanoscale morphologies.

End Functional Polymers and Miktoarm Copolymers by Controlled Polymerization Methods

Prakash P. Wadgaonkar
Polymers and Advanced Materials Laboratory, Polymer Science and Engineering Division,
National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India.
Email: pp.wadgaonkar@ncl.res.in
Tel: +91-20-25902306; Fax: +91-20-25902615

End-functional polymers and miktoarm copolymers are of great interest as they find applications as precursors to block copolymers and as rheology modifiers, respectively. End-functional polymers and miktoarm copolymers could be prepared using different techniques such as anionic and cationic polymerizations but due to stringent reaction conditions and some limitations associated with these techniques, polymer chemists have shifted their interest in recent times to controlled radical polymerization methods such as RAFT, NMP and ATRP. Of these techniques, ATRP is a robust and versatile synthetic technique which allows preparation of molecular brushes, stars, block copolymers, and end functional polymers with high chain end fidelity and precisely controlled structures.

We have designed and synthesized several new functional group containing ATRP and ROP initiators and multifunctional initiator cores possessing different types and specific number of initiating site for preparation of miktoarm copolymers. Commercially available 4, 4′-bis (4-hydroxyphenyl) pentanoic acid, which in turn is derived from levulenic acid –a platform chemical obtained from biomass- and 5-hydroxy isophthalic acid were used as the starting materials. Both 4, 4′-bis (4-hydroxyphenyl) pentanoic acid and 5-hydroxy isophthalic acid contain phenolic and acid groups which were effectively utilized in various aspects of chemical transformations for synthesis of the desired initiators. New initiators for ROP and ATRP containing various functional groups such as allyloxy, aldehyde, propargyloxy, and azido were designed and synthesized. These functionalized initiators were utilized for synthesis of end-functional polymers. The MFI-cores were designed and synthesized using simple organic transformations and utilized to obtain miktoarm copolymers (A_2B, AB_2, A_2B_2 and A_3B) *via* combination of suitable polymerization techniques. [1-4]

References:

[1] P. S. Sane, B. V. Tawade, I. A. Parmar, S. Kumari, S. Nagane, P. P. Wadgaonkar; *J. Polym. Sci. Part- A Polym Chem,* **2013**, 51, 2091
[2] P. S. Sane, B. V. Tawade, D. V. Palaskar, S. K. Menon, P. P. Wadgaonkar; *React and Funct polym*, ***2012***, *72,* 713
[3] P. S. Sane, D. V. Palaskar, P. P. Wadgaonkar; *Eur Polym J,* **2011**, 47, 1621
[4] D. V. Palaskar, P. S. Sane, P. P. Wadgaonkar; *React and Funct Polym***, 2010**,70, 931

Multicomponent Polymerization for New Polymer Synthesis

Xin-Xing Deng, Lei Li, Yao-Zong Wang, An Lv, Fu-Sheng Du, Zi-Chen Li
Key Laboratory of Polymer Chemistry & Physics of Ministry of Education,
Department of Polymer Science & Engineering, College of Chemistry,
Peking University, Beijing 100871, CHINA

Isocyanide based multicomponent reactions (IMCRs) are very efficient atom-economical reactions that can assemble three or more different components into one molecule in a one-pot process, and have therefore been playing important roles in many fields.[1,2] Among the IMCRs, Passerini reaction, a three component reaction first described in 1921, has been proved to be a powerful synthetic method that can yield an ester-amide linkage from a carboxylic acid, an aldehyde and an isocyanide (**Figure 1**). [1,2] It is thus quite advantageous to use this reaction to prepare polymers with different architectures and functional groups in a very efficient and straightforward way. Unfortunately, this highly efficient reaction has been overlooked for a long time in polymer synthesis; only until quite recently, synthesis of polyesters by this reaction has been reported. [3] We extended the scope of Passerini reaction in polymer science as a multicomponent polymerization method. In this talk, I will describe several synthetic approaches to different functional polymers based on Passerini reaction. This will include linear poly(ester-amide), [4] polyamides, [5] star polymers, [6] graft copolymers, photo-degradable polymers as well as multi-block copolymers containing segments with poly(ester-amide)main chains with ordered sequences (**Figure 2**).

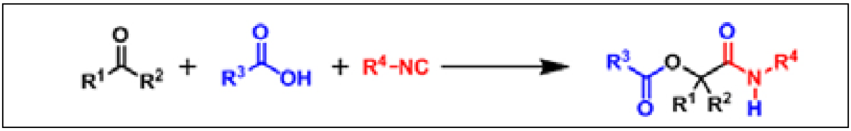


Figure 1. General Passerini reaction

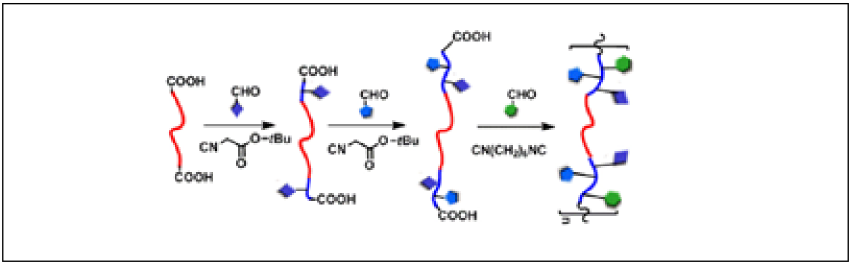


Figure 2. General synthetic procedure for multi-block copolymer sysnthesis

References:
[1]. Zhu, J., Bienayme, H., Eds., *Multicomponent Reactions*, Wiley-VCH, Weinheim, 2005.
[2]. A. Domling, *Chem. Rev.*, **2006**, *106*, 17.
[3]. O. Kreye, T. Toth and M. A. R. Meier, *J. Am. Chem. Soc.*, **2011**, *133*, 1790.
[4]. X. X. Deng, L. Li, Z. L. Li, A. Lv, F. S. Du, Z. C. Li, *ACS Macro Letters* **2012**, 1300.
[5]. Y. Z. Wang, X. X. Deng, L. Li, Z. L. Li, F. S. Du, Z. C. Li, *Polym. Chem.* **2013**, *4*, 444.
[6]. L. Li, X. W. Kan, X. X. Deng, C. C. Song, F. S. Du, Z. C. Li, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 865.

Tailored Hybrid Nanostructures of Polybenzimidazole for PEM Fuel Cell

Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad 500 046, INDIA
** E-mail: tjsc@uohyd.ernet.in ; tjscuoh@gmail.com*

Motivation of the current studies comes from the fact that despite the myriad studies on polybenzimidazole (PBI) based proton exchange membranes (PEM) for fuel cell operating above 100°C, the development of membranes with higher proton conductivity without compromising mechanical stability has continued to be the prime challenge. Our group has developed and been working on several strategies to address this key challenge. Briefly our approaches are: (1) synthesis of tailor made PBI structures, (2) development of a novel fabrication process called *'Gel Process'*, (3) blending of PBI with suitable polymers, and (4) formation of PBI hybrid nanostructures/nanocomposites with inorganic fillers [1-3].

In this presentation, I wish to share our recent contributions towards the development of PEM membranes designed from tailor made organic/inorganic hybrid PBI nanostructures. Nanostructures of polymers with inorganic fillers e.g. clays, silica etc. have attracted great interests because of remarkable improvement in properties. A judicious choice of polymer structure and functionality along with inorganics structures are the key factors to have favourable interactions which yield to nanocomposites. In this presentation, I wish to highlight the preparations, structures and properties of oxy-polybenzimidazole (OPBI), a heterocyclic polymer with ether linkage in the backbone, nanocomposites with varieties of clays and silica particles. Structurally different clays and nano sized silica particles have been used after appropriate organic modifications which induce the compatibility of these inorganic fillers with the PBI/OPBI. We observed that the structure of the inorganics dictates the nanocomposites structures and hence the properties. Newly developed organic/inorganic hybrid nanostructure membranes displayed very high proton conducting behaviour at 160°C and remarkably high thermal, mechanical, and oxidative stabilities.

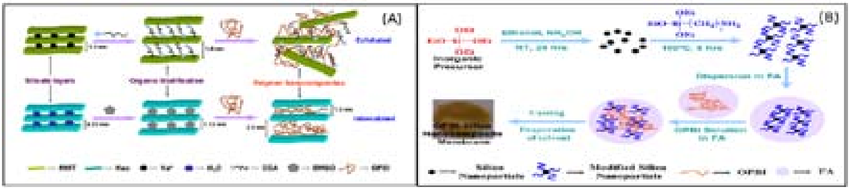


Figure 1. OPBI nanocomposites with clays (A) and surface modified silica (B)

Acknowledgement: We gratefully acknowledge financial support by DST, India

References

[1] Ghosh, S.; Maity, S.; Jana, T. *J. Mater. Chem.*, 21 **(2011)** 14897.
[2] Ghosh, S.; Sannigrahi, A.; Maity, S.; Jana, T. *J. Phys. Chem. C*, 115 **(2011)** 11474.
[3] Hazarika, M.; Jana, T. *ACS Appl. Mater. Interfaces*, 4 **(2012)** 5256.

Design of Novel Polymeric Materials for Biomolecular Immobilization

Amitav Sanyal*
Department of Chemistry, Bogazici University, Bebek 34342, Istanbul, Turkey
amitav.sanyal@boun.edu.tr

Reactive polymers are indispensible building blocks for fabrication of novel platforms for biomolecular immobilizations since they can be designed to accommodate a high density and wide variety of functional groups. Over the past few years our research has focussed on the design of novel polymeric platforms that allow efficient biomolecular immobilization in a tailored manner [1]. We have aimed to design polymeric materials that would allow one to attain spatial and temporal control in immobilization. As one of the approaches, we have utilized the Diels-Alder cycloaddition-cycloreversion based strategy to access polymeric materials containing thiol-reactive maleimide groups [2]. Maleimide is well known to participate in polymerization reactions; hence, the electron deficient alkene needs to be protected during polymerization. A Diels-Alder reaction between maleimide and furan is utilized to mask the reactive double bond. After the fabrication of polymeric materials, the maleimide group is unmasked to expose the thiol reactive alkene unit. A combination of synthetic reactions with fabrication strategies can be used to obtain three-dimensional reactive polymeric structures with micron and sub-micron features. As an alternative approach, we have expanded the strategy to include other reactive functional groups such as dienes and alkenes to obtain polymeric materials that can be easily decorated with (bio)molecules [3,4]. Utilization of these building blocks does not involve protection-deprotection steps. Furthermore, using a diene or dienophile containing polymer allows fabrication of surfaces that allow release of conjugated molecules upon heating. Reversible attachment and detachment of appropriate molecules can be done several times without damaging the polymeric surface. The presentation will disclose several metal-free conjugation strategies for immobilization of biomolecules on various polymeric platforms in a reversible or non-reversible manner.

References:

[1] Kosif, I.; Park, E. J.; Sanyal, R.; Sanyal, A. *Macrmolecules* 43 (**2010)** 4140.
[2] Sanyal, A. *Macromol. Chem. Phys.* 211 (**2010**) 1417.
[3] Gevrek, T. N.; Ozdeslik, R. N.; Sahin, G. S.; Yesilbag, G.; Mutlu, S.; Sanyal, A. *Macromol. Chem. Phys.* 14 (**2012**) 166.
[4] Yilmaz, I. I.; Arslan, M.; Sanyal, A. *Macromol. Rapid Commun.* 33 (**2012**) 856.

What Do We Learn from the Materials Science of DNA –First Examples of High Temperature Organic Ferromagnets

Young-Wan Kwon, Jung-Il Jin
KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Korea
Phone : +82-2-3290-4045, Fax : +82-2-921-0688, E-mail : jijin@korea.ac.kr

Materials Science of DNA is in its infant stage although DNA has been enjoying for the past 60 years the pivotal importance in bioscience and biotechnology. Their unique structural and functional characteristics, however, are teaching us that DNAs can be extremely useful materials that can be advantageously utilized in self-assembly, molecular recognition, molecular wire, formation of metal nanoparticles, optics and optoelectronics, and organic molecular magnets.

This presentation consists of three main parts. In the first part, optical and optoelectronic properties of natural and modified DNAs will be discussed. DNA can be chemically modified in various ways to produce versatile materials that can be more easily handled when compared with natural ones. Natural DNAs are water soluble and natural counter ions of DNA phosphate anions are sodium ions (Na^+). If the sodium ions are replaced with long alkyl quaternary onium ions, such as ammonium ions, DNA becomes soluble in common organic solvents and is able to form high quality films. We employed long alkyl ammonium ions containing various terminal functional groups in the alkyl chains in order to render useful optical or optoelectronic properties. Carbazole, styrylpyrene, and chalcone groups[1-4] are representative examples. We studied fluorescence, this film transistor, and light-emitting diodes properties of such modified DNAs.

In the second part, magnetic properties of natural and modified DNAs[5] will be discussed. Especially, the room temperature ferromagnetism of metal-complexed DNAs and DNAs intercalated with stable organic free radicals will be discussed. Detailed studies of their electron paramagnetic resonance and magnetization were made by EPR spectroscopy and SQUID magnetization measurement.

In the last part, utilization of organic discotic liquid crystals as mimics of DNA in the development of high temperature ferromagnetic compositions[6] will be discussed. Discotic LCs (DLCs) are composed of columns of stacked, flat disc-like molecules. When we mixed DLCs with low levels of iron(III) phthalocyanine or stable organic free radicals, the composites were found to be ferromagnetic even at room or higher temperatures.

We also are studying the magnetic properties of polyconjugated polymers doped with paramagnetic dopants. Preliminary report on the results will be included in this presentation.

These findings open a new approach in developing high temperatures, organic ferromagnetic compositions that should be able to find applications in modern magnetic data storage and display devices.

[1] U. -R. Lee, J. -E. Lee, M. -J. Cho, K. -H. Kim, Y. -W. Kwon, J. -I. Jin, and D. -H. Choi, *J. Polym. Sci. A: Polym. Chem.*, 2009, **47(20)**, 5416–5425.
[2] D.-H. Choi et al., J. Polym. Sci. Part A : Polym. Chem., 2010, **48**, 1913- 1918
[3] D.-H. Choi et al., Appl. Phys. Lett., 2010, **96**, 103307
[4] D.-H. Choi et al., Polymer, 2008, **49**, 5417-5423
[5] Y. -W. Kwon, C. H. Lee, D. -H. Choi, and J. -I. Jin, *J. Mater. Chem.*, 2009, **19**, 1353-1380.
[6] C. H. Lee, Y. -W. Kwon, D. -H. Choi, Y. H. Geerts, E. -K. Koh, J. -I. Jin, *Adv. Mater.*, 2010, **22(39)**, 4405–4409.

Polymer Nanocomposites for Electromagnetic Interference (EMI) Shielding Applications

Veena Choudhary
Centre For Polymer Science and Engineering, Indian Institute of Technology, Delhi
Hauz Khas, New Delhi 10016, India

Electromagnetic interference [EMI] refers to disturbances caused by electromagnetic radiation that arises due to mobility of charged particles in electronic devices. EMI is undesirable because it interrupts, obstructs and limits the effective performance of electronics and electrical equipment [1]. Some well known examples include interference withn TV signals, mobile phone communication difficulties as well as degradation and loss of data. [2-4] However, EMI is ubiquitous due to the rapid proliferation of electronic devices such as computers and cellular phones. Depending on the intensity and frequency of radiation, EMI may also adversely affect human health causing cancer, reproductive malfunction, cataracts and changes in behaviour and development of children having thinner skulls and rapidly dividing cells [5,6]. Effective EMI shielding is important for the protection of public health. Hence, continued efforts have been made over the past two decades to reduce EMI using a number of strategies and variety of materials including metals, carbon based materials, conducting polymers, dielectric/magnetic materials [7-15]. These studies clearly showed that no single material can take care of all the aspects of shield e.g. strength, weight, cost, processability, level of shielding and stability under wide variety of environmental conditions. The discovery of various nanomaterials and their unique properties have been exploited to develop materials for shielding applications. Polymer nanocomposites have attracted enormous world-wide attention due to their light weight, flexibility of design and acceptance of wide variety of fillers[16-17]. This lecture will discuss the basics of EMI shielding/microwave absorption, techniques for the measurement of shielding effectiveness and potential materials for EMI shielding applications. The work carried out in our laboratories on polymer nanocomposites based on thermoplastic/thermosetting resins as matrix and carbon nanotubes (CNTs), graphene, dielectric ($BaTiO_3$, TiO_2 etc.) or magnetic (γ-Fe_2O_3, Fe_3O_4, $BaFe_{12}O_{19}$ etc.) materials as fillers will be highlighted in this lecture.

References:

[1] Huang, J.C., Advances in Polymer Technology 1995 14, 137
[2] Al-Saleh,M.H.; Sundararaj,U.; Carbon 2009, 47, 1738
[3] Regev,O.; Elkati,P.N.B.; Loos,J.; Koning, C.E. Advanced Materials 2004, 16, 248
[4] Yang, Y.; Gupta Mool, C.; Dudley Kenneth,L.; Lawrence Roland,W. Nano letters 2005, 5 2131
[5] Boice John,D. Jr.; Tarone Robers,E., Journal of the National Cancer Institute, 2011, 103, 1211
[6] Augner,C.; Gnambs,T.; Winker,R.; Barth,A. Science of the Total Environment, 2012, 424, 1
[7] Joo, J. and Epstein, A.J., Appl. Phys. Lett., 1994, 65, 2278.
[8] Colaneri, N.F. and Shacklett, L.W., IEEE Trans. Instrum. Meas., 1992, 41, 291.
[9] Schulz, R.B., Plantz, V.C. and Brush, D.R., IEEE Trans 1988, 30, 187.
[10] Saini, P., Choudhary, V., Sood, K.N. and Dhawan, S.K., J. Appl. Polym. Sci. 2009, 113, 3146.
[11] Saini, P., Choudhary, V., Singh, B.P., Mathur, R.B. and Dhawan, S.K., Mater. Chem. Phys. 2009, 113, 919.
[12] Saini, P., Choudhary, V. and Dhawan, S.K., Polym. Advn. Technol. 2010, 21, 1.
[13] Singh, P., Babbar, V.K., Razdan, A., Srivastava, S.L. and Goel, T.C., Mater. Sci. Eng. B 2000, 78, 70.
[14] Singh, P.; Babbar, V. K., Razdan, A., Srivastava, S.L. and Goel, T. C., Mater. Sci. Eng. B 1999, 67, 132.
[15] Ajayan, P.M., Stephan, O., Colliex, C. and Trauth, D., Science 1994, 265, 1212.
[16] Rozenberga, B.A., and Tenn, R., Prog. Polym. Sci. 2008, 33, 40.
[17] Alexandre, M., Dubois, P., Mater. Sci. Engg., R: Rev. 2000, 28, 1.

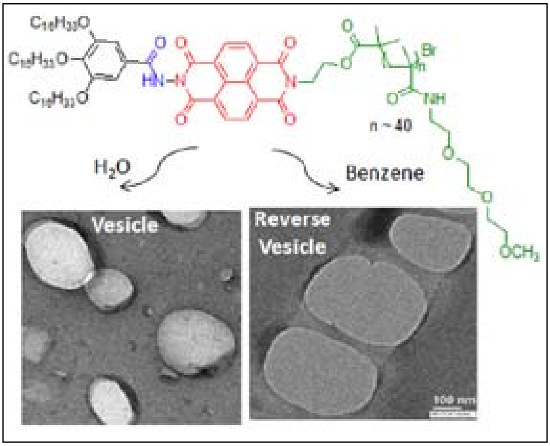
Luminescent Invertible Polymersome by Naphthalene-Diimide (NDI)-end-Functionalized Amphiphilic Polymer

Anindita Das and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the Cultivation of Science, Kolkata, INDIA-70032
** psusg2@iacs.res.in*

Over the last three decades, wealth of knowledge has been developed in the area of supramolecular-assembly and photophysical properties of various pi-conjugated chromophores. In parallel self-assembly of amphiphilic block copolymers has been probably the most celebrated topic of research among polymer chemists and even beyond owing to very high relevance in many areas including biology and materials science. Surprisingly even in this era of various exciting hybrid materials (polymer-peptide conjugates, polymer-protein conjugates, inorganic-organic hybrid materials) too little is known regarding impact of specific supramolecular interactions in a suitably designed pi-conjugated chromophore in terms of dictating structure formation of an amphiphilic macromolecular system.

In recent past we have synthesized a novel chromophore-conjugated macromolecular amphiphilic system consisting of a trialkoxy-benzhydrazide functionalized naphthalene-diimide (NDI) building block at the chain end of a water soluble non-ionic polymer. It shows vesicle and reverse vesicle assembly in water and oil, respectively, with bunch of interesting features such as aggregation-induced enhanced emission, excellent container property for both hydrophobic and hydrophilic dye, remarkable thermal and kinetic stability.

Supramolecular design criteria, self-assembly studies and future implications of this novel polymeric structure will be included in this presentation.



References

[1] Das, A.; Ghosh. S. *Revised Manuscript submitted.*

Photoinduced Deformation Behavior of Polymeric Colloidal Crystals

Mun Ho Kim, Jong-Jin Lee, Doo-Jin Byun, Kil-Yeong Choi*
Reliability Assessment Center for Chemical Materials, Korea Research Institute of Chemical Technology,
141 Gajeong-ro, Yuseong-gu, Daejeon 305-600, Republic of Korea
(kychoi@krict.re.kr)

Since most polymers are not inherently stable to light, their photochemical behavior remains a subject of constant interest. In this study, we investigated the photoinduced deformation behavior of polymeric colloidal crystal films. At first, three-dimensional (3D) colloidal photonic crystals was prepared and exposed to a light with a relatively low ultraviolet energy that closely mimics natural sunlight. As a consequence of photochemical reactions containing chain-scission, photoaging induced morphological changes in the film surface including changes in the size, surface roughness, shape, and packing structure of PS particles. These structural modifications came about the deterioration of optical properties (photonic bandgap) during photoaging. Based on our results and observations, a plausible correlation between the evolutions of the optical properties and the structural modifications during photoaging was established. Finally, the compositional modifications of the surface based on oxygen incorporation behavior caused by the photooxidation process are discussed based.

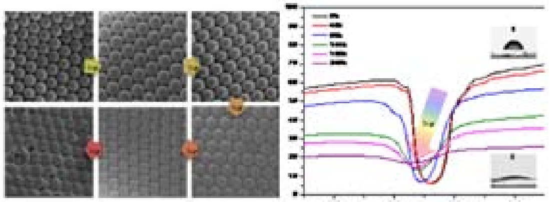


Figure 1. SEM images of 3D colloidal crystals before and after photoaging, and their transmittance spectra.

As a second approach, we investigated the photo-induced deformation behavior of a polymeric colloidal monolayer with interparticle bridges. A PS colloidal monolayer with interparticle bridges was prepared and exposed to the UV light. As a consequence of photochemical reactions containing chain-scission, UV irradiation induced morphological changes in the monolayer surface including changes in the size, shape, and packing structure of PS particles. By manipulating the UV irradiation time, fine tuning of size and shape of the interstice in the monolayer was achieved. In these procedures, the interparticle bridges play an important role. Finally, the compositional modifications of the surface based on oxygen incorporation behavior caused by the photooxidation process were discussed and a plausible photochemical reaction mechanism was proposed.

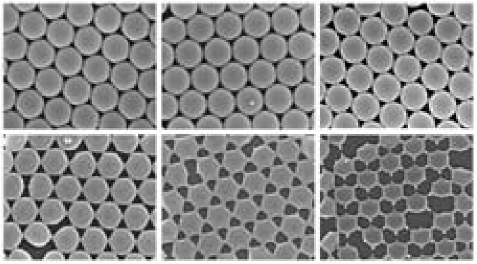


Figure 2. SEM images of PS colloidal monolayers before and after UV irradiation

We believe that these results would give a fundamental guideline for the application of polymeric colloidal crystals.

References

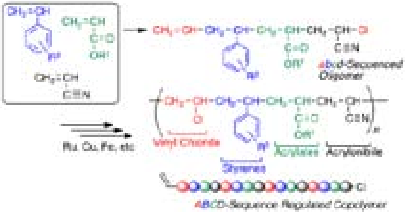
[1] Kim, M. H.; Lee, J. J.; Byun, D. J.; Choi, K. Y. *Journal of Colloid and Interface Science*, 393 (**2013**) 66.
[2] Kim, M. H.; Lee, J. J.; You, J. E.; Byun, D. J.; Choi, K. Y. *Journal of Colloid and Interface Science*, Submitted.

Transition Metal-Catalyzed Step-Growth and Living Radical Polymerizations for Tailored Polymeric Structures

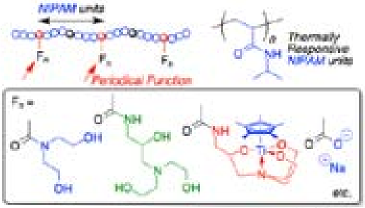
Kotaro Satoh* and Masami Kamigaito
Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

The metal-catalyzed atom transfer radical addition (ATRA or Kharasch reaction) is a highly efficient carbon–carbon bond forming radical reaction. Nowadays, this chemistry is widely applied to radical addition polymerizations of vinyl monomers that developed into the metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP) and to open a new era of precision polymer synthesis [1,2]. Recently, we have found a new class of step-growth radical polymerization of the designed monomer bearing a reactive carbon–halogen bond and an unconjugated carbon–carbon double bond in a single molecule, which is also based on atom transfer radical addition similarly to controlled/living radical polymerization [3].

In this paper, the step-growth radical polymerization was evolved into the two systems for preparing tailaored polymeric structures, i.e., sequence-regulated vinyl copolymer and periodically-functionalized polymer. The former is a novel strategy for preparing sequence-regulated vinyl copolymers by step-polymerization of sequence-regulated vinyl oligomers prepared from common vinyl monomers as building blocks, such as styrene, acrylate, acrylamide, acrylonitrile, and vinyl chloride (Scheme 1) [4,5]. In the later part, the simultaneous chain- and step-growth radical polymerization was investigated by copolymerizing step-growth monomers with common vinyl monomers, i.e., the step-polymerization was simultaneously compatibilized with the metal-catalyzed atom transfer radical polymerization, which resulted in the polymers with periodic functional moeities (Scheme 2) [6,7].



Scheme 1. Synthesis of Sequence-Regulated Vinyl Copolymers by Step-Growth Radical Polymerization.



Scheme 2. Periodically Functionalized Polymer by Simultaneous Chain- & Step-Radical Polymerization.

References:
[1] Kamigaito, M; Ando, T; Sawamoto, M. *Chem. Rev.* 101 (**2001**), 3689.
[2] Satoh, K.; Kamigaito, M.; Sawamoto, M. **2012**. Polymer Science: A Comprehensive Reference, Matyjaszewski, K. Möller, M. eds., vol. 3, pp. 429-461, Elsevier BV, Amsterdam, Netherlands.
[3] Satoh, K.; Mizutani, M.; Kamigaito, M. *Chem. Commun*. 2007, 1260.
[4] Satoh, K.; Ozawa, S.; Mizutani, M.; Nagai, K.; Kamigaito, M. *Nat. Commun*., 1 (**2010)**, 6.
[5] Satoh, K.; Abe, T.; Kamigaito, M. *ACS. Symp. Ser.*, 1100 (**2012**), 133.
[6] Mizutani, M.; Satoh, K.; Kamigaito, M. *J. Am. Chem. Soc.* 132 (**2010**), 7498.
[7] Mizutani, M.; Satoh, K.; Kamigaito, M. *Macromolecules,* 44 (**2011**), 2382.

Supramolecular Comb Polymer Assemblies using Tailored Semiconducting Materials

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

Nanostructured organic semiconductor materials which are also solution processable, has been an ultimate aim in the area of organic and large area electronics. Donor-acceptor block copolymers have the potential to microphase separate and form well-defined arrays which are tens of nanometers in size. But in actual practice, this is seldom achieved due to the poor solubility of the block copolymers and the challenging synthesis involved. In this regard, use of non covalent interaction between a preformed polymer and suitably functionalized organic semiconductor molecules is a novel concept. The talk will elaborate on the methodology adopted in our research group whereby suitably functionalized n type organic semiconductor materials could be organized into lamellar structure in the domain range 5 to 10 nm using the concept of supramolecular assembly with pre formed high molecular weight polymer by simple solution mixing of the two components. Comb polymers were constructed by supramolecular organization of unsymmetrical perylene as well as naphthalene bisimides with Poly(4-vinyl pyridine) (**P4VP)** through non-covalent interaction to form well-defined arrays which were tens of nanometers in size. The advantage of this approach was the ability to retain the crystallinity of the small semiconducting molecule at the same time combine the processability afforded by the polymer.

References

[1] Narayan, R.; Kumar, P.; Narayan, K.S.; Asha, S. K. Adv. Func. Mater.(2012) DOI: 10.1002/adfm.201202366.
[2] Benjamin J. Rancatore, Clayton E. Mauldin, Shih-Huang Tung, Cheng Wang, Alexander Hexemer, Joseph Strzalka, Jean M. J. Fre´chet, and Ting Xu. Acs. Nano 4 (2010) 2721

Side Chain Amino Acid/Peptide Containing Stimuli Responsive 'Smart' Polymers

Priyadarsi De
Polymer Research Centre, Department of Chemical Sciences, IISER-Kolkata,
BCKV Campus Main Office, Mohanpur - 741252, Nadia, West Bengal, India
E-mail: p_de@iiserkol.ac.in

Amino acids are the most important building blocks of the naturally occurring bio-macromolecules, the proteins and the peptides, which can generate highly ordered hierarchical structures. The primary structure of the bio-macromolecules is held together by covalent linkage of amino acids, whereas, their secondary (*α*-helix and *β*-sheet) and higher order structures (tertiary and quaternary) are constructed by intra- and inter-chain association such as hydrogen bonding, electrostatic, hydrophobic-stacking, dipolar interactions, etc. Their highly ordered structure is greatly influenced by the property associated with primary structures, namely amino acids sequence, chain chirality, and amphiphilicity. Therefore, incorporation of naturally occurring amino acid residue in the synthetic polymer may create a new class of non-biological macromolecule with bio-mimetic structure and property. Also, combination of a biomolecule with an amino acid/peptide side chain containing polymer will produce new materials that can synergistically combine the individual properties of the two constituents, leading to novel materials with sophisticated properties. It is also possible to "tailor-make" new polymeric materials with special functions (such as, 'smart' pH-responsiveness) using amino acid moiety to meet the demands on the market of advanced materials for drug delivery and biotechnology applications. Topic of discussion will focus on underutilized amino acid monomers to prepare previously inaccessible adaptive materials (Figure 1) with controlled architecture using reversible addition-fragmentation chain transfer (RAFT) polymerization [1-4].

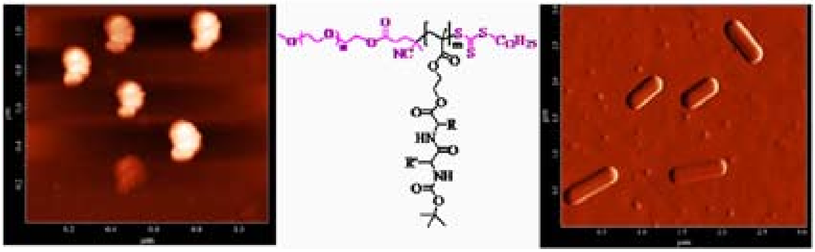


Figure 1. Atomic force microscopy (AFM) images of side-chain peptide containing block copolymers.

References:

[1]. Kumar, S.; Roy, S. G.; De, P. *Polym. Chem.* 3 (**2012**) 1239
[2]. Kumar, S.; Acharya, R.; Chatterji, U.; De, P. *J. Mater. Chem. B* 1 (**2013**) 946
[3]. Roy, S. G.; Acharya, R.; Chatterji, U.; De, P. *Polym. Chem.* 4 (**2013**) 1141-1152
[4]. Bauri, K.; Roy. S.G; Pant, S.; De, P. *Langmuir* 29 (**2013**) 2764

Utilizing Efficient Chemical Reactions to Prepare Multifunctional Polymers and Reactive Nanoporous Membranes

Anzar Khan*
Department of Materials, Swiss Federal Institute of Technology, Zurich-8093, Switzerland
**anzar.khan@mat.ethz.ch*

Development of new polymer synthesis methods that proceed with supreme fidelity and high levels of control over the nature, number, and placement of functional groups are highly desired in the area of functional soft materials synthesis.[1] Towards this end, a variety of protocols have been developed. Of particular note are the robust, efficient, and orthogonal chemistry (REO) approaches that rely on simple yet high yielding chemical reactions for the construction of complex materials.[1] Among these, thiol-based synthesis strategies have been very successful due to their insensitivity towards water and oxygen, quantitative yields, mild conditions, and ready availability of a wide range of thiol-based precursors.[1-3] For instance, thiol-ene, thiol-yne, thiol-bromo, thiol-fluoro, and thiol-isocyanate reactions have been used for efficient preparation of functionalized linear polymers, dendrimers, and hyperbranched polymers. Surprisingly, reaction between a thiol and an epoxy group,[4-5] despite the success in industrial and biomedical applications, is overlooked in macromolecular synthesis. The distinguishing feature of this process is the formation of a reactive hydroxyl group upon coupling reaction. This attribute can be exploited for a second functionalization event and hence a variety of dual-functional materials can be obtained from epoxy-containing reactive scaffolds. In the first part of this presentation, we will discuss synthesis of multifunctional homopolymers, random copolymers, and block copolymers through thiol-epoxy chemistry.[7-9]

In the second part, we will discuss the use of efficient and reversible reactions in the preparation of reactive nanoporous materials.[10] In this regard, synthesis and self-assembly behaviour of phase-separating block copolymers[11] connected through an oxy-imine[12] or a hydrazone-based[13] reversible covalent bond will be presented. Furthermore, the exchange dynamics of the reversible linkage to obtain nanoporous membranes with tunable pore chemistries will be examined.

References
[1] Iha, R.K.; Wooley, K.L., Nystrom, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.*, 109 (**2009**), *109*, 5620, and references therein.
[2] Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. *Chem. Soc. Rev.*, 39 (**2010**), 1355, and references therein.
[3] Lowe, A. B.; Harvison, M. A.; *Aust. J. Chem.*, 63 (**2010**), *63*, 1251, and references therein.
[4] Nishikubo, T.; Kameyama, A.; Kashiwagi, K. *Polymer Journal*, 26 (**1994**), 864.
[5] Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. *Polymer*, 48 (**2007**), 1526.
[6] De, S.; Khan, A.: *Chem. Commun.*, 48 (**2012**), 3130.
[7] De, S.; Stelzer, C.; Khan, A. *Polym. Chem.* 3 (**2012**), 2342.
[8] Brändle, A.; Khan, A. *Polym. Chem.* 3 (**2012**), 3224.
[9] Gadwal, I.; Khan, A. *Polym. Chem.* 4 (**2013**), 2440.
[10] Ulbricht, M. *Polymer*, 47 (**2006**), 2217.
[11] Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.*, 41 (**1990**), 525.
[12] Rao, J.; De, S.; Khan, A.: *Chem. Commun.*, 48 (**2012**), 3427.
[13] Rao, J.; Khan, A. *Polym. Chem.* 4 (**2013**), 2691.

Advances in Polymer Electrolytes for Lithium-ion Batteries

Gouri. C
Head, Lithium-ion and Fuel Cell Division, PCM Entity, Vikram Sarabhai Space Centre,
Thiruvananthapuram – 695022, Kerala. Tel: 0471-2562778; Fax: 0471-2562115;
Email: gouri_cheruvally@vssc.gov.in, gouri_c@yahoo.com

Lithium-ion batteries (LIBs) have emerged as the most important energy storage device suitable for varying applications including aerospace, automobiles and consumer electronics. The LIB performance is decided mainly by the characteristics of the electrodes, electrolyte and separator. Polymers play key roles in LIBs in the form of functional materials 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 LIB technology is based on the shuttling of Li^+ ions between the electrodes within the cell during charge-discharge reactions. The Li^+ ion transport is accomplished by using a suitable electrolyte with appreciable ionic conductivity along with an ion-conducting separator. This lecture refers to the advancement in the area of polymer electrolytes (PEs) achieved in our laboratory. The studies were focused on the development of suitable PEs with sufficient mechanical strength, high ionic conductivity at ambient temperature and good compatibility with the Li-ion cell electrodes. Different PEs such as (i) the dry, solid-type based on the blend of poly(ethylene oxide) (PEO) and lithium salt, (ii) the composite PEs incorporating high surface area nano-sized ceramic particles, and (iii) the gel/plasticized PEs based on a polymer host membrane activated with liquid electrolytes were explored extensively.

The gel PEs exhibit appreciable ionic conductivity under ambient conditions. However, generally they have poor mechanical strength. The properties of gel PEs depend significantly on the nature and properties of the polymer membranes used to form them, which in turn, vary with their formation techniques. Electro-spinning was investigated to realize host membranes for PEs with desired properties based on polymers such as poly(acrylonitrile) (PAN) and poly(vinylidenefluoride) (PVdF). The electrospun polymer membranes consist of thin fibers of micron/sub-micron diameters with very high specific surface area. Since the interlaying of fibers generate large porosity with fully interconnected pore structure facilitating the easy transport of ions, they serve as good host matrices for gel PEs.

For addressing the safety concerns arising due to the usage of volatile and flammable liquid electrolytes that are presently used in Li-ion cells, PEs incorporating non-volatile and non-flammable room temperature ionic liquids have also been explored and the lecture discusses these aspects to.

Semifluorinated sulfonated high performance polymers for proton exchange membrane materials

Susanta Banerjee
Materials Science Centre, IIT Kharagpur, India-721302
Email: susanta@matsc.iitkgp.ernet.in

Fuel cells are considered as one of the promising clean energy technologies in the context of present and future energy challenges. Proton exchange membranes (PEMs) are one of the key components of fuel cells act primarily as solid electrolyte. In this regard, Dupont's Nafion®, sulfonated tetrafluoroethylene based copolymers are the most commonly used materials because of their excellent oxidative and chemical stability along with high proton conductivity. However, deterioration in the conductivity and the mechanical strength at temperature above 80 °C, and high preparation cost of Nafion® urge the necessity to develop alternative proton conducting polymers. Therefore, hydrocarbon-based polymers have been investigated intensively by many researchers. As a common limitations, these hydrocarbon polymers bear a trade-off between proton conductivity (ion exchange capacity values), and mechanical and dimensional stability. Also, poor electrochemical stability in harsh fuel cell conditions is another reported drawback of prime concern in these hydrocarbon based polymers. In this context, as a middle approach is to prepare semifluorinated polymers. These semifluorinated polymers can balance the advantages and disadvantages of hydrocarbon-based polymers and perfluoro-polymers; they are expected to reduce preparation costs and have excellent proton conductivity as well as good resistance against hydrolytic and oxidative degradation. From this point of view, our group is working on different semifluorinated sulfonated co-poly(ether sulfone)s (SPAEs) and co-poly(ether imide)s (SPIs) in which different trifluoromethyl substituted comonomers were used. The trifluoro methyl groups are effective in improving the oxidative stability and the tensile properties of SPAE and SPI membranes. They showed good solubility due to the synergetic effects of the pendant trifluoro methyl groups in the backbones, which disrupted the regularity of the molecular chains and hindered the dense chain stacking. Also, trifluoro methyl groups increased the hydrophobicity, and helped in lower water uptake and lower swelling and excellent hydrophobic hydrophilic nano phase separated morphology. We have studied the different SPAEs structures in terms of the effect of sulfonation content, fluorine content, and bulky rigid group incorporation. Increasing fluorine content resulted in improved conductivity and better water management, whereas polar group incorporation helped in exclusion of water with moderate conductivity. A good balance between conductivity and dimensional and mechanical stability is achieved for these copolymers. The proton conductivity upto 108 mS/cm and 129 mS/cm were achieved at 90°C for the SPAE and the SPI membranes respectively; close to the proton conductivity of Nafion®.

References:

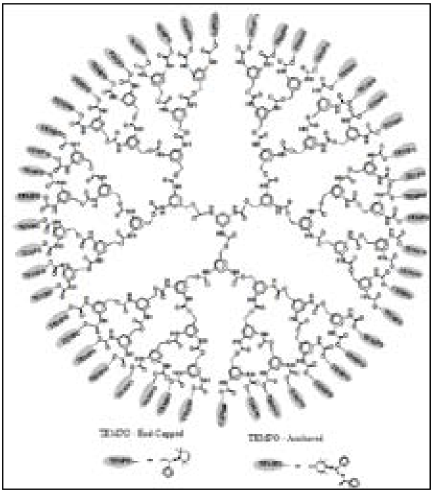
[1] Phthalimidine based new fluorinated sulfonated poly(arylene ether sulfone)s copolymer proton exchange membranes R. Mukherjee, A. K. Mohanty, **S. Banerjee***, H. Komber, B. Voit, *J. Membr. Sci. (2013) Vol. 435, pages 145-154*. ii) Highly fluorinated sulfonated poly(arylene ether sulfone) copolymers: synthesis and evaluation of proton exchange membrane properties, A. K. Mohanty, E. A. Mistri, **S. Banerjee***, H. Komber, B. Voit, *Ind. & Eng. Chem. Res. (2013) Vol. 52,pages 2772-2783*. iii) Synthesis and characterization of new fluorinated Poly(ether imide) copolymers with controlled degree of sulfonation for proton exchange membranes, E. A. Mistri, A. Mohanty, **S. Banerjee***, *J. Membr. Sci.(2012) Vol. 411-412, pages 117-129*. iv) Synthesis and characterization of novel fluorinated poly(arylene ether sulfone)s containing pendant sulfonic acid groups for proton exchange membrane materials, A. Mohanty, E. A. Mistri, A. Ghosh, **S. Banerjee***, *J. Membr. Sci. (2012) Vol. 409-410, pages 145-155*. v) Naphthalene dianhydride based semifluorinated sulfonated copoly(ether imide)s: Synthesis, characterization and proton exchange properties, E. A. Mistri, A. Mohanty, **S. Banerjee***, H. Komber, B. Voit, *J. Membr. Sci.(2013) http://dx.doi.org/10.1016/j.memsci.2013.03.015*

Oral

Successful Synthesis of Unimolecular Initiator End-Capped and Anchored Perfect Polyurethane Dendrimer Up to Fourth Generation

S.Veerapandian, A. Sultan Nasar*
Department of Polymer Science, University of Madras, Guindy Campus, Chennai-60025
*E.Mail ID:drasultannasar@yahoo.com

The discloser of polymers with controlled chain structure, complexity and star-like topology is ambitious in current research [1-7]. An executable protocol based on dendritic growth strategy and living polymerization mechanism could produce this kind of materials. However, the most exciting challenge in achieving this task is to made available suitable multi-functional core molecules. In our laboratory, a novel, facile and highly efficient approach for the synthesis of dormant TEMPO unimolecular initiator (dormant styrenyl TEMPO) end-capped and anchored polyurethane dendrimers up to fourth generation, consisting of simplest aryl-alkyl urethane repeat unit, has been developed. The blocked isocyanate core and building block containing hydroxy group were synthesized in a two-steps reactions. The divergent iterative methodology adopted yielded amine-terminated polyurethane dendrimer at second step and this was modified into blocked isocyanate terminated dendrimer in the next step avoiding formation of isocyanate group. The blocked isocyanate moiety possessing easily cleavable blocking agent facilitated the dendrimer construction and functionalization into dendritic unimolecular initiators via carbamate interchange reaction. The number of functionalities up to 48 of **G4** dendrimer were achieved accurately and conformed by ^{1}H NMR, MALDI-TOF-MS spectroscopies.



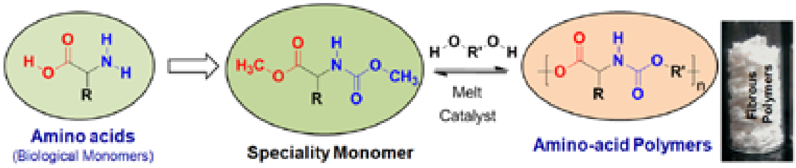
References:

[1]. Brigitt, I.V.; Albena, L. Chem.Rev. 109 (2009) 5924.
[2]. Valrie, S,; Robert, J,; Christophe, D. Chem.Rev. 108 (2008) 1104.
[3]. Per, B.Z,; Yasuyuki, K,; Masayoshi. O. Chem.Rev. 108 (2008) 3747.
[4]. Craig, J.H,; Anton, W.B,; Eva, H. Chem.Rev. 101 (2001) 3661.
[5]. Krzysztof, M,; Jianhui, X, X. Chem.Rev. 101 (2001) 2921.
[6]. Masami, K,; Tsuyoshi, A,; Mitsuo, S. Chem.Rev. 101 (2001) 3689.
[7]. Nikos, H,; Marinos, P.; Stergios, P,; Hermis, I. Chem.Rev. 101(2001) 3747.

Polymers Based on Amino acids: Plastic Materials from Bio-resources

S. Anantharaj, Moumita Gupta and M. Jayakannan*
Department of Chemistry
Indian Institute of Science Education & Research (IISER-Pune)
Dr. HomiBhabha 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. However, the non-availability of efficient polymer synthetic routes makes these bio-resources less attractive for commercial exploration. 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. The end group analysis via MALDI-TOF-MS confirmed that the monomers were thermally stable under the experimental condition. The new process is capable of making wide range of polymer architectures such as di- and tri-block copolymers and hyperbranched polymers and so on.The new polymers were self-organized as β-sheet or poly proline type-II in aqueous or organic solvents. Thermal properties of polymers such as glass transition temperature and crystallinity could be readily varied using different L-amino acid monomers or diols in the feed. Thus, the new melt condensation approach will open up new platform of research activates based on amino acids in the polymer literature.



New Dual Ester-Urethane Condensation Chemistry

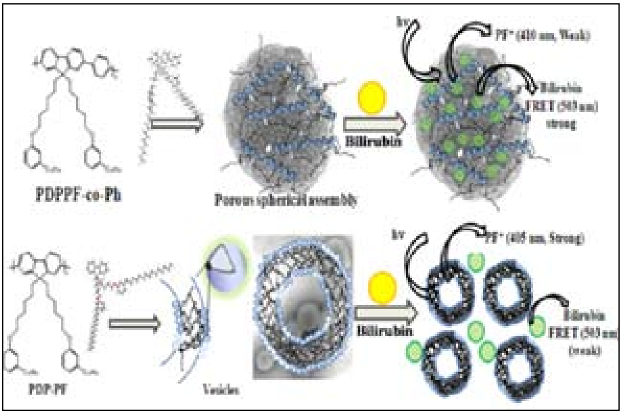
References:

1. Anantharaj, S.; Jayakannan, M. Polymers from Amino acids: Development of Dual Ester-urethane Melt Condensation Approach and Mechanistic Aspects. *Biomacromolecules*, **2012**, *13*, 2446- 2455.
2. Deepa, P.;Jayakannan, M. Solvent Free and Non-isocyanate Melt Transurethane Reaction for Aliphatic Polyurethanes and Mechanistic Aspects*J. Polym. Sci. Part-A: Polym. Chem***. 2008**, *46*, 2445-2458.

Selective, Nanomolar Sensing of Bilirubin using Tailor-made Polyfluorenes: Synergistic Effect of Porous Spherical Morphology and FRET

T. Senthilkumar and S. K. Asha.*
Polymer Science & Engineering Division, National Chemical Laboratory, Pune-411008
Email: sk.asha@ncl.res.in

The amplified signal response and sensitivity of conjugated polymers make them suitable for applications as chemical and biosensors.[1] Bilirubin, a breakdown product of haemoglobin, is an important biomolecule, which if present in abnormal levels in body fluids is an indicator for disturbance in bile drainage. Therefore, monitoring the bilirubin concentration in body fluids is a vital step in diagonising liver disorders and jaundice. The clinically practiced semi-quantitative determination of bilirubin in urine samples is based on colour change from yellow to red produced by the diazotization reaction of bilirubin and sulphanilic acid using spectrophotometer.[2] This method is time-consuming, in addition to interference from other haeme protein residue present in the sample influencing the diazotization reaction. We have developed polyfluorene fluorescence based bilirubin sensor that detects unbound bilirubin with high selectivity and sensitivity.[3] Two new polyfluorenes functionalized with pentadecyl phenol (PDP) homo- (PDP-PF) and copolymer (PDPPF-co-Ph) were synthesized, which were found to self assemble into vesicles and porous spherical assemblies respectively in solid state as well as in solution. Steady state fluorescence measurements gave a fluorescence quenching of polymer as well as increase in emission of bilirubin (FRET) with highest energy transfer efficiency of 86 % leading to emission colour change from blue to green. The open porous spherical assembly of PDPPF-co-Ph enabled better adsorption of the analyte, leading to high energy transfer. Structural analogues such as biliverdin and porphyrin showed poor fluorescence quenching efficiency, thus highlighting the selectivity and sensitivity upto nanomolar of the FRET based sensing of the bilirubin by newly designed polyfluorene.



References:

[1]. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* 100 (**2000)** 2537.
[2]. Van den Bergh, A. A. H.; Snapper, J.; *Deutsh. Arch. Klin. Med.* 110 (**1913)** 540.
[3]. Senthilkumar, T.; Asha, S. K. *Macromolecules* **2013, DOI**:10.1021/ma4000946.

Recoverable Thermoresponsive Ruthenium Benzylidene compounds for Metathesis Reaction: Synthesis and Catalytic Activity

Debasis Samanta,* Pentela Nagaraju, P. Murugan, Asit Baran Mandal,*
Polymer Science Division, CSIR-CLRI, Chennai-20, India
E-mail: abmandal@hotmail.com, debasis.samanta@gmail.com

A compound or material is called thermo responsive when it undergoes physical change in presence of external thermal stimuli. Poly (N-isopropyl amide) falls in this category. Due to the thermo-responsive behaviour, polyNIPAM is less soluble in water at elevated temperature. This interesting property has been exploited for several applications like catalyst/enzyme recovery.[1] In this case, a reaction can be performed in ambient temperature in presents of a soluble thermo responsive catalyst, and after completion of the reaction temperature of the medium can be elevated so that the catalyst can be precipitated out, recovered and reused. For olefin metathesis reaction the most used catalyst is Ruthenium benzylidene catalyst, which is expensive and difficult to remove completely from the medium. Hence, by incorporating the thermo responsive tag (using "click reaction") to this catalyst, easy recovery, reusability and removal should be possible and easy. In this context, recently we reported immobilization of polymer on surface by "click" reaction[2] and acid responsive microcapsules using functionalized CNTs.[3]

In the presentation we will discuss about our recent advancement in the development of thermo responsive ruthenium based metathesis catalyst. We will present schematic synthetic procedure for the suitable ligands followed by the preparation of thermo responsive catalyst (17). Challanges in the characterization of those compounds will also be discussed. The catalytic activity of the catalyst and strategy of recovery (Figure 1) will also be discussed.

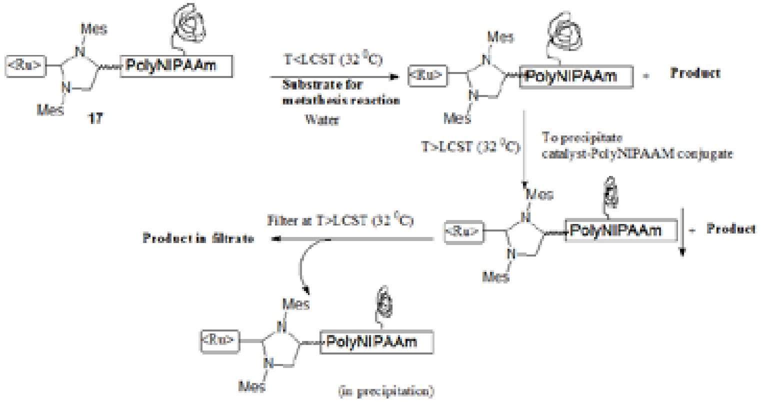


Figure 1. Strategy of recovery of thermo-responsive catalyst

References:

[1]. Chen, G. H.; Hoffman, A. S. *Bioconjugate Chem.* 4 (1993) 509
[2]. Samanta, D.; Murugan, P.; Ananthakrishnan, S. J.; Somanathan, N.; Das, S. K.; Jaisankar, S. N.; Mandal, A. B. *Chem. Commun.* 48 (2012) 12068.
[3]. Samanta, D.; Sankar, R. M.; Jaisankar, S. N.; Alam, M. S.; Mandal, A. B. *Chem. Commun.* 47 **(**2011) 11975.

Acknowlegement:
Financial support from Department of Biotechnology, Govt. of India (No. BT/PR643/GBD/27/413/2012) is gratefully acknowledged.

Versatile Sulfhydryl-Chemistry at the Chain-End of a Synthetic Polylactide

Mijanur Rahaman Molla and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the Cultivation of Science, Kolkata, INDIA- 700032
Email: psumrm@iacs.res.in

Polylactide is an important class of macromolecule in biomedical application such as surgical sutures, drug delivery systems and internal bone fixation due to its well-known biocompatible and biodegradable properties. Thus synthetic strategies for producing versatile functional polylactides are highly desirable.

We have recently demonstrated ring opening polymerization (ROP) of a lactide monomer using a simple initiator containing a pyridyl disulfide functional group.[1] This produced well-defined polymers with chain end functionality which could produce highly reactive thiol groups under mild condition in presence of a reducing agent. The free thiol group was utilized for incorporation of various chain end functionalities using high-yielding thiol-maleimide, thiol-acrylate and thiol-ene coupling reactions. In all cases quantitative functionalization could be established by end group analysis using UV/vis and NMR spectroscopic tools. This strategy was extended further to synthesize an amphiphilic block copolymer by coupling the thiol-terminated polylactide with acrylate end-functionalized polyethylene oxide (PEO). Interestingly the connecting functional group (β-thiopropionate) in-between the two blocks was found to be acid labile and consequently the block copolymer could be fragmented to two parent polymers in presence of an acid.

Further we also explored chain end modification by reaction of a thiol containing chromophore naphthalene diimide (NDI) with the pyridyl disulfide group at the terminal of the as synthesized polymer. The resulting NDI-conjugated polymer showed white light emission due to simultaneous emission from free and excimeric NDI chromophore attached to polylactide in sharp contrast to blue emitting monomeric NDI. Further NDI-functionalized polylactide also showed uniform spherical nano-structured assembly on solid surface.

Synthesis, quantitative end-group functionalization and photophysical properties probed by various spectroscopic and microscopic studies will be the topic of this presentation.

References:

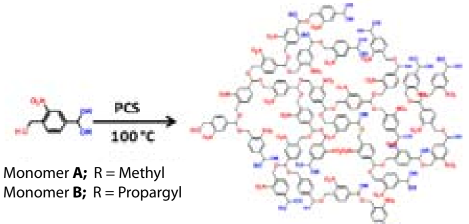
[1]. Molla, M. R.; Ghosh, S. *Macromolecules* **2012**, *45,* 8561-8570.

Photodegradable hyperbranched polyacetal: Exploring its potential as a positive photoresist and for reactive photo-patterning

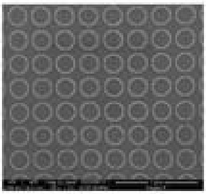
Saptarshi Chatterjee and S. Ramakrishnan*
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore 560012, INDIA
raman@ipc.iisc.ernet.in

Among the various photoresponsive groups, *o*-nitrobenzyl unit has been the recent focus of attention of polymer chemists because of its potential for structural adaptation [1]. *o*-Nitrobenzyl moiety cleaves readily under 365 nm irradiation and generates *o*-nitrosobenzaldehyde; in the polymer context, this linkage has extensively been used for destabilizing aggregates, such as micelles and vesicles, formed by block copolymers, and for altering the LCST behaviour of polymeric systems [2]. Random copolymers based on acrylates, carrying *o*-nitrobenzyl ester protecting groups have been used to create photopatterns, which were subsequently used as templates to pattern proteins on substrates; clearly photopatterning, especially when combined with clickable handles, hold interesting potential for generating substrates for a variety of biological applications [1].

Hyperbranched polymers are a class of dendritic macromolecules that possess properties distinct from those of linear analogues; for instance, they exhibit low melt and solution viscosity and possess a large number of potentially modifiable peripheral groups. Recently, we designed an AB_2 monomer carrying a hydroxyl group and a dimethyl acetal unit, which upon melt polymerization generated an acid-labile hypebranched polyacetal [3]. Interestingly, it was found that the rate at which the polyacetal degrades is strongly influenced by the nature of the peripheral groups. In this study, we describe, for the first time, the synthesis of a photodegradable hyperbranched nitro-polyacetal via a melt trans-acetalization polymerization. Self-condensation of monomer **A** under melt polymerization condition using pyridinium camphorsulfonate (PCS) as a catalyst yields a hyperbranched polyacetal, wherein each repeat unit carries an *o*-nitrobenzyl junction; this HBP exhibited photolability which permitted us to use this as a photoresist to generate patterns by exposure to 365 nm light. Monomer **B**, on the other hand, carrying a dipropargyl acetal moiety instead of dimethyl acetal, permitted us to generate photo-patterned substrates onto which click reaction using an appropriate organic azide was possible. Exploiting this property, clickable micropatterned substrates were generated; as a test case, an organic fluorescent dye was clicked onto the patterned substrate and examined by fluorescence microscopy.



Monomer **A;** R = Methyl
Monomer **B;** R = Propargyl



SEM image of a photo-patterened substrate.

References

[1] Zhao, H.; Sterner, E. S.; Coughlin, E. B.; Theato, P. *Macromolecules* **2012,** *45*, 1723.
[2] Han, D.; Tong, X.; Zhao, Y. *Macromolecules* **2011**, *44*, 437.
[3] Chatterjee, S.; Ramakrishnan, S. *Macromolecules* **2011**, *44*, 4658.

Synthesis and Characterization of PCL-b-PCCMA by Combining ROP with ATRP

Ravindra M Patil[a,b], Anil A Ghanwat[b], Satyanarayana Ganugapati[a],
Rudhramyna Gnaneshwar[a*]
a. Syngene International Ltd, Biocon Park , Plot No. 2&3, Bommasandra Industrial Estate - Phase- IV
Bommasandra-Jigani Link Road, Bangalore 560 099, India.
b. School of chemical Sciences, Solarpur University, Solapur, 413 255, India
E-mail: rudhramyna.gnaneshwar@syngeneintl.com

A number of applications (in coatings, in Li^+ ion batteries etc.) and as biomedical materials (in controlled drug delivery, as self-healing materials etc.) will greatly benefits from research on (co) polymers bearing reactive functionalities that are capable of chemical transformations upon usage[1]. We herein report the synthesis of cyclic carbonate end functional PCL-b-PCCMA co-polymers by using bromopolyesters, initially synthesized by ring-opening polymerization (ROP) of poly(ε-caprolactone) (PCL), as macroinitiators for the atom transfer radical polymerization (ATRP) of cyclic carbonate methyl methacrylate (CCMA) in presence of copper bromide and 2,2′-bipyridyl at 80°C in toluene for 16 h. Further these 5-membered cyclic carbonate pendent groups reacted with amine such as 2-phenylethylamine enabled the hydroxy urethane pendant functional block copolymers without the use of the relatively more hazardous isocyanates and without any by-product.

References

[1]. (a). Abraham, G. A.; Gallardo, A.; San Roman, J.; Fernandez-Mayoralas, A.; Zurita, M.; Vaquero, J. *J. Biomater. Res. A* **2003**, *64*, 638-647. (b). Li, Y. Y.; Zhang, X. Z.; Cheng, H.; Zhu, J. L.; Cheng, S. X.; Zhuo, R. X. *Macromol. Rapid Commun.* **2006**, *27*, 1913-1919. (c). Hong, S. W.; Kim, K. H.; Huh, J.; Ahn, C. H.; Jo, W. H. *Macromol. Res.* **2005**, *13*, 397-402. (d).Shanmugananda, M. K.; Zhang, Q.; Remsen, E. E.; Wooley, K. L. *Polym. Mater. Sci. Eng.* **2001**, *84*, 1073-1074. (e). Ghosh, B.; Urban, M.W. Science 2009, 323, 1458-1460 (f). Jana, S.; Yu, H.; Parthiban, A.; Chai, C. L.L. J. Polym. Sci Part A: Polym Chem **2010**, 48, 1622-1632**.**

Synthesis of Chiral Polysilanes using UV-irradiation Technique

Km. Meenu, Dibyendu S. Bag and A. K. Saxena
Defence Materials and Stores Research and Development Establishment (DMSRDE)
DMSRDE P.O., Kanpur-208013 INDIA

Polysilanes represent a novel class of materials with unique electronic and optical properties as result of an extensive electron delocalization along Si-Si polymer backbone [1]. They are also used as photoresists, photoconducting materials, and SiC ceramic precursors [2-3]. The properties of these polymers are affected by the substituents attached to the polymer chain, the degree of polymerization and polymer chain conformation [4-5]. It is also well known that polysilanes upon UV-irradiation give rise to silyl macroradicals which are capable of initiating radical polymerization [6-7]. In this investigation, we have synthesized chiral polysilanes by UV-irradiation of poly(methylphenylsialne) in the presence of a chiral vinyl monomer, (R)-N-(1-phenylethyl) methacrylamide (R-NPEMAM). Polymerization of the chiral monomer by the silyl macroradicals generated by the UV-irradiation obtained chiral polysilanes. Purified samples of chiral polysilanes were characterized by FTIR, UV-Vis and Circular Dichroism (CD) spectroscopy. The appearance of N-H str. (3432 cm^{-1}) and C=O str. (1648 cm^{-1}) of CONH of the chiral mer unit in FTIR spectra of the synthesized samples indicated chiral polysilanes. The Si-Si bond appeared at 464 cm^{-1}. Two absorbances at 233 and 270 nm in the UV-Vis spectra of such polymers are due the aromatic rings associated with the polysilane and R-NPEMAM chiral unit; whereas the absorbance due to Si-Si σ-conjugation appears at 324 nm.

The circular dichroism (CD) was studied on a JASCO J-810L CD spectropolarimeter in THF solvent at 25°C (Fig.1). The cotton effect observed at 276 nm is due to the chiral aromatic ring of the R-NPEMAM unit which is obvious. Moreover, we also observe here a cotton effect at 325 nm. However, polysilane used here is not chiral and does not exhibit any cotton effect. This cotton effect at 325 nm is thus appeared due to the Si-Si conjugation which became helical due to the chiral block at the one or both the ends of the chiral polysilane. Hence this induced circular dichroism (ICD) is observed at 325 nm. Such chiral polysilanes having tunable optical activity by induced chirality may find application in optoelectronics.

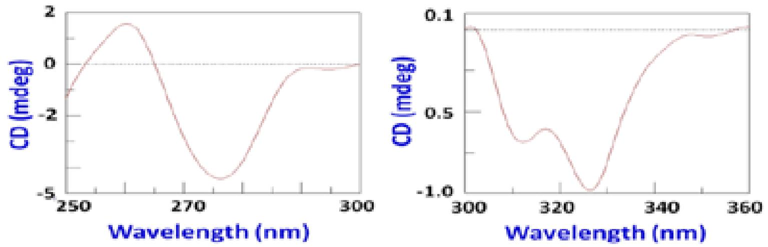


Fig.1 CD spectra of a chiral polysilane in THF (conc. 0.005 gm/dl) at 25°C

References:

[1]. Miller, R. D.; Michl, J. *Chem. Rev.* 89 (**1989**) 1359

[2]. Michl, J.; West, R. **2000**. Silicon-Containing Polymers, ed. R. G. Jones, W. Ando, J. Chojnowski, p. 499, Kulwer:Dordresht: The Netherlands

[3]. Hayase, S. Prog. Polym. Sci. 28 (**2003**) 59

[4]. Harrah, L. A.; Zeigler, J. M. *Macromolecules* 20 (**1987**) 601

[5]. Hsiao, Y-L.; Waymouth, R. M. *J. Am. Chem Soc.* 116 (**1994**) 9779

[6]. West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* 13 (**1986**) 35

[7]. Kminek, J.; Yagci, Y.; Schnabel, W. *Polym. Bull.* 29 (**1992**) 277

Development of Polymeric Core-shell Particles and their Nanocomposites with Graphene Oxide using RAFT Polymerization

Niranjan Yeole*, S N Raju Kutcherlapati, Harish Reddy Inta, Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad-500 046
E-mail: niranjan.yeole@gmail.com, tjscuoh@gmail.com

The synthesis of well-defined polymers and complex architectures has been greatly facilitated due to recent development in controlled radical polymerization (CRP) technique, which has opened up new possibilities in design and preparation of functional nanostructures.

Successful one-pot synthesis of polystyrene (PS) particles composed of amphiphilic block copolymer, obtained from poly(hydroxyethyl methacrylate) (PHEMA) based macro-RAFT agent, is developed as a simple and robust method for the preparation of nano-sized core-shell nanoparticles along with adjustment of core-shell dimensions. Initially generated hydrophilic PHEMA macro-RAFT agents are then chain-extended *in-situ* with a hydrophobic monomer (styrene) to form nanoparticles with core-shell morphology. Core-shell dimensions can be readily tuned by varying hydrophilic monomer concentration and polymerization time for the formation of PHEMA based macro-RAFT agent.

In addition to polymer nanoparticles synthesis, surface modification by Graphene Oxide (GO) is under progress. GO was prepared and immobilized with RAFT agent. The hydroxyl groups of GO were attached to the RAFT agent through an esterification process. The resultant modified GO was used for the preparation of PS/GO nanocomposites in surfactant free emulsion polymerization (SFEP) and emulsion polymerization. PS-GO can be generated in different hydrophilic monomer based copolymer matrices, yielding a new class of GO/polymer composites.

Acknowledgement: NY thanks the University Grants Commission, New Delhi for providing Dr. D. S. Kothari Postdoctoral Fellowship.

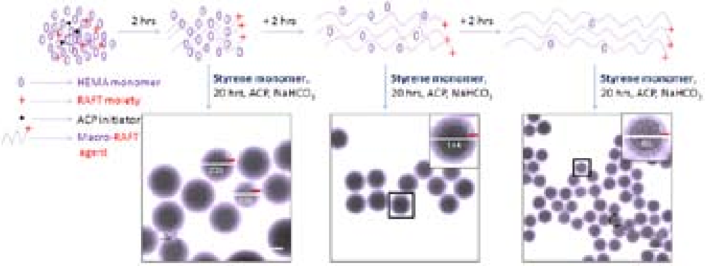


Figure 1. Schematic representation of one-pot synthesis of core-shell polymer nanoparticles using poly(HEMA) based macro-RAFT.

References

[1] Chaduc, I.; Zhang, W.; Rieger, J.; Lansalot, M.; D'Agosto, F.; Charleux, B. *Macromol. Rapid Commun.* 32 **(2011)** 1270.
[2] Chaduc, I.; Girod, M.; Antoine, R.; Charleux, B.; D'Agosto, F.; Lansalot, M. *Macromolecules* 45 **(2012)** 5881.
[3] Beckert, F.; Friedrich, C.; Thomann, R.; Mülhaupt, R. *Macromolecules* 45 **(2012)** 7083.
[4] Etmimi, H.; Tonge, M.; Sanderson, R. *J Polym. Sci. Part A: Polym. Chem.* 49 **(2011)** 1621.
[5] Yeole, N.; S N Raju, K.; Harish Reddy I.; Jana, T. (manuscript under preparation).

Biodegradable Hyperbranched Polymers with Acid-labile Ketal Linkages: Design, Synthesis and Biological Evaluation

Rajesh A. Shenoi[a], Jayaprakash K. Narayanannair[b], Jasmine L. Hamilton[a], Benjamin F. L. Lai [a], Muhammad Imran ul-haq[a], Kallanthottathil G. Rajeev[b], Muthiah Manoharan[b] and Jayachandran N. Kizhakkedathu[a, c]*
[a]Centre for Blood Research and Department of Pathology and Laboratory Medicine, University of British Columbia, Vancouver BC, Canada
[b]Alnylam Pharmaceuticals, Cambridge MA, USA
[c]Department of Chemistry, University of British Columbia, Vancouver BC, Canada.
**E-mail: jay@pathology.ubc.ca*

Aim: Multifunctional, biocompatible and biodegradable polymers with specific degradation linkages that undergo controlled degradation in response to various physiological stimuli is critical for the development of targeted drug delivery systems, bioconjugates and as scaffolds for tissue engineering. Among these, pH sensitive polymers are of particular interest due to the wide range of applications such as tumor targeting and the endolysosomal delivery of proteins, nucleic acids and anti-inflammatory agents. The purpose of the present study was to develop a novel class of multifunctional and biodegradable polymers with acid-labile ketal linkages and investigate their in vitro and in vivo degradation behavior.

Methods: We designed and synthesized several novel AB_2 type epoxide monomers with structurally different ketal groups. The ketal-containing biodegradable polymers were synthesized by the anionic ring opening multibranching polymerization of these ketal-containing epoxide monomers with glycidol. A series of polymers of varying molecular weight and ketal content were synthesized by the proper choice of the polymerization conditions. The pH dependent degradation of the polymers was studied in different buffers using NMR and GPC analysis. The degradation behavior of fluorescently-labeled polymers was studied within the cells using confocal microscopy. The in vivo degradation, biodistribution and clearance of the polymers were investigated by intravenous administration of tritium-labeled polymer in mice.

Results: The newly developed ketal-containing biodegradable polymers demonstrated controlled degradation profiles depending on the pH, temperature and structure of the ketal groups. A range of hydrolysis half lives from a few minutes to a few hundred days depending on the ketal group structure was achieved. The polymers as well as their degradation products were found to be highly biocompatible as measured by several assays. The polymers were also rapidly internalized by the cells and underwent degradation within the acidic compartments within the cells. When intravenously administered in mice, the biodegradable polymer of molecular weight of 100 kDa showed an order of magnitude lower plasma circulation half life than non-degradable polymer of similar molecular weight. This demonstrated its degradation in vivo and rapid clearance from circulation. There was negligible tissue accumulation (less than 0.5 % of the injected amount) of the biodegradable polymer and most of the injected amount (more than 80%) was cleared through urinary and fecal excretion pathways. We are currently exploring the utility of these biodegradable polymers for drug delivery and bioconjugation strategies.

Conclusions: We developed a new series of well-defined, neutral, multifunctional, biocompatible and biodegradable polymers and demonstrated that their degradation could be controlled by varying the structure of the acid-labile ketal group. The excellent biocompatibility, in vivo degradation and clearance behavior of these polymers make them suitable for the development of multifunctional nanomedicine.

Novel Synthesis of Poly(lactic acid) Stereocomplex Nanoparticles with Different Morphology by Self Assembly

S.B. Idage, B.B. Idage, A.K. Lele*

Polymers & Advanced Materials Laboratory, Polymer Science & Engineering Division
National Chemical Laboratory, Pune - 411 008, INDIA
*E-mail : ak.lele@ncl.res.in

We have demonstrated the formation of new type (1D) of super structures from Poly(lactic acid) (PLA) stereocomplex nanoparticles with different architectures and morphology by a simple technique using Poly(D-lactic acid) (PDLA) and Poly(L-lactic acid) (PLLA) of different molecular weights. The nanoparticles were characterized by FT-IR and Raman spectroscopy, CP/MAS ^{13}C NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray diffraction (WXRD), particle size distribution (PSD) and scanning electron microscopy (SEM).

The FT-IR and Raman spectra clearly showed an evidence for formation of Poly(lactic acid) stereocomplex nanoparticles. CP/MAS ^{13}C NMR spectra show an appearance of a new peak at 173.3 ppm for carbonyl carbon due to stereocomplexation. PLA stereocomplex nanoparticles showed melting point (Tm) in the range of 225-230^{o}C along with PLLA and PDLA which has Tm of 180^{o}C confirms the exclusive formation of stereocomplex crystals than the formation of PDLA and PLLA homo crystals. The thermal stability of PLA stereocomplex is increased from 270 to 310^{o}C due to stereocomplexation. PLA stereocomplex nanoparticle size varies from 112 to 291 nm and it depends on the molecular weights of the PLLA and PDLA enantiomers used for the nanoparticles synthesis.

The dependence of PDLA and PLLA enantiomer molecular weight on PLA stereocomplex morphology is clearly evidenced by scanning electron microscopy (SEM). The scanning electron micrographs showed the formation of nanoparticles by aggregation/fusion to each other with PLLA and PDLA with different mol. wt. chain length showing different shape of nanoparticles which leads to formation of highly branched/fern type structures with high mol. wt. and flower type structures with stating branched core with low as well as medium mol. wt. chain lengths

References

[1] Toshiyuki Kida, Kenta Kondo and Mitsuru Akashi, Chem. Commun., 48, 2319 (2012).
[2] Yukiko Furuhashi, Yoshiharu Kimura and Naoko Yoshie, Polymer Journal, 38 (10), 1061 (2006).

Ion and molecularly imprinting polymer/membrane technology and its application in the remediation of contaminated aquatic environments

Titus A.M. Msagati and Bhekie B. Mamba
Department of Applied Chemistry, Faculty of Science, University of Johannesburg,
Doornfontein Campus, P.O. Box 17011, Johannesburg, South Africa, 2028
tmsagati@uj.ac.za

Ion and molecularly imprinting has become one of the fast growing technologies that have gained a lot of attention recently especially in the area of materials science, medicine as well as others. The The ion imprinted polymers (IIPs), molecularly imprinted polymers (MIPs) and molecularly imprinted membranes (MIMs) are synthesized on the principles of enzyme phenomenon whereby an ion or a polymer or membrane is altered by polymerization that takes place in the presence of a template that will later be removed to create cavities that will recognize only the analyte of interest. This specific and selective affinity for the target species decreases the chances of competition from other different types of species. The imprinting technique started with the discovery of the bulk polymerization method where by the monomer, initiator, crosslinker and template are mixed together and allowed to polymerize, and then the resulting polymer ground and sieved to get particles with sizes suitable for the polymer's application. The imprinted functionalities (ion/molecularly/membrane) have got some attractive qualities for use in environmental applications which include their stability, inexpensive and have a wide range of synthesis options with each suiting a certain unique application. In this paper we report on the synthesis, characterization and applications of IIPs for As and Se, MIPs for dioxins, phthalate esters and microcystins as well as the potential MIMs for hydrophobic organic compounds in aquatic environments..

Poster

TP1

Cardo poly(ester – imide)s containing cyclohexylidene moiety

A. A. Ghanwat[1], V. P. Ubale[2], P. P. Wadgaonkar[3] and N. N. Maldar[1*]
1. School of Chemical Sciences, Solapur University, Kegaon, Solapur- 413 255.
2. D.B.F. Dayanand College of Arts and Science, Solapur-413 002.
3. Division of Polymer Science and Engineering, National Chemical Laboratory, Pune-411 008.
Email: maldar_nn@rediffmail.com

A novel aromatic diamine containing a cardo cyclohexylidene moiety and preformed ester linkage, viz; 1, 1-bis (3- aminobenzoyloxy phenyl) cyclohexane; m-BPCDA, was prepared through reaction of 1, 1 –bis (4-hydroxy phenyl) cyclohexane and two moles of m- nitrobenzoyl chloride followed by catalytic (Pd/C) hydrogenation. The structures of novel m-BPCDA and its precursor; bis(ester-Nitro) derivative were confirmed by FTIR, NMR and mass spectra. A series of new poly(ester-imide)s was synthesized by polycondensation of m-BPCDA with commercially available aromatic dianhydrides such as pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic dianhydride (BTDA), hexafluoro-isopropylidene diphthalic anhydride (6-FDA), biphenyl tetracarboxylic dianhydride (BPDA), oxydiphthalic anhydride (ODPA) in N-methyl-2-pyrrolidone (NMP) by low temperature solution polycondensation. Poly(ester – imide)s were characterized by FTIR spectroscopy, solubility, inherent viscosity, thermal analysis (TGA, DSC) and X- ray diffraction studies. Inherent viscosities of these poly (ether -imide)s were in the range of 0.20 to 0.27 dL / g indicating moderate molecular weight built -up. These polymers had good solubility in (hot / at room temperature) polar aprotic solvents namely DMAc, NMP, DMF etc. X –ray diffraction pattern of polymers suggested that introduction of pendant cyclohexylidene group containing diester linkage and meta catenation may have disrupted the chain regularity and packing leading to amorphous nature. The above observation also support solubility properties of the polymers investigated. Glass transition temperatures of poly(ester – imide)s were in the range of 184 to 224 ^{0}C when analyzed by DSC; whereas thermogravimetric analysis of polymers under nitrogen atmosphere showed no weight loss below 308 ^{0}C indicating that poly(ester – imide)s had excellent thermal stability. The structure -property correlation among the poly(ester – imide)s was studied. These polymers could find potential applications as processable high temperature materials.

Key Words:
1, 1-Bis (3- aminobenzoyloxy phenyl) cyclohexane, Soluble-Cardo-poly(ester – imide)s, thermal properties, XRD.

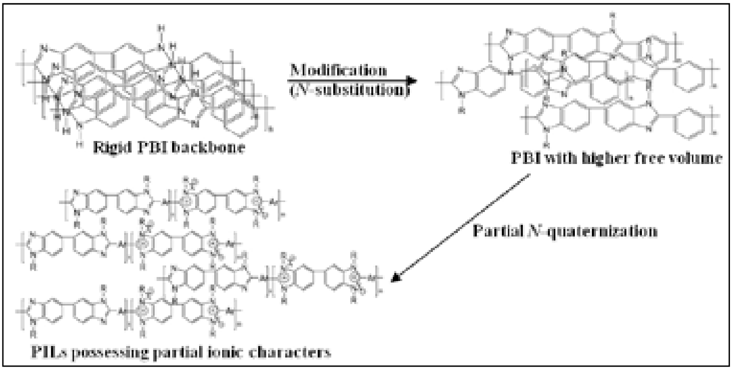
TP2

Polymeric Ionic Liquids Possessing Partial Ionic Character: Synthesis and Gas Permeation Studies

Anita S. Rewar, Rupesh S. Bhavsar, K.Sreekumar and U.K.Kharul*
Polymer Science and Engineering Division, National Chemical Laboratory, Pune-411008 (India)
uk.kharul@ncl.res.in

Capture of CO_2 from flue gases produced by the combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Chemisorbing processes are considered to be the most feasible method and are already at an advanced stage of development but they have some disadvantages [1], but gas separation membranes are attracting more and more attention as a possible alternative because of its advantages over the other processes [2].This work aims to develop new polymeric ionic liquids (PILs) possessing partial ionic characters for gas separation membrane material. PIL, a class of polymeric materials having unique characteristics of combining large variety of anions and cations widens spectrum of their applicability in various fields [3]. Alike ionic liquids, they possess high CO_2 sorption capability and high CO_2 sorption desorption rate [1]. The requirement of PILs for gas permeation application of possessing film forming property will be conveniently utilized while tuning anionic and cationic sites in PILs based on rigid backbone polybenzimidazoles (PBIs) [4]. It was studied that quantitative *N*-quaternization of PBI though exhibits excellent film forming property; their permeability towards different gases are much lower (due to close chain packing as a result of high ionic character) than *N*-substituted PBIs [5]. In this work, it is demonstrated that a balance of chain attraction (ionic character) & chain repulsion (*N*-substitution by bulky *tert*-butyl benzyl group) is required to get high rate of gas permeation and it occurs at lower degree of substitution (13 %). We have also studied the effect of anion variation (NTf_2, BF_4 and acetate) on gas permeation properties in resulting PILs.

Partial *N*-quaternization of PBI would possess higher free volume; owing to both, (i) reduced ionic character and (ii) *N*-alkylation by bulky substituent. Though this would lead to high gas permeability; it would be prudent to understand effects of such kind of combination on physical properties of resulting polymers and their CO_2 separation characteristics.



References

1. Tang J.; Radosz M. and Shen Y., *Macromol.,* 41**(2008)** 493.
2. Aaron D. and Tsouris C., *Sep. Sci. and Tech*, 40 (**2005)** 321
3. Mecerreyes D.; *Prog. Polym. Sci.,* 36 **(2011)** 1629.
4. Kharul U. K.; Kumbhakar S.C.; Bhavsar R. S. And Shevate R. H., WO **2012**/035556
5. Kumbhakar S.C.; Islam M.N.; Potrekar R.A. and Kharul U. K., *Polymer,* 50 **(2009)**1403-1413.

TP3

Synthesis and Aggregation Behaviour of Poly(methyl methacrylate)-*b*-Polytyrosine Block Copolymer

Anupam Saha, Tapas K. Paira, Sanjib Banerjee, Madhab Dule and Tarun K. Mandal *
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
** E-mail: psutkm@iacs.res.in*

The combination of polymers with peptides /proteins to make bioconjugates is an emerging multidisciplinary field of research that has increased attention to the scientific community due to their higher value-added functional applications in various fields such as nanomaterials, biomedical-related areas and tissue engineering.[1] Polymer bio-conjugates has potentially interest in the formation of self-assembled micro/nano structures. Recently, controlled radical polymerization (CRP) techniques have been largely used to construct different types of polymeric architectures. Also, the ring-opening polymerization (ROP) of α-amino acid N-carboxyanhydride (NCA) has been the highly popular technique to prepare variety of well-defined polypeptide based hybrid copolymers.[2]

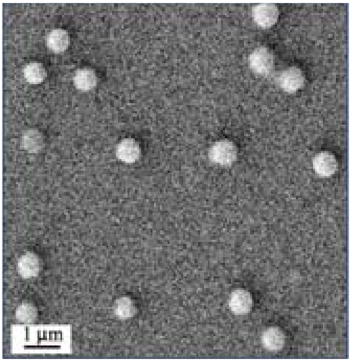


Figure 1. FESEM image of self-assembled PMMA-*b*-Ptyr block copolymer conjugate.

Taking the impressive advances of CRP and ROP to prepare polymer bio-conjugates, we report the synthesis of a new type of biohybrid material, poly(methyl methacrylate)-*b*-polytyrosine (PMMA-*b*-Ptyr) block copolymer using a combination of atom transfer radical polymerization (ATRP), "click" chemistry and ring-opening polymerization (ROP) of tyrosine N-carboxyanhydride. The synthesized polymer bioconjugate is characterized by GPC, NMR and FTIR techniques. The aggregation behaviour of PMMA-*b*-Ptyr copolymer is studied in N,N-dimethylformamide (DMF). Nearly monodispersed spherical particles are obtained via aggregation of PMMA-*b*-Ptyr copolymer molecules, as observed by field emission scanning electron microscope (FESEM), transmission electron microscopy and dynamic light scattering (DLS) analysis (Figure 1).

References

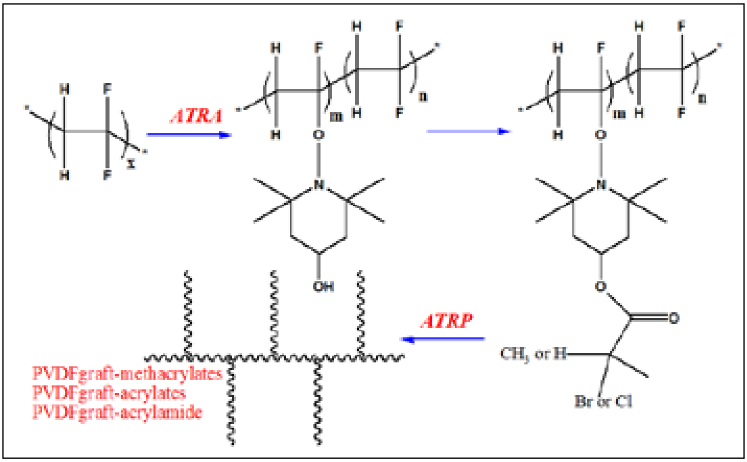
[1] Le Droumaguet, B.; Nicolas, J. *Polym. Chem.*, 1 (**2010)** 563.
[2] Dimitrov, I.V.; Berlinova, I.V.; Iliev, P.V.; et al. *Macromolecules*, 41 (**2008**) 1045.

TP4

A Novel Synthetic Route for Preparation of PVDF based Graft Copolymers

Atanu Kuila, Dhruba P. Chatterjee, Rama K. Layek and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700032, INDIA
E-mail: psuakn@iacs.res.in

Graft modification of PVDF is by far the best method for tailoring properties of PVDF based materials. Atom Transfer Radical Polymerization (ATRP) has been mostly used for tethering graft polymeric chains on PVDF backbone in most of the literature reports. However, yield of co-polymer and degree of control exerted on polymerization is rather poor in these reports.[1,2] Here we report a novel technique for grafting of various polymeric chains derived from vinyl monomers[mainly (meth)acrylates].The strategy involved Atom Transfer Radical Addition(ATRA) [3] of 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl radical(4-HydroyTEMPO) on PVDF backbone, by copper based catalyst system, followed by coupling of suitable acyl halide moieties to develop model initiating sites for ATRP of vinyl monomers. After this a 'grafting from' strategy has been applied for polymerizing different monomers by ATRP with copper based catalyst system at 60^0 C, to develop a variety of PVDF based graft co polymeric system. Characterisation of the synthesized polymers carried out using FTIR, FTNMR, GPC, DSC and XPS techniques. Degrafting of the grafted polymeric chains on PVDF backbone followed by their molecular weight characterization has been done for PVDF-g-Polymethylmethacrylate(PVDF-g-PMMA) system. A linear first order rate of monomer disappearance during grafting alongwith linear increase of molecular weight of the graft copolymers and low PDI is observed. PVDF-g-PMMA copolymers thus synthesized have been further used to initiate polymerization of methoxyethoxyethyl-methacrylate (MeO_2MA) to prepare PVDF-g-(PMMA-b-PMeO_2MA) under similar conditions.



References

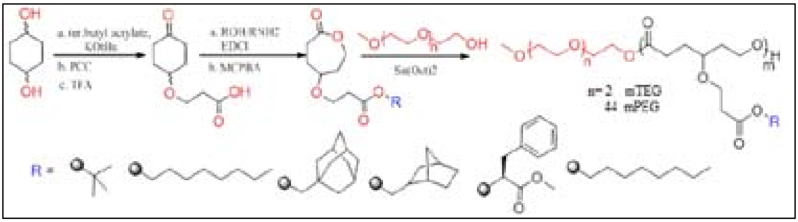
[1] Hester, J. F.; Banerjee, P.; Won, Y.Y.; Akthakul, A.; Acar, M. H.; Mayes, A. M. *Macromolecules* 35 (**2002**) 7652.
[2] Samanta, S.; Chatterjee, D. P.; Manna, S.; Mandal, A.; Garai, A.; Nandi, A. K. *Macromolecules,* 42 (**2009**) 3112.
[3] Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z**.** *Macromolecules* 31 (**1998**) 5955.

TP5

γ-Substituted Poly(caprolactone)s: Design, Synthesis and Polymer Self-organization

Bapurao Surnar and M. 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

Aliphatic polyesters are important class of polymers for applications in biomedical and pharmaceutical industry. Ring-opening polymerization (ROP) of cyclic ester is one of the extensively employed synthetic methodologies for aliphatic polyesters. ROP facilitates formation of narrow molecular weight distribution (PDI) as well as block and graft copolymer architectures. The present work highlighted the synthesis and structural analysis of new classes of γ-substituted caprolactones (monomers) having hydrophilic and hydrophobic substitution. The ring opening polymerization of caprolactones (caprolactone, substituted polycaprolactone) performed by using $Sn(Oct)_2$ as a catalyst and methoxypolyethylene glycol (mPEG 2K) and methoxytriethylene glycol (mTEG) as initiators. The monomers 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. The newly synthesized γ-substituted polycaprolactones are thermally stable up to 250-280 °C. Substituted polycaprolactones having adamentane, norbornane, octyloxy, octylamine units were found to be amorphous in nature. Selective syntheses of random and triblock substituted co-polymers were also achieved. The random block copolymers were found to be amorphous whereas triblocks are crystalline in nature. Further studies were carried out to understand the roles of chain hydrophilic/ hydrophobicity, self-assembled nano- aggregates in water and Zeta potential, etc. Thus, the current design molecular design provides new opportunity to tune the structure-property relationships of the aliphatic polymers based on polycaprolactones.



References :

1. James T.; Greg G. Qiao, *Macromolecules* 39 (**2006),** 9018-9027.
2. Trollas M,; Victor Y,;David M,; Robert DM,; James L.Hedrick. *Macromolecules* 33 (**2000),** 4619-4627.

TP6

Controlled Radical Polymerization of *N*-phenylitaconimide with Methyl Methacrylate: Experimental and Theoretical Study

Chetana Deoghare[§], R. N. Behera*, Rashmi Chauhan*
Department of Chemistry, BITS, Pilani – K. K. Birla Goa Campus, Goa-403726 INDIA
[§]Presenting author email:chetskm@gmail.com
**Corresponding authors email: rchauhan@goa.bits-pilani.ac.in / rbehera@goa.bits-pilani.ac.in*

The incorporation of imides such as itaconimides in the polymer backbone is reported to enhance glass transition temperature and thermal stability of resulting polymers [1]. The copolymerization of *N*-substituted itaconimides with monomer such as 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 [2]. It will be of interest to synthesize these copolymers using atom transfer radical polymerization (ATRP) process which is known to give polymers with known architecture with active chain ends [3]. In this work, we report the copolymerization of *N*-phenylitaconimide (PI) and MMA using CuBr/Bipy catalyst in anisole at 80^0C and ethyl-α-bromoisobutyrate (EBiB) as initiator. Also, we have investigated the possibilities of potential new initiators R-X (3°, 2° and 1° alkyl halides having structural resemblance to PI) for the copolymerization process using density functional theory (DFT) method.

The structural and molecular characterization of the synthesized copolymer of PI with MMA has been done by ^{1}H-NMR and gel permeation chromatography, respectively. The linear first-order kinetics of monomer with time as well as linear evolution of the molecular weight with conversion confirms controlled polymerization. We study the (C-X) bond dissociation energy for the potential initiators (R-X, X: Cl, Br, I) as well as the current one (EBiB) in gas phase as well as in polar solvent using B3LYP/6-31+G(d) method. Comparison of equilibrium constants for the initiation of ATRP process (K_{ATRP}) of the investigated initiators show that many of them have K_{ATRP} values comparable to that of EBiB and thus can be of potential initiators for the studied copolymerization process.

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.

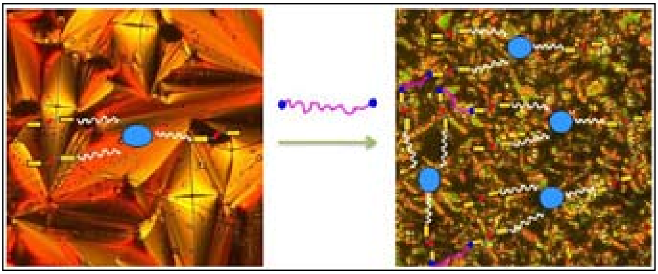
TP7

Star Shaped Liquid Crystalline Azobenzene: Monomers to polymers

Chinmay G. Nardele and Asha S. K.*
*Polymer Science and Engineering division, National Chemical laboratory,
Pune-411 008 INDIA

Hyperbranched polymers (HBPs) are an interesting class of materials due to their very close resemblance with dendrimers in many physical and chemical properties like high solubility, low viscosity and the presence of large number of functional groups. The simple one pot synthesis of HBPs from a AB_x or A_x+B_y monomers make an advantage over dendrimers which require tedious multistep synthesis. The hyperbranched liquid crystalline polymers (HBLCPs) are a structural classification of liquid crystal polymers where the mesogen can be introduced during or after polymerisation in a branched structure. The structural uniqueness of HBLCPs help to get faster switching response in devices compared to the main or side chain LC polymers. Azobenzene is a well known mesogen as well as photoresponsive chromophore that can undergo photoisomerization. Liquid crystalline materials containing azobenzene has generated a lot of research interest and they are widely used in the preparation of optical shutters, optical displays, photocontrollable coatings, etc.

Here we are describe the design and synthesis of a novel HBLCPs having disk like phloroglucinol connected to a calamatic (rod shape) azobenzene mesogen. The monomer design consisted of either a three arm (B_3) or four arm (B_4) star shaped molecules. In the B_3 type monomers the phloroglucinol core was connected to three polymerisable azobenzene arms via flexible methylene spacer of five or ten unit alkyl spacer length whereas the B_4 type monomers had a dimeric phloroglucinol structure with four polymerisable azobenzene arms. In all monomers the terminal azobenzene was suitably substituted with methyl carboxylic ester which was polymerized with tetraethylene glycol (A_2 type monomer) by transesterification route to get the hyperbranched polymers. The structural characterizations of both the monomers and the polymers were done using ^{1}H-NMR and ^{13}C-NMR. The molecular weights of polymers were determined by GPC analysis. The thermal stability of all monomers and polymers were analysed using TGA and the phase transitions were studied using differential scanning calorimetry (DSC) coupled with polarised light microscope (PLM). The star shaped monomers and polymers exhibited LC behaviour, with the three arm star shaped monomers showing smectic LC phases whereas the dimeric four armed monomer showed switching phase behaviour from smectic to discotic LC. Interstingly, the hyperbranched polymer of B3 monomer having five methylene spacer with TEG diol also showed smectic to discotic LC phase transition which was stable at even room temperature.



References:

1) Marcos, M.; Martin-Rapun, R.; Omenat, A.; Serrano, J. L. *Chemical Society Reviews* **(2007)** 36 1889

TP8

Self-Curing, High Temperature PhthalonitrileThermosets – Synthesis, Cure Characteristics and Network Formation

Dhanya Augustine, Dona Mathew*, C.P.Reghunadhan Nair
Polymers and Special Chemical Group, PCM Entity, Vikram Sarabhai Space Centre
Email id : *dona_mathew@vssc.gov.in*

The present study is focused on realizing self- cure promoting, high temperature phthalonitrile polymers with low cure temperature and short cure times comparable to epoxies without impeding the high temperature capability of phthalonitrile resins. With this view, different compositions of amine-incorporated, self-curing novolac-phthalonitrile systems (APN) were realized using appropriate synthesis strategy and characterized. The cure characteristics of the different compositions were monitored by DSC and rheometry. Incorporation of amine functions facilitated acceleration of the cure reaction. Thus, about 130 °C decrease in cure initiation was achieved with the incorporation of 20 mol % of amine functionalities into novolac-phthalontirile oligomer. Analysis of the cured products indicated that, the cure reaction proceeds through amine-mediated reaction of nitrile groups, resulting in formation of heterocyclic intermediates like isoindoline, triazine and phthalocyanine networks [1]. Cured networks of amine functionalized phthalonitrile systems were highly thermally stable (T_i~ 420 °C) and yielded char residue about 79 % at 900 °C. Thermosetting blends of APN with epoxy novolac (EPN) and diglycidyl ether of Bisphenol A (Gy 250) were formulated and their cure behavior was monitored by FTIR, DSC and rheological analysis. DSC scans of the blends showed three exotherms corresponding to the curing of epoxy-amine, epoxy-phthalonitrile and amine-phthalonitrile systems in the temperature ranges of 80 °C, 150 °C and 250 °C and thereby altering the cured network structure (epoxy-amine adduct, oxazoline formation) and consequent properties of phthalonitrile systems [2]. The study revealed that the APN/epoxy blends exhibited good processability without significant compromise in their thermal stability. Self-curing APN/epoxy thermosets will be an excellent high performance matrix.

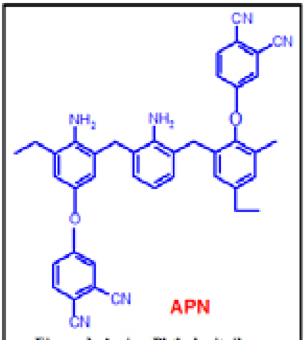


Figure 1. Amino-Phthalonitrile

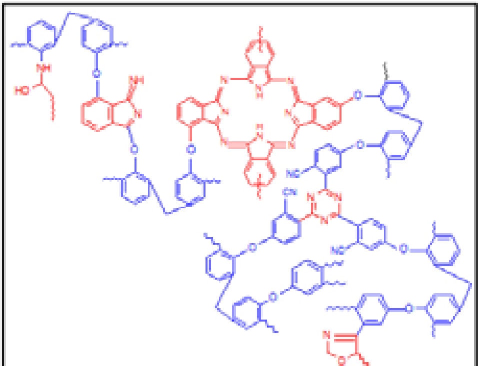


Figure 2. Probable network structure of Epoxy-amino phthalonitrile

References
[1]. Sumner, M; Sankarapandian, M; Mc Grath, J and et al. *Polymer*, 43 (**2002**) 5069
[2]. Hang, G; Yanke, Z; Zhiran, C and et al. *High perf polym*, June **2012** (published online)

TP9

Addition Curable Fluorosilicones for Space Applications– Synthesis, Characterization and Viscoelastic Studies

[a]Indulekha K*, [a]Ann Mathew, [a]Prasanta Kumar Behera, [b]Soumyamol P.B, [a]R.S.Rajeev
[a]Polymers and Special Chemicals Division
[b]Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Thiruvananthapuram-695022 INDIA
**corresponding author; email: k_indulekha@vssc.gov.in*

Fluorosilicones are a class of high performance polymers which combines the properties of siloxanes and fluorocarbon polymers for applications requiring low temperature flexibility, high temperature stability and fuel resistance. Up to now, fluorosilicone rubber containing a 3,3,3-trifluoropropyl (TFP) group [$-CH_2CH_2CF_3$] has found large-scale commercial application.[1] Various methods, such as the ring-opening polymerization of cyclosiloxanes,[2] hydrolysis and condensation of dichlorosilane which is bonded with methyl and fluorine alkyl,[3] have been employed for the preparation of the gum for fluorosilicone rubber.

This paper describes the synthesis and characterization of hydrocarbon resistant poly(dimethyl-co-methyltrifluoropropyl) siloxanes. A series of vinyl terminated poly(dimethyl-co-methyltrifluoropropyl) siloxane with varying fluorine content were synthesized via anionic ring opening copolymerisation of octamethylcyclotetrasiloxane (D4) and 1,3,5-trimethyl-1,3,5-tris (3,3,3-trifluoropropyl) cyclotrisiloxane (F3) in presence of a chain terminator, 1,3-divinyltetramethyldisiloxane as shown in Fig.1.

The resultant vinyl functional siloxane was curable in the form of an elastomer via platinum catalysed hydrosilylation mechanism using a hydride crosslinker. The synthesized polymers were characterized by FT-IR, 1H NMR and 29Si NMR. Based on 1H NMR and 29Si NMR analyses, it was found that the composition of each copolymer was almost equal to the feed ratio, and the sequence distribution of each polysiloxane followed random statistics. It was found that the glass transition temperatures (Tg) of the copolysiloxanes increased with the increase in fluorine content which was evident from the positive shift in Tg from -120°C to -65 °C in dynamic mechanical analysis. The synthesiszed polymers were compounded using inorganic fillers and studied for their mechanical and thermal properties. The thermal data showed that copolymeric systems exhibited good thermal stability with peak decomposition temperature above 500°C. The swelling studies in different hydrocarbons of varying carbon numbers showed that the introduction of -CH2CH2CF3 groups greatly improved the hydrocarbon resistance of the polymer. The studies showed that copolymeric siloxane systems with trifluoropropyl pendant units can be used as solvent resistant coatings with broad service temperature range for aerospace applications by appropriate compounding.

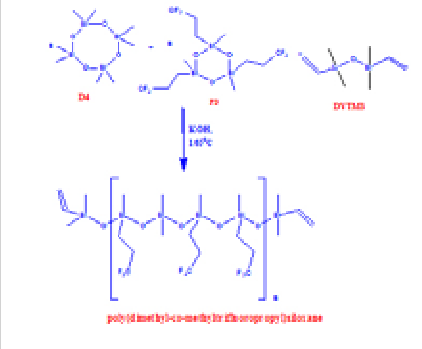


Figure 1. Synthesis of fluorosilicone copolymer

References

[1] Chaffee, R. G.; Siegel, R. A.; Voci, R. J. *U. S. Pat., 5171773*, **1992**
[2] Barrere, M.; Maitre, C.; Dourges, M. A.; Hemery, P. *Macromolecules*, 34 **(2001)** 7276–7280.
[3] Furukawa, Y.; Shin-Ya, S.; Miyake, H.; Kishino, H.; Yamada, M.; Kato, H.; Sato, M., *J. Appl. Polym. Sci.*, 82 **(2001)** 3333–3340.

TP10

Recognition of 5-Fluorouracil (5-Fu) by Multiwalled Carbon Nanotubes

Jeena Abraham, Beena Mathew*
School of Chemical Sciences, Mahatma Gandhi University, Kottayam-656560
Jeenaabraham23@gmail.com

Molecularly imprinted polymers (MIPs) are special polymers that are attained by the polymerization of a monomer with a crosslinker in the presence of a template molecule. Molecular recognition sites are formed after the extraction of the template molecule from the polymerized material. The formed cavities are complementary to the template in size and shape for the subsequent rebinding process. Through the formation of the MIP on the surface of MWCNTs, the accessibility of the analyte to binding sites can be improved, and the binding time can be reduced.

A novel MWCNT supported with homogeneous 5-Fluoro uracil imprinted outer layer for its selective recognition was synthesized. For fabricating MIPs on MWCNT, the vinyl group was first introduced on the surface of MWCNT, which directed the selective polymerization of functional monomers and crosslinkers in the presence of 5-FU on the MWCNT surface. Various analytical techniques confirmed the homogeneous formation of MWCNT MIP binding sites; 5-FU imprinted carbon nanotube showed its specific rebinding. In the kinetic study, it was found that the rate of adsorption 5- FU increased rapidly in the initial stage and then reduced after it reached equilibrium. Compared a to pseudo first order model, a second order kinetic equation gave a better fit for the adsorption kinetic data. The adsorption increased with increasing 5-FU concentration. The results showed that the adsorption process obeys a Langmuir adsorption isotherm. The fabricated system showed remarkable selectivity towards 5-FU from other structurally related compounds such as thymine and uracil. The fabricated polymer also conduct in chromatographic separation,

References

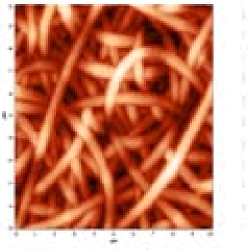
1. Rezaei, B.; Mallakpour, S.; Rahmanian.; *J Iran Chem Soc*, 7,(**2010**), 1004.
2. Li Xu.; Zhi-feng Xu.; *J Polym Res*,19, (**2012**), 9942.

TP11

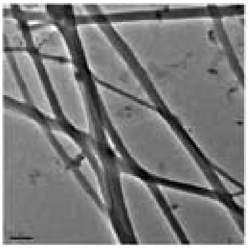
Electrospun Nanofiber Based Colorimetric Sensor For Formaldehyde Detection

K. Kavitha[a] and D. Ravi Shankaran[b]*
[a] *Department of Biomedical Engineering, PSG College of Technology,*
Peelamedu, Coimbatore-641 004, INDIA
[b]*Nano-Bio Materials and Sensors Laboratory, PSG Institute of Advanced Studies,*
Peelamedu, Coimbatore-641 004, INDIA
** drs@ias.psgtech.ac.in; dravishankaran@hotmail.com*

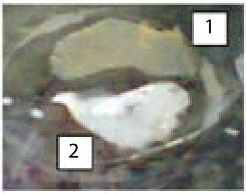
There is a great interest in the synthesis of polymeric nanofibers for various applications. Among the wide variety of polymers, polymethylmethacrylate (PMMA) is promising for diverse applications owing to its excellent chemical, physical, biological, optical and thermal properties. Here, we have fabricated PMMA based nanofibers by facile electrospinning technique. Electrospinning is a versatile method for producing functional nanofibers with desired characteristics [1]. Various experimental parameters such as polymer concentration, distance between the tip to collector, voltage applied, flow rate have been optimized to achieve reproducible nanofibers. We obtained PMMA nanofibers in the diameter range of 50-500nm. Optical microscopy, atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) techniques were used to characterize the as-spun nanofibers. Thus formed PMMA nanofibers have been evaluated for colorimetric sensing of formaldehyde [2]. Detection of formaldehyde is important for various applications such as environmental monitoring, food quality assessments and medical diagnostics. The fabricated fibers were treated overnight with Fluoral-P and Polyethylenimine (PEI). Thus treated fibers shows specific color change (white to yellow) when exposed to formaldehyde vapors. This method provides a simple and low-cost device for formaldehyde detection unlike the conventional methods which requires time consuming sample preparation and sophisticated instrumentation.



AFM image of optimised fibers



TEM image of optimised fibers



Response of Fluoral-P/PEI treated (1) and Untreated (2) samples when exposed to HCHO

References
[1] Bhardwaj, N.; Kundu, S. C.*Biotechnology advances 28*(3) (**2010**) 325-347.
[2] Chigome, S.;Torto, N. *Analytica chimica acta 706*(1) (**2011**) 25-36.

TP12

Castor oil Polyurethane/Siloxane Cross-Linked Structures: Influence of Siloxane Cross-Linking on its Properties

K. Seeni Meera, R. Murali Sankar, A. Murali, S. N. Jaisankar and Asit Baran Mandal*
Polymer Division, Council of Scientific and Industrial Research (CSIR) –
Central Leather Research Institute (CLRI), Adyar, Chennai 600020, Tamil Nadu, India.
**E-mail: abmandal@hotmail.com; abmandal@clri.res.in*
Tel.: +91-44-24910846/0897; Fax: +91-44-24912150.

The development of polyurethane (PU) materials based on bio-renewable resources is of current interest, due to the environmental pollution, high price and depletion of petroleum raw materials [1,2]. Of which, castor oil (CO) is the widely used vegetable oil as a raw materials in paints, coatings, lubricants and also used in implants and therapeutic agents [3]. The unique property of castor oil containing 90% ricinoleic acid bearing hydroxyl group, which acts as a tri-hydroxyl functioned monomer [4].

Recently, combination of polyurethane and siloxane received much attention due to its biostability and mechanical stability. Siloxane linkage (SiO_2 chain) obtained by sol-gel process has its own properties like low glass transition, minimum surface energy, less moisture permeability and less toxicity [5,6]. Siloxane linkages provide applications to different fields viz., self-cleaning processes, leather coatings, clotting prevention in artificial blood vessels, cultural heritage, and monument surface protection [7,8].

Figure 1. Structure of castor oil polyurethane/ siloxane cross-linked structure.

Our aim is to combine both the properties of polyurethane and siloxane to have better biocompatibility as well as thermal stability. Here, we have synthesised castor oil based PU/siloxane cross-linked films using isophorone diisocyanate, dibutyltin dilaurate and 3-aminopropyl trimethoxysilane in $CHCl_3$ at 70 °C under N_2 atmosphere. by sol-gel process [9]. Figure 1 represents the structure of castor oil polyurethane/siloxane cross-linked structures.

FT-IR spectra proved the strong crosslinking interaction between PU and siloxane moieties, which shift the peak positions of PU N-H and C=O groups [10]. Solution ^{1}H-NMR spectra confirm the formation of polyurethane/siloxane structure and solid state ^{29}Si CP/MAS NMR spectra reveal the formation of siloxane network structure. The activation energy parameters for the degradation process of PU films were calculated using Kissinger method, which evidence that the thermal stability increases with the increase of siloxane content. Hydrophobicity and homogeneity of the PU surface were analysed by contact angle measurements. UV-vis measurements prove that all the PU samples exhibit more than 85% transmittance. Moisture sorption reveals the moisture adsorption capacity of the films. SEM-EDX analysis shows the surface morphology and elements present in the films. AFM analysis evidenced that increasing siloxane content decreases the surface roughness from 13.4 (PU 1.0) to 4.7 nm (PU 1.5). These new kinds of PU materials may have applications in lens coatings and optical fibre, etc [11].

References

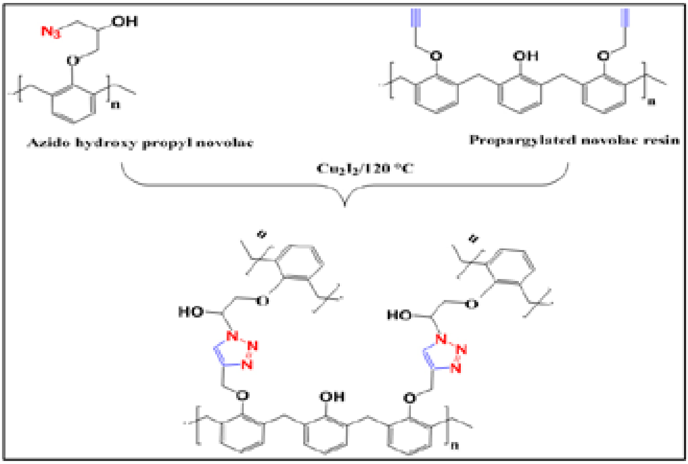
[1] Karak, N.; Rana, S.; Cho, J.W. *J. Appl. Polym. Sci.* 112 (**2009**) 736.
[2] Babu, B. R.; Meera, K. S.; Venkatesan, P.; Sunandha, D. *Water Air Soil Pollut*. 211 (**2010**) 203.
[3] Ogunniyi, D.S. *Bioresour. Technol*. 97 (**2006**) 1086.
[4] Xia, Y.; Larock, R.C. *Polymer* 51 (**2010**) 2508.
[5] Meera, K. M. S.; Sankar, R. M.; Jaisankar, S. N.; Mandal, A. B. *Colloids Surf., B* 86 (**2011**) 292.
[6] Li, C.-Y.; Chen, J.-H.; Chien, P.-C.; Chiu, W.-Y.; Chen, R.-S.; Don, T.-M. *Polym. Eng. Sci.* 47 (**2007**) 625.
[7] Seeni Meera, K. M.; Murali Sankar, R.; Murali, A.; Jaisankar, S. N.; Mandal, A. B. *Colloids Surf., B* 90 (**2012**) 204.
[8] Milanesi, F.; Cappelletti, G.; Annunziata, R.; Bianchi, C.L.; Meroni, D.; Ardizzone, S. *J. Phys. Chem. C* 114 (**2010**) 8287.
[9] Seeni Meera, K.; Murali Sankar, R.; Jaisankar, S.N.; Mandal, A. B. *J. Phys. Chem. B* (**2013**) DOI: 10.1021/jp3097346.
[10] Murali Sankar, R.; Seeni Meera, K.; Mandal, A. B.; Jaisankar, S. N. *High Perform. Polym.* 25 (**2013**) 135.
[11] Tan, H.; Yang, D.; Xiao, M.; Han, J.; Nie, J. *J. Appl. Polym. Sci.* 111 (**2009**) 1936.

TP13

Syntactic Foam Composites based on Phenolic Resin Cured via Click Chemistry

K. Sunitha, Dona Mathew*, C.P.Reghunadhan Nair
Polymers and Special Chemical Group, PCM Entity, Vikram Sarabhai Space Centre
Email id: *dona_mathew@vssc.gov.in*

Phenolic-triazole-epoxy matrix resin based syntactic foam composites of varying compositions were realized through click chemistry [1]. Propargylated novolac (PN), Bisphenol A bisazide (BABA) and azido hydroxyl propyl novolac (AHPN) were synthesized, characterised and coupled via azide-alkyne click reaction forming triazole linked phenolic-epoxy networks [2]. Catalytic curing of the propargylated novolac and the azido compounds in presence of Cu_2I_2 was initiated at 40-65°C as shown in scheme 1. Glass transition temperature of (Tg) of the cured networks varied from 70°C to 75°C in the case of BABA-PN and 75°C to 80°C in the case of AHPN-PN. Cure reaction of the systems was followed by rheokinetics evaluations which revealed single stage curing pattern. Silica fibre- reinforced syntactic foam composites of density 0.55g/cc were processed using these resin systems and glass microballoon as fillers. Their mechanical properties and impact strength were correlated to the composition of the blends. Thermal stability of the cured BABA-PN and AHPN-PN blends were evaluated and correlated to the structure and composition of the cured networks. The syntactic foam composites cured at 120°C possessed comparable mechanical properties and superior impact resistance compared to their phenolic resin based counter parts. These syntactic foam composites pose a promising alternative to phenolic resin based systems foams for possible aerospace applications owing to this better processability and comparable thermal and mechanical properties.



References

[1]. Tsarevsky NV; Bernaerts KV; Dufour B; Du Prez FE;Matyjaszewski K. *Macromolecules*, 37(**2004**) 9308.

[2]. Bindu RL; Reghunadhan Nair CP; Ninan KN. *Polym Inter* 50 (**2001**) 651.

TP14

Synthesis and Characterization of Phthalonitrile Resin Containing Bismaleimide Group

K.Kumudha and Dr.M.Sarojadevi*
Department of Chemistry, Anna University,
Chennai-600025 INDIA
msrde2000@yahoo.com

Phthalonitriles are one of the leading candidates for use in composite structures where thermally stable, high performance resins are required. Phthalonitriles constitute a class of high-temperature polymers that has a number of exceptional properties such as high glass transition temperatures (Tg), outstanding thermal and thermo-oxidative stability, excellent mechanical properties, good moisture resistance and superior fire resistance [1].

Bismaleimides are another type of thermosetting polymers. The main drawback of bismaleimides is their brittleness [2]. To reduce the brittleness and improve the toughness of BMI resins, an attempt was made, to copolymerize phthalonitriles and bismaleimides [3]. 4-Nitro Phthalonitrile, 4-amino phenoxy phthalonitrile, various aromatic diamines, corresponding bismaleimides were synthesized. Synthesized bismaleimides were treated with 4-aminophenoxy phthalonitrile, to prepare bisphthalonitrile monomer containing bismaleimide group. Structures of all the synthesized compounds were confirmed by FT-IR, NMR techniques. Thermal properties of the phthalonitrile copolymers weres analyzed by DSC and TGA techniques.

References

[1] Keller TM, Dominguez DD. Polymer, 46 (2005) 4614-8.

[2] Ying-Ling Liu, Yu-Jane Chen. Polymer 45 (2004) 1797-1804.

[3] Juhua Zhang, Xinhua Liu, Huarong Wen, Meili Xie & Xingxian Cai. Polymer International 42 (1997) 363-366.

TP15

Fundamental Insights into Dimer emission from 100 % Pyrene loaded Methacrylate Comb Polymers: TRES and Temperature dependent Fluorescence

Kaushlendra Kumar and Asha S.K.*
Polymer Science and Engineering Division,
National Chemical Laboratory
Pune-411008

The molecular self-assembly of polymers into microstructures through secondary interactions like hydrogen bonding or hydrophilic- hydrophobic balance is an area of research that has attracted a lot of interest. The investigation of self-organization among the polymers can be done by morphological as well as photophysical studies. The origin of excimer formation in novel comb methacrylate homopolymers having a fluorophore pyrene as pendant is discussed in great detail. Their self organization behaviour was extensively studied by the photophysical investigations. The photophysics of the polymers for the very dilute solutions in DMF were investigated by steady state emission, fluorescence decay studies, time resolved emission (TRES), variable temperature emission studies. It was observed that the polymer **PPH** having non-hydrogen bondable ester linkage in the hanging (pendant) chains formed excimer completely via static mechanism only and these ground state aggregated species were stable even at higher temperatures. The polymer **PIP** having short chain and hydrogen-bondable urethane linkage formed excimer via contribution of both static as well as dynamic mechanism. The other hydrogen bondable urethane methacrylate polymers having a linear linker (**PHHP**) and kinked linker (**PIHP**) formed excimer mostly via dynamic mechanism with small contribution from static route. The TRES carried out for these polymers provided significant insight into excimer formation in these 100 % Pyrene homopolymers. The findings presented here will help in fundamental understanding of the role of architectural differences in the self-organization process.

References:

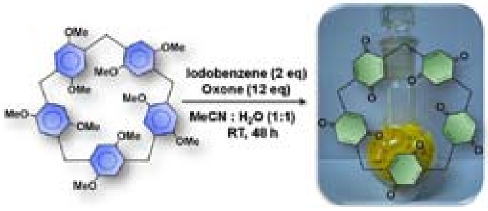
1) Kaushlendra, K.; Asha, S. K. *Langmuir* **2012**, *28*, 12731.
2) Kaushlendra, K.; Deepak,V. D.; Asha, S. K. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1678.
3) Deepak, V. D.; Asha, S. K. *J. Phys. Chem. B* **2009**, 113, 11887.
4) Rekha, N.; Asha, S. K. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 2996.

TP16

An Easy and Multi-Gram Synthesis of Pillar[5]quinone and its Solvent Mediated Self-Assembly

Kilingaru I Shivakumar and Gangadhar J Sanjayan*
Division of Organic Chemistry, National Chemical Laboratory,
Pune-411008 INDIA

Pillar[n]arenes[1,2] are a new class of $[1_n]$ paracyclophanes with similar composition to that of calix[n]arenes but having different structural features. Pillararenes, unlike few other macrocycles, possess exceptional molecular symmetry with electron rich cavity, are easy to functionalize and have good solubility in organic solvents. Pillararenes have found applications in the fabrication of (*pseudo*) rotaxanes or poly(*pseudo*)rotaxanes, supramolecular dimers or polymers, artificial transmembrane proton channels, and as fluorescent sensors and molecular recognizers.



Scheme 1. Synthesis of Pillar[5]quinone from DMpillar[5]arene

The oxidized form of pillar[5] arene *viz.* pillar[5]quinone (P[5] Q)[3,4] (Scheme.1) is structurally very much intriguing, not only because all the five quinone rings are part of the cyclamer backbone, but also due to the symmetrical crowning of the periphery by ten carbonyl oxygen atoms. Indeed, computational studies have suggested that P[5]Q could showcase intramolecular charge transfer upon excitation of electrons from HOMO to LUMO, owing to the large difference in the electron distribution between them.[5] Furthermore, P[5]Q-derived systems have been predicted to be promising candidates for trapping anionic halogens.[5] All these properties and their potential applications make P[5]Q a highly useful building block for researchers. From this perspective, ready access to P[5]Q in substantial quantities would clearly be of considerable importance.

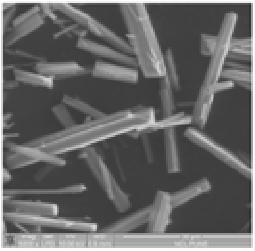


Fig. 1 SEM image of P[5]Q-TCE

We have developed an environmentally benign, chromatography free, easy-to-operate strategy to synthesize and isolate the macrocyclic quinone P[5]Q in multi-gram scale[4]. Isolation was effected simply by crystallization from 1,1,2,2-tetrachloroethane (TCE). P[5]Q formed TCE mediated rod shaped supramolecular ensemble[6] (Fig.1) as evident from surface analyses (SEM, TEM and AFM). The crystal structure[6] obtained from the synchrotron-aided PXRD simulation gave more insight into the solvent-mediated self- assembly. Thermal studies[6] revealed physical property changes of the self-assembly. Cyclic voltammetry[6] (CV) was performed to find out the redox behavior of the macrocyclic polyquinone. The obtained voltammogram revealed the complex redox behavior of P[5]Q.

References:

[1]. Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* 130 (**2008**) 5022.
[2]. (a) Cragg, P. J.; Sharma, K. *Chem. Soc. Rev.* 41 (**2012**) 597. (b) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. Acc. Chem. Res. 45 (**2012**) 1294.
[3]. Cao, D.; Kou, Y.; Liang, J.; Chen, Z.; Wang, L.; Meier, H. *Angew. Chem. Int. Ed.* 48 (**2009**) 9721.
[4]. Shivakumar, K.I.; Sanjayan, G.J. *Synthesis* 45 (**2013**) 896.
[5]. Lao, K.-N.; Yu, C.-I. J. Comput. Chem. 32 (**2011**) 2716.
[6]. Shivakumar, K.I.; Harris, K.M.D.; Sanjayan, G.J. (manuscript to be communicated)

TP17

pH-Responsive Polymersome from a Tri-Block Copolymer Synthesized in One Pot

Krishna Dan and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the Cultivation of Science Jadavpur, Kolkata-700032
Email: psusg2@iacs.res.in

Various "click" reactions have made strong impact in synthesis of functional polymers during last decade. Thiol-acrylate Michael addition reaction satisfies all criteria of a so called "click" reaction such as quantitative yield, mild reaction condition and generation of no by-products. Additionally it produces a β-thio propionate linker in the resulting material which in known to undergo hydrolytic cleavage selectively in acidic pH and at a very slow rate. For this reasons, we have been interested in exploring this particular reaction [1] to make pH-responsive amphiphilic macromolecules.

Recently we have demonstrated synthesis of telechelic polymer using (**P1**, Scheme 1) thiol-acrylate Michael addition reaction between a hydrophobic di-thiol and di-acrylate with stoichiometric imbalance so that the P1 contained free thiol functional groups in both ends. It was subsequently added with acrylate terminated PEO (**P2**, Scheme 1) in same reaction pot to generate amphiphilic ABA type triblock copolymer **P3** (Scheme 1). **P3** showed vesicular assembly in aqueous medium and could encapsulate both hydrophobic and hydrophilic guest molecules. Due to the presence β-thio propionate group in the polymer backbone, the vesicles could be disassembled under mild acidic condition (pH ~ 5.0). [2] This resulted in sustained release of encapsulated pyrene selectively at pH 5.4 while no such release was observed at pH ~ 7.0. It is noteworthy that in cancer cells pH is acidic compared to healthy cells. Thus mild acid-induced slow disassembly may find relevance in targeted drug delivery application particularly considering synthetic ease at which the polymer could be made in one pot. This presentation will elaborate on synthesis detail and pH responsive self-assembly studies of this newly developed system in our group.

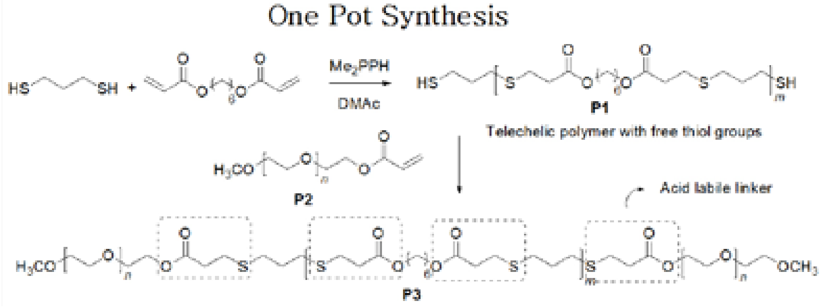


Figure 1. One pot synthesis of amphiphilic tri-block copolymer (P3)

References

[1] Shin, J.; Matsushima, H. J.; Chan, W.; Hoyle, C. E. *Macromolecules* 42, (**2009)**, 3294.
[2] Dan, K.; Bose, N.; Ghosh, S. *Langmuir* 27, (**2011)**, 612-617.

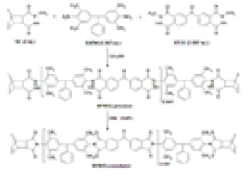
TP18

PMR-15 Type Polyimides With Non-carcinogenic Diamines

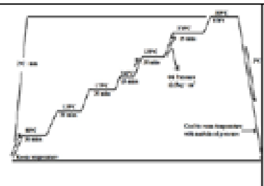
M. Selladurai[a], C.P.R. Nair[b], Dona Mathew[b], P. Sundararajan[c] and M. Sarojadevi[a]
[a] *Department of Chemistry, Anna University, Chennai - 600 025, India*
[b] *Polymers and special chemicals division, VSSC, Trivandrum, India*
[c] *Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa,Ontario K1S 5B6, Canada*
* *msrde2000@yahoo.com*

During the last four decades, high performance polymers and fiber-reinforced polymer composites, being light weight, have found increased application in aerospace structural components as replacement for metals. The PMR-15 system developed by NASA is an attempt to combine the advantages of both systems: an addition mechanism with minimum volatile formation during cure [1]. PMR-15 is prepared in two stages from the monomers viz. 2-carbomethoxy-3-carboxy-5-norbornene (nadic ester, NE), 4,4′-methylene dianiline(MDA) and the dimethyl ester of benzophenone tetracarboxylic acid (BTDE). Though the PMR-15 are easily processed, they undergo extensive microcracking and the monomer methylene dianiline (MDA) is a mutagen and a suspected carcinogen. For this reason the Occupational Safety and Health Agency (OSHA) has established rigid regulations for the safe handling of materials containing MDA[2].

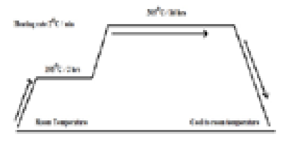
It has been demonstrated that introduction of bulky alkyl groups on both phenyl rings of MDA especially in the ortho positions significantly reduces or eliminates mutagenic activity [3]. Hence, in the present study three aromatic diamines with methyl groups ortho to the amino group were prepared and used in the place of MDA to make PMR-15 type of resins. Modified PMR-15 type prepolymers were made by reacting a diamine (3.084 mmoles) with mono-methyl ester of cis-5-norbornene-endo-2,3-dicarboxylic acid (2 mmol) and di-methyl ester of 3,3′,4,4′-benzophenonetetracarboxylic acid (2.084 mmole). The structure of the prepared diamines and prepolymers were studied using elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques. The cure behaviour of the prepolymers were studied using DSC analysis and FT-IR. The thermal stability of the polymers was studied by TGA. Carbon fiber reinforced composites were made. The fiber content, void content, density, T_g and mechanical properties of the composites were studied.



Scheme for the preparation of the prepolymer



Cure schedule for the preparation of the composites



Post cure schedule for the preparation of the composites

Acknowledgements

The authors gratefully acknowledge Dr.K.Adhinarayanan and Dr.G.Periyasamy of Anabond Ltd, Chennai, for the unlimited support to carry out this project.

References

[1] Peter Delvigs, David L Klopotek and DeNise Hardy-Green, *High Perform. Polym.* 13 (2001) 301–312.

[2] US Dept. of Health and Human Services 1986 *Methylenedianiline: Current Intelligence Bulletin* **47**.

[3] R. Benigni, L. Passerini ,*Mutation Research,* 511 (2002) 191–206.

TP19

Synthesis, Characterization and Evaluation of Maleimido Undecanoate as a Polymerizable Surfactant in the Emulsion Copolymerization of Styrene and n-Butyl Acrylate

M. V. Reddy, N. Rajender, K.I.Suresh*
Polymers and Functional Materials Division,
CSIR- Indian Institute of Chemical Technology,
Tarnaka, Hyderabad - 500007, A. P. (state), India.
E mail: kisuresh@iict.res.in

Emulsion polymerization is one of the most important techniques for preparing polymers, from an industrial point of view, to prepare film forming lattices. In emulsion polymerisation, it is necessary to introduce surfactants in the recipe for control both the particle size and the stability of the lattices. However the presence of these species, which are generally low molecular weight compounds interacting with polymeric particles through adsorption involving weak H or π boding, may result in adversely affect the lattice stability and the final polymer properties[1]. For instance, lack of stability under conditions, such as high shear, freezing, or high ionic strength, may arise from the use of conventional surfactants. Furthermore, these amphiphilic molecules may migrate through the matrix upon film formation and affect the overall properties of the final polymeric material such as adhesion, water sensitivity and gloss. Migration of these molecules may also lead to their association and agglomeration leading to phase separation and increase in anisotropy in the final polymer that may affect its mechanical properties. The use of polymerizable surfactants (surfmers) can avoid these issues as they display the amphiphilic properties of standard surfactants and also chemically reactive (eg: covalently bound) with the growing polymer chains [2,3].

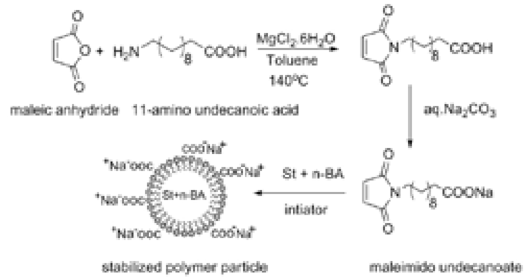


Figure 1:Schematic of the Synthesis of Polymerizable Surfactant and the prepared particles

This study deals with the synthesis, characterization and evaluation of a newly synthesized polymerizable surfactant (surfmer), starting from11-aminoundecanoic acid, which can be prepared from castor oil, a renewable resource. The prepared surfactant (Figure1) was characterized by ^{1}H, ^{13}C, mass and FT-IR techniques. The micellization behaviour of aqueous solution was studied by surface tension measurements. Dispersions of styrene and n-butyl acrylate with varying surfmer content were prepared. The particle size and polydispersity of the latex was analyzed by dynamic light scattering. The surfactant effect on the stability of the dispersions and particle size was studied. With increasing surfmer content the particle size decreased but the conversions increased. Film Properties were studied by TGA, DSC and techniques.

References:

[1]. Gilbert, R.G.(1995) Emulsion Polymerization : A Mechanistic Approach.; Academic Press: London.
[2] Sindt, O.; Gauthier, C.; Hamaide,T.; Guyot,A. *Journal of Applied Polymer Science* 77(**2000**) 2768.
[3]. Suresh, K, I.; Gesche, F.; Rolf, S.; Eckhard, B. *J Surfact Deterg* 15 (**2012**) 207

TP20

CNSL based polyols for polyurethane systems

Mukesh Kathalewar, Dr. Anagha Sabnis*
Department of Polymer & Surface Engineering, Institute of Chemical Technology,
Nathalal Parekh Marg, Matunga, Mumbai-400019, India.
** Dr. Anagha Sabnis: email: as.sabnis@ictmumbai.edu.in*

In ages of depleting fossil oil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development. Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars, wood and others.[1-2] Products obtained from these renewables are as diverse as pharmaceuticals, coatings, packaging materials or fine chemicals, to only name a few.[2-3] Cashew nut shell liquid (CNSL), an agricultural by-product abundantly available in tropical countries such as India, is one of the major and economical resources of naturally occurring phenols. CNSL can be regarded as a versatile and valuable raw material for wide applications in the form of brake linings, surface coatings, paints, and varnishes as well as in polymer production.[4-5]

In the current investigation, diglycidyl ether of cardanol (NC-514) was used for preparation of polyols with variable functionalities. The glycidyl moiety in NC-514 was modified with various secondary amine compounds having pendant hydroxyl groups. The purified products were evaluated for hydroxyl number, FTIR and ^{1}H NMR.

These polyols were then cured with different polyisocyanate curing agents on mild steel substrates. The coatings were evaluated for mechanical (scratch hardness, pencil hardness, impact resistance, taber abrasion, tape adhesion, flexibility etc.), thermal (Differential scanning calorimetry (DSC) Thermo-gravimetric analysis (TGA)), chemical (solvent resistance, water resistance) and anticorrosive (Electrochemical impedance spectroscopy, tafel) properties. The study conducted revealed that these precursors could be successfully used as polyols for polyurethane systems wherein its hydrophobic nature and the excellent chemical resistance could be beneficial.

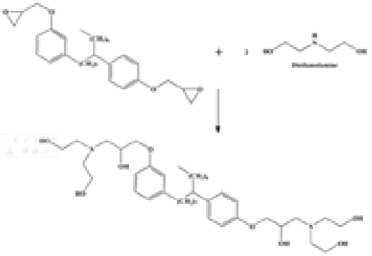


Figure 1: Schematic representation of synthesis of CNSL based polyol

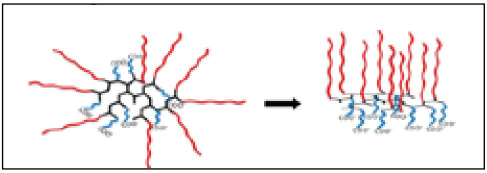
References
[1] Meier, M.; Metzger, J.; Schubert, U. *Chemical Society Reviews*, 36 (**2007**) 1788.
[2] Joseph, S.; John M.; Pathen L.; Thomas, S. *Hdb Environmental Chemistry* DOI: 10.1007/698_2009_21.
[3] Raquez, J.; Deleglise M.; Krawczak P. *Progress in Polymer Science*, 35 **(2010)**, 487.
[4] Lubi, M.; Thachil, E. *Designed Monomers and Polymers,* 3, **(2000)**, 123.
[5] Vasapollo, G.; Mele, G.; Sole, R. *Molecules*, 16 (**2011)** 6871.

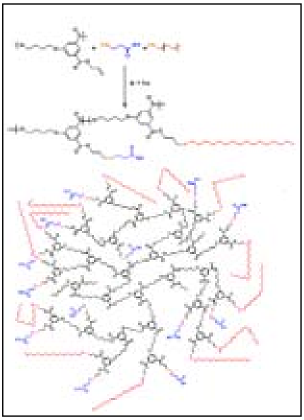
TP21

Hyperbranched Surfactants - *Hypersurfs*

N. S. Shree Varaprasad, Saheli Chakraborty and S. Ramakrishnan*
Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore-560012 INDIA
** raman@ipc.iisc.ernet.in*

Hyperbranched polymers (HBP) are highly branched structures that have demonstrated remarkable conformational adaptability to generate a variety of interesting constructs, such as core-shell, Janus structures, etc; this adaptability may be considered one of the most important virtues of these systems that make them strong rivals to the more structurally symmetric, but difficult to access, Dendrimers [1]. Designing simple strategies to place desired functionality at the periphery of HBPs would therefore be very important for imparting useful application-oriented properties; in view of this, we recently developed a simple approach to prepare peripherally azide-yne clickable polyesters [2], which when clicked with a variety of organic segments yielded interesting core-shell and Janus systems [3]. In the present study, we explore the possibility of preparing hyperbranched surfactants, namely *hypersurfs,* by randomly clicking both hydrophobic alkyl segments and ionic groups on the periphery of HBPs using the thiol-ene click reaction; the reorganization of these segments due to the adaptability of the backbone, we expect, would generate amphiphilic molecules that can behave like a collection of surfactants stitched together.





Diallyl, 5-(4-hydroxybutoxy) isophthalate was polycondensed via melt transesterification to obtain a HBP with numerous clickable allyl groups at the periphery; the periphery of the HBP was randomly clicked with the required quantities of hexadecane thiol and 3-mercaptopropionic acid using the thiol-ene click reaction. Proton NMR spectra clearly revealed the completion of the click reaction.

The ability to reorganize and segregate the hydrocarbon chains and the ionic carboxylic acid groups in an aqueous solution at high pH was examined by Langmuir isotherms; further, AFM imaging of the monolayers transferred on to a silicon substrate were carried out. DSC studies also confirmed the self-segregation of the hexadecyl segments, as evident from the melting transition associated with the alkyl chain crystallization. DLS studies revealed that the average size of the aggregates were in the range ~100-200 nm and the ζ potential, as expected, varied with the mole-fraction of the carboxylic acid. The results of these studies and a few of the other properties of these novel *hypersurfs* will be presented.

References

[1] Frechet, J. M.; Tomalia, D. A. Dendrimers and Other Dendritic Polymers; Wiley: New York, 2001.

[2] Ramkumar, S. G.; Rose, K. A. A.; Ramakrishnan, S. *J. Polym. Sci., Part A: Polym. Chem.* 2010, 48, 3200–3208.

[3] Ashok Z. Samuel, S. Ramakrishnan, *Macromolecules*, 2012, 45, 2348-2358.

[4] Raj Kumar Roy and S. Ramakrishnan, *J. Polym. Sci., Part A: Polym. Chem.* 2011, 49, 1735–1744.

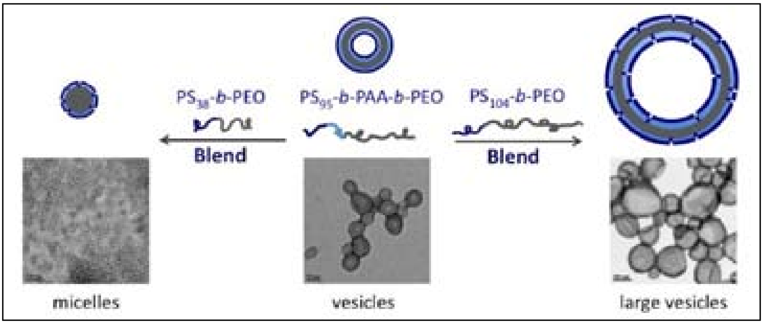
TP22

Controlling Morphologies of Amphiphilic ABC Triblock and AC Diblock Copolymer Binary Mixture in Aqueous Medium

Naganatha G. Patil and Ashootosh V. Ambade*
Polymer Science and Engineering Division, CSIR-National Chemical Laboratory,
Pune-411 008 INDIA

Amphiphilic block copolymers are widely studied for their self-assembly into different morphologies [1]. The structures formed are mainly influenced by hydrophilic weight fraction (W_{philic}) that represents the packing parameter. A given block copolymer shows a particular self-assembly based on W_{philic} under given preparation conditions and it is difficult to tune this parameter to get different morphologies with the same block copolymer. An interesting strategy to tune the block copolymer morphology in solution is to blend it with a homopolymer or copolymer in varying ratios [2]. This method also circumvents the need to synthesize a series of block copolymers. It provides an opportunity to prepare multifunctional polymeric materials such as drug delivery vehicles by blending appropriately functionalized polymers. Further, the morphology may be altered by the influence of interchain interactions such as hydrophobic interaction, among others, between the blended polymers [3].

ABC triblock copolymers impart complexity to the morphology that is desirable for aforementioned investigations by virtue of an additional block and hence are of great interest [4,5]. Here we report blends of amphiphilic ABC triblock copolymers with AC diblock copolymers to obtain different morphologies in aqueous solution in controllable manner by tuning the W_{philic} of ABC/AC binary mixtures. An unsymmetrical ABC triblock copolymer, which is composed of a terminal hydrophobic block and two adjacent hydrophilic blocks was synthesized by controlled polymerization method. The chain lengths of hydrophilic blocks were kept constant and that of hydrophobic block is varied. The obtained morphologies were characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques.



References

[1] Zhang, L.; Eisenberg, A. *Science*, 268 (**1995**) 1728.
[2] Liu, X.; Wu, J.; Kim, J.-S.; Eisenberg, A. *Langmuir*, 22 (**2006**) 419.
[3] He, F.; Gadt, T.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* 133 (**2011**) 9095.
[4] Stoenescu, R.; Meier, W. *Chem. Commun*. (**2002**) 3016.
[5] Reynhout, I. C.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *J. Am. Chem. Soc.*129 (**2007**) 2327.

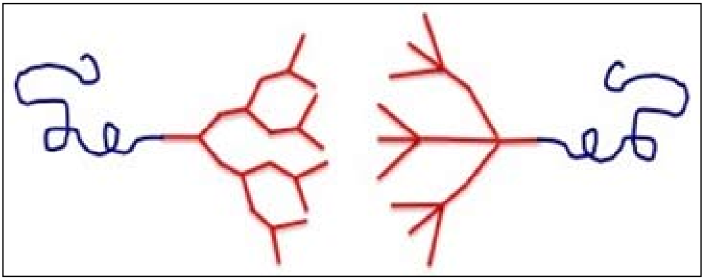
TP23

Studies on Aggregation Behaviour of Linear-Dendritic Copolymers

Nagendra Kalva and Ashootosh V. Ambade*
Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune – 411008 INDIA

Linear dendritic block copolymers are well-defined macromolecular analogues of small molecule surfactants. The first examples on self-assembly of linear dendritic block copolymers in solution were reported by Fréchet and co-workers in 1992 [1]. They synthesized AB diblock and ABA triblock linear dendritic copolymers based on poly benzyl ether dendrons and linear PEO polymer. Later, Hammond and co-workers studied PAMAM –PEO linear dendritic copolymer self assembly into micelles [2]. Recently, Del Barrio et al. reported a series of linear dendritic copolymers based on azobenzene containing bis-MPA dendrons as hydrophobic block and PEO linear polymer as a hydrophilic block which self assembled into cylindrical micelles, sheet-like micelles as well as vesicles [3]. These and other reports compare the aggregation properties of linear-dendritic polymers within a series only with respect to dendron generation.

Surfactants form wide range of aggregates in solution. Aggregation of these amphiphiles has been studied by structural variations such as sizes and multiplicity of the hydrophobic tail and hydrophilic head groups [4], branching within the hydrophobic tail and its location, and location of phenyl ring within the hydrophobic tail [5] to understand their effect on micellar properties like critical micelle concentration (cmc) and aggregation number. However, effect of such subtle structural changes on the micellar properties of amphiphilic linear-dendritic copolymers has not been reported. Here, we present the design and synthesis of linear-dendritic copolymers with subtle variations in the hydrophobic dendron to afford head groups with different sizes and shapes and studies on their aggregation behaviour. Two types of dendrons based on different branching pattern and similar chemical structure were synthesized and attached to a hydrophilic polymer of constant chain length. The micellar assemblies of these polymers were studied by cmc, dye encapsulation, and Dynamic Light Scattering (DLS) techniques to investigate the effect of headgroup structure on aggregation.



References:

[1] Gitsov I, Wooley KL, Fréchet JMJ. *Angew Chem Int Ed Engl.,* 3 (**1992)** 1200.

[2] Iyer, J.; Fleming, K..; Hammond, P. T. *Macromolecules,* 31 (**1998)** 8757.

[3] Barrio, J. D.; Oriol, L.; Sanchez C.; Serrano, J. L.; Cicco A. D.; Keller P.; Li, M.H. *J. Am. Chem Soc.*, 132 (**2010)** 3762.

[4] Bhattacharya, S.; De, S. *Chem. Commun.,* (**1996)** 1283.

[5] De.S.; Aswal, V.K,; Ramakrishnan, S. *Langmuir,* 26 (**2010)** 17882.

TP24

Synthesis of Kojic Acid based End-functionalized Polymers having Biological Activities

P. Kure, D. Damodara, S. Alex, D. Palaskar* and G. Satyanarayana*
Syngene International Ltd
Biocon Park, Plot 2 & 3, Bommasandra Industrial Area Phase IV
Bommasandra - Jigani Link Road
Bangalore - 560099, INDIA
** Satyanarayana.Ganugapat@syngeneintl.com and Dnyaneshwar.Palaskar@syngeneintl.com*

Kojic acid **(Figure. 1)** is a natural chemical compound consisting of 4-pyranone as a basic backbone. It has several biological activities such as mild inhibitor for pigments, antifungal, chelator for transition metals, scavenger of radicals, etc[1]. Hence, use of kojic acid in tailor made polymers can enhance their properties[2].

In the present work, we synthesized 2-(chloromethyl)-5-methoxy-4H-pyran-4-one **(CMMP, Figure 2)** and a new O-ethyl S-((5-methoxy-4-oxo-4H-pyran-2-yl)methyl) carbonodithioate **(RAFT-KA, Figure 3)** using very simple organic reaction transformations on kojic acid. The obtained CMMP has an ability to function as an Atom Transfer Radical Polymerization (ATRP) initiator. RAFT-KA could act as a Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization agent. Both CMMP and RAFT-KA will be used in the polymerization of styrene and methyl methacrylates to achieve end-functionalized polystyrene (PS) and poly(methyl methacrylate) (PMMA) with a predetermined molecular weight and relatively narrow molecular weight distributions. Kojic acid as an end group in PS and PMMA will be analyzed by FTIR, ^{1}H-NMR and GPC.

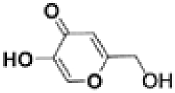


Figure 1: Kojic acid

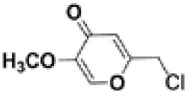


Figure 2: CMMP

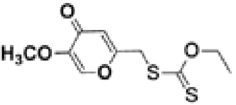


Figure 3: RAFT-KA

References

[1] Putty-Reddy Sudhir, Hui-Fen Wu and Zi-Cong Zhou, *Rapid Commun. Mass Spectrom.*, 19 **(2005)** 209.

[2] Bungo Ochiai, Miyuki Kamiya, Takeshi Endo, *J. Polym. Sci. Part A: Polym Chem.* 50 **(2012),** 3493.

TP25

Synthesis and Characterization of Poly[2-(acetoacetoxy)ethyl methacrylate] Bearing Pendant β-Dicarbonyl Functionalities

Prithwiraj Mandal, Nikhil K. Singha*
Rubber Technology Centre, Indian Institute of Technology Kharagpur
Kharagpur- 721302, West Bengal, India
E-mail address: nks8888@yahoo.com

2-(acetoacetoxy)ethyl methacrylate (AEMA) is an interesting monomer, because of the presence of pendant β-dicarbonyl moieties. These β-dicarbonyl groups are commonly involved in H-bonding and have affinity towards metal ions and have major application potential in the areas of biomedical applications, organic-inorganic hybrid materials and biomineralization processes [1-3]. In 2003 Schlaad et al. prepared homopolymers and block copolymers based on 2-(acetoacetoxy)ethyl methacrylate via RAFT radical polymerisation, as they failed to polymerize AEMA successfully via ATRP using CuBr/ (Me_6TREN), or CuBr/(dNbpy) at 90 °C. The polymerization was not controlled under the ATRP conditions they used [4]. G. Chen et al. synthesized poly[2-(acetoacetoxy)ethyl methacrylate] latexes by miniemulsion polymerization technology and observed that PAEMA latexes emitted visible fluorescence under UV light when ammonia was introduced [5].

This investigation reports the atom transfer radical copolymerization (ATRP) of 2-(acetoacetoxy) ethyl methacrylate (AEMA), a monomer bearing β-dicarbonyl in its pendant group. In this case AEMA was polymerized at ambient temperature via ATRP using CuX/bpy (bpy = 2,2`-bipyridine) as catalyst. It was observed that with decreasing catalyst concentration the polymerization reaction was more controlled leading to polymers with controlled molecular weight and narrow polydispersity index. The chemical structure of the polymer was confirmed by ^{1}H NMR spectroscopy. Chain extension experiment indicated that the PAEMA prepared via ATRP had well defined active bromide end group. Conventional free radical polymerization (FRP) of AEMA led to gel formation. The thermal properties of the polymers were studied by TGA and DSC analysis.

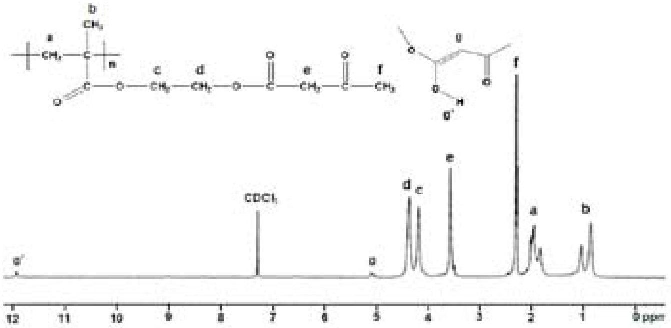


Figure 1. ^{1}H NMR spectrum of PAEMA

References

[1] Schlaad, H.; Krasia, T. Antonietti, M. *J. Am. Chem. Soc.,* 126 (**2004**), 11307.
[2] Kaliyappan, T.; Kannan, P. *Prog. Polym. Sci.,* 25 (**2000**), 343.
[3] Cölfen, H. *Macromol. Rapid Commun.,* 22 (**2001**), 219.
[4] Krasia, T.; Soula, R.; Börner, H. G.; Schlaad, H. C*hem. Comm.,* (**2003**), 538.
[5] He, J.; Zhang, T-Y.; Chen, G. *J. Colloid Interface Sci.,* 373 (**2012**), 94.

TP26

Synthesis, spectral and chelating properties of azo polymeric ligand derived from bis(2 -hydroxy benzaldehyde ethylenediimine) and diazonium salt of 4-amino phenol

R.Keerthiga, S.Vijayalakshmi, P.Kandasamy, M.Sasidaran, T.Kaliyappan
Polymer Research Laboratory, Department of chemistry,
Pondicherry Engineering College, Pillaichavady, Puducherry, India- 605014
Email: tkaliyappan2001@yahoo.com

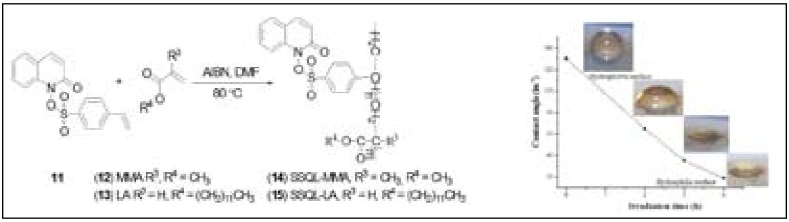
A chelating polymer poly((4-hydroxy azobenzene) bis(2-hydroxyl benzaldehyde ethylenediimine-formladehyde)) (poly(4-HAB2-HBE-F)) was synthesized by polycondensation of bis(2-hydroxyl benzaldehyde ethylenediimine) and diazonium salt of 4-amino phenol with formaldehyde in presence of oxalic acid as catalyst. Polychelates were obtained when the DMF solution of the polymer containing few drops of ammonia was treated with the aqueous solution of Cu (II)/Ni (II). Elemental analysis of the polychelates indicates the metal- ligand ratio was 1:2. The polymer metal complexes were characterized by FT-IR, ^{1}H NMR, XRD, TGA and DSC. The newly synthesized formaldehyde resin proved to be selective chelating ligands for heavy metal ions. The metal uptake efficiency of the formaldehyde resin at different pH and concentration of electrolyte were also studied.

TP27

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

Rakesh Banerjee, Md. Iqbal, ND Pradeep Singh* and Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur,
West Bengal-721302 INDIA

Over the past few decades, photoacid generators (PAGs) have gained enormous interest due to their immense applications in microlithographic industry. [1] PAGs are the key material used in the field of photoresists for semiconductor fabrication. [2] On photoirradiation of polymer film containing a PAG, results in generation of acid, which catalyses certain important chemical transformations within the polymer film such as deprotection of functional groups, initiation of polymerization or cross linking process. [3] We have synthesized three different classes of photoresponsive homopolymers and their copolymers with methyl methacrylate, styrene, ethyl acrylate, etc. using the well-known free radical polymerization techniques. [4] 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 presentation 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] a) Yamato, H.; Asakura, T.; Nishimae, Y.; Matsumoto, A.; Tanabe, J.; Birbaum, J.-Luc.; Murer, P.; Hintermann, T.; Ohwa, T. *J. Photopolym. Sci. Technol*. 20, **(2007)** 637. b) Yi, Y.; Ayothi, R.; Ober, C. K.; Yueh, W.; Cao, H. *Proc. SPIE*, **2008**, *6923*, 69231B-1.

[2] a) Ayothi, R.; Yi, Y.; Cao, H. B.; Yueh, W.; Putna, S.; Ober, C. K. *Chem. Mater. 19*, (**2007**), 1434. b) Innocenzi, P.; Kidchob, T.; Falcaro, P.; Takahashi, M. *Chem. Mater*. 20, **(2008)**, 607. c) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* 3, **(1991)**, 394.

[3] a) J. M. Torres, C. M. Stafford, B. D. Vogt, *Soft Matter* 8, **(2012)**, 5225-5232; b) H. Y. Koo, H. J. Lee, J. K. Kim, W. S. Choi, *J. Mater. Chem*. 20, **(2010)**, 3932-3937; c) H. Ito, *Adv. Polym. Sci.* 172, (**2005**), 37-245.

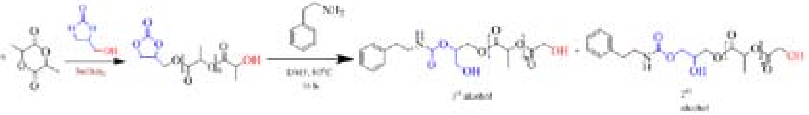
[4] a) M. Ikbal, A. Jana, N.D. Pradeep Singh*, R. Banerjee, and D. Dhara*, *Tetrahedron* 67, **(2011)**, 3733-3742. b) M. Ikbal, R. Banerjee, S. Atta, D. Dhara*, A. Anoop*, and N. D. Pradeep Singh* *J. Org. Chem* 77, **(2012)**, 10557-10567. c) M. Ikbal, R. Banerjee, S. Atta, A. Jana, D. Dhara, A. Anoop and N. D. Pradeep Singh, *Chemistry - A European Journal* 18, **(2012)**,11968-11975.

TP28

Synthesis and Characterization of α-Hydroxy, ω-(Cyclic carbonate)- Telechelic Poly(D, L-Lactide)

Ravindra M Patil[a,b], Anil A Ghanwat[b], Satyanarayana Ganugapati[a], Rudhramyna Gnaneshwar[a*]
a. Syngene International Ltd, Biocon Park , Plot No. 2&3, Bommasandra Industrial Estate - Phase- IV
Bommasandra-Jigani Link Road, Bangalore 560 099, India.
b. School of chemical Sciences, Solarpur University, Solapur, 413 255, India
E-mail: rudhramyna.gnaneshwar@syngeneintl.com

End functional polymers with controlled architecture and narrow molecular weight distribution are of great importance as they are useful precursors for preparing different polymer architectures[1] and also utilized in variety of applications such as protective coatings, macromolecular surfactants and adhesives. PLA is currently used in a number of biomedical applications, such as sutures, stents, dialysis media and drug delivery devices. It is also being evaluated as a material for tissue engineering. ROP of D,L-lactide is initiated by 4-(hydroxymethyl)-1, 3-dioxolan-2-one and catalyzed by $Sn(Oct)_2$ in toluene at 110°C to yield α-hydroxy, ω-(cyclic carbonate) telechelic PLA with relatively narrow PDI is demonstrated. The end group's structure derived from the alcohol initiator such as glycerol carbonate is confirmed by NMR, FTIR and MALDI TOF MS. Cyclic carbonate end group reaction with amine such as 2-phenylethylamine enabled the hydroxy urethane ends functional PLA without the use of the relatively more hazardous isocyanates and without any by-product.



D, L-Lactide α-Hydroxy, ω-(cyclic carbonate) telechelic PLA Hydroxy urethane end functional PLA

References

[1]. Tasdelen M. A.; Kahveci M. U.; Yagci Y. *Prog. Polym. Sci.* 36, [**2011**], 455.

TP29

A facile one-pot Reactive Solution Blending Approach for Main Chain Donor-Acceptor Polymeric Materials

S. Kumari Nisha and S. K. Asha*
National chemical Laboratory, Pune-411008
E-mail: sk.asha@ncl.res.in

The π stacking interaction in semiconducting materials is a major hurdle to develop film forming polymers especially for n type semiconducting materials like perylene bisimides (PBI). Incorporation of PBI into main chain polymer scaffold would generate mechanically robust materials which can replace the poor film forming fullerene derivatives as the electron acceptor and transport material in plastic solar cells. Although a number of PBI main-chain polymers have been reported, most of them are only soluble in special solvents such as concentrated sulphuric acid or m-cresol, mainly due to the strong π-stacking interaction. We have demonstrated a successful reactive solution blending strategy for the chemical incorporation of fluorescent chromophores like perylene bisimide (**PBI**) and oligo(p-phenylene vinylene) (**OPV**) into the backbone of an engineering thermoplastic polyester [poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate)] (PCCD) [1-2]. Random copolyester incorporating both the acceptor (**PBI**) and donor (**OPV**) moieties were also synthesized and the photophysical properties of this donor-acceptor polyester were studied. **Figure 1** shows the photographs of the free standing films prepared from these copolyesters. The transesterification by reactive solution blending approach is easily adoptable for a wide range of suitably functionalized donor or/and acceptor molecules resulting in tunable photophysical properties with film forming ability.

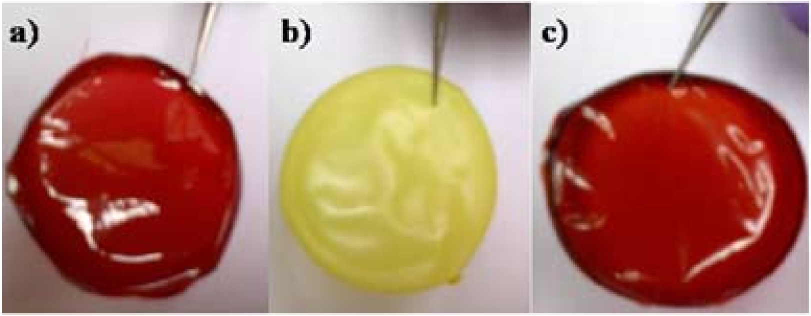


Figure 1. Photograph of (a) PBI copolyester, (b) OPV copolyester and (c) PBI-OPV copolyester drop casted from a 1 weight % solution in chloroform.

References:
[1]. Nisha, S. K.; Asha, S. K. *Patent Application* (**2012**) WO 2012/111026 A1.
[2]. Nisha, S. K.; Asha, S. K. *J. Polym. Sci. A Polym. Chem.* 51 (**2013**) 509.

TP30

Triazole Crosslinked Propargyl Terminated Polytetramethylene as Solid Propellant Binder: Thermal and Mechanical Characterization

S.Reshmi*, S.Gayathri and C.P.Reghunadhan Nair

Polymers and Special Chemicals Group, Propellants, Polymers, Chemicals and Materials Entity
Vikram Sarabhai Space Centre, Thiruvananthapuram-695022

** Corresponding author: e-mail s_reshmi@vssc.gov.in, reshmiskurup@gmail.com, Polymers and Special Chemicals Group, PCM Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram-695022, Kerala, India, Tel: +914712565558, Fax-+91471-2564203*

In a solid propellant formulation, oxygen rich binders are essential for certain specialised applications such as gas generator and pyrogen igniter propellants. In literature there have been reports on polytetramethylene oxide (PTMO) based binders for the processing of composite solid propellants [1-2]. However, the major disadvantage of this polymer is the side reaction with moisture leading to evolution of gaseous products that result in very high viscosities of the propellant as well as porosity in the cured propellant, when the curing is done by reaction with diisocyanates. The introduction of a new cure mechanism based on 'click reaction' in PTMO can resolve these issues. For this purpose, functional modification of PTMO was done by anchoring a 'clickable' propargyl group at the chain end PTMO. Curing of PTMP was effected by reacting with glycidyl azide polymer (GAP) to yield crosslinked triazole network in the presence of cuprous iodide (Cu_2I_2) as catalyst. The catalysed system was chosen for studies as the uncatalysed cure reaction occurs at ~110°C and is not conducive for propellant applications as the safe operational temperatures for curing of solid propellants is in the range of 40-60°C. The cure reaction of PTMP with GAP for catalysed system occurs in the range of 52-210°C with an enthalpy of 149 ±10 J/g. The kinetics of cure reaction was evaluated by the variable heating rate method of Ozawa and the kinetic parameters were determined.

Tensile properties of the cured PTMP-GAP compositions were correlated to the composition. The typical mechanical properties obtained for PTMP-GAP cured polymer network for an alkyne-azide equivalence ratio of 1:1 gives a tensile strength of 4 kg/cm^2, elongation of 20% and modulus of 25 kg/cm^2. Composite solid propellant was processed using the new binder and was characterised for burn rate and mechanical properties.

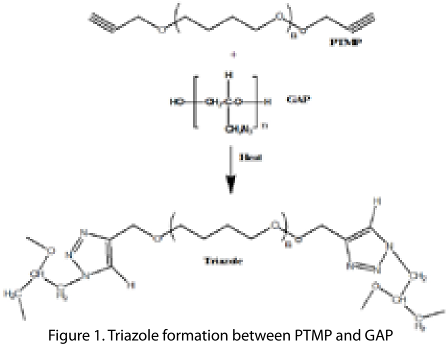


Figure 1. Triazole formation between PTMP and GAP

References

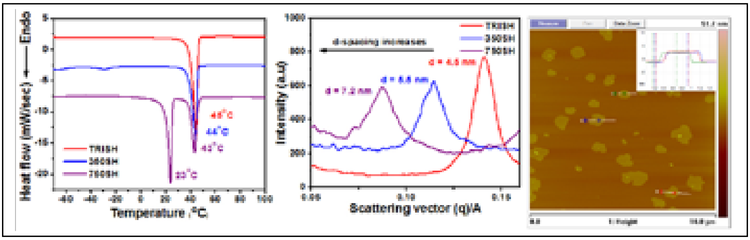
[1] Kohga, M.; .Miyano. T; Kojima, T, *Journal of Propulsion and Power,* 22 (**2006)** 1418.
[2] Kohga, M.; .Okamoto. K, Combustion *and Flame,* 158 (**2011)** 578.

TP31

Periodically Grafted Amphiphilic Copolymers Based On Itaconic Acid

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

Self-assembly of macromolecules provides an efficient pathway for the generation of objects from nanometer to micrometer dimensions with a predictable and controllable morphology. Depending on their morphologies, such self-assembled systems could be utilized for applications in nanotechnology, electronics, drug delivery etc. [1]. Amphiphilic copolymers comprising a hydrophobic segment and a hydrophilic segment undergo self assembly into highly ordered structures due to the high propensity for phase segregation between the two immiscible segments. Wagener and coworkers have prepared amphiphilic graft copolymers based on a polyethylene backbone and hydrophilic pendant oligoethylene glycol segments placed at regular intervals along the backbone. However, their study focused on solid state properties in particular, the influence of the lateral substituent on the crystalline morphology of the alkylene segment using WAXS measurements [2, 3]. Recently, a novel class of periodically grafted amphiphilic copolymers were synthesized from our group wherein pendant hexaethylene glycol monomethyl ether units were periodically placed along a hydrophobic alkylene polyester backbone. When the intervening alkylene segment was adequately long, such as 22-carbon chain, the polymer exhibited a strong tendency to self-assemble and adopt a folded zigzag conformation and such a folded form can be considered as a PEGylated wax nanobundle as the intervening alkylene segments undergo crystallization to generate a paraffinic-type crystal [4]. In order to examine the effect of the pendant hydrophilic oxyethylene segment length on the phase segregation behaviour of the hydrophobic alkylene segment, we prepared a series of periodically grafted amphiphilic copolymers where the length of the oligoethylene glycol segment was systematically varied. Linear polyesters were synthesized based on itaconic acid, a biosourced and renewable monomer, by melt polycondensation and the subsequent utilization of the *exo*-chain double bond in the itaconate moiety for post polymerization modification by the Michael reaction resulted in amphiphilic copolymers containing hydrophilic oxyethylene segments grafted at precise intervals along a hydrophobic alkylene polymer backbone. DSC measurements revealed that longer oxyethylene segments induced more effective phase separation and consequent crystallization of the hydrophobic alkylene segment. AFM and SAXS studies confirmed the formation of folded zigzag structures; the height of the flat entities in the AFM images increased with the PEG segment length, as did the lamellar spacing determined by SAXS.



References

[1] Rodriguez-Hernandez, J.; Checot, F.; Gnanou, Y.; Lecommandoux,S. *Prog. Polym. Sci.*, 30 (**2005**) 691
[2] Berda, E. B.; Wagener, K. B. *Macromol. Chem. Phys.*, 209 (**2008**) 1601
[3] Berda, E. B.; Lande, R. E.; Wagener, K. B. *Macromolecules*, 40 (**2007**) 8547
[4] Roy, R.K.; Gowd, E.B.; Ramakrishnan, S. *Macromolecules*, 459 (**2012**) 3063

TP32

Mesoporous Polymer/Carbon Nanospheres Synthesized via Surface-Confined Atom Transfer Radical Polymerization for Applications as Functional Materials

Sanjib Banerjee, Tanmoy Maji, Tapas K. Paira and Tarun K. Mandal*
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India
E-mail: psutkm@iacs.res.in

Ordered mesoporous materials (pore size: 2-50 nm) are a very interesting field of research because these materials have an extremely high surface area and large pore volume. This makes the materials useful for applications in separation, adsorption, chemical sensor, catalysis and synthesis of host–guest functional material.[1, 2] Also, they are highly desirable for optical sensor applications, energy storage and information processing and as Magnetic Resonance Imaging (MRI) contrast agents.[3] Among them, mesoporous polymer (MP) materials has potential use in electronics, controlled release and heterogeneous catalysis.[4] Mesoporous carbon (MC) materials are also used as an adsorbent of bio and organic molecules, catalyst supports, component of fuel cells and component of Li ion batteries.[5]

We have developed a facile approach for the production of mesoporous polymer nanospheres (MPN) and mesop orous carbon nanospheres (MCN) with faithful shape retention of the initiator-modified silica nanospheres (MSIN) template via surface-confined atom transfer radical polymerization (SC-ATRP). First, mesoporous silica-polymer hybrid nanospheres (MSPN) are prepared via SC-ATRP of methacrylate monomers from MSIN using CuCl/CuCl$_2$/PMDETA as the catalyst in xylene at 105 ^{o}C. Subsequent removal of the hard silica template results in the production of MPN. Further, carbonization of the MSPN hybrid, followed by removal of the silica template resulted in the production of MCN. Field emission scanning electron microscopic and transmission electron microscopic analyses of the obtained MPN/MCN materials revealed that they completely retain the size, shape and mesoporous network of the template MSIN nanospheres. The synthesized mesoporous poly(methyl methacrylate) nanospheres (MPMMAN) and MCN materials have high surface area of 520 and 658 m^2 g^{-1} respectively. This technique further allows fabrication of functional MPN material which are successfully used as "clickable" mesoporous materials for the synthesis of triazole functionality with potential antimicrobial activity, in efficient removal of ionic contaminates with binding capacity of 0.345 mmol g^{-1} and in glucose-sensing with a high binding capacity of 29.6 mmol g^{-1}.

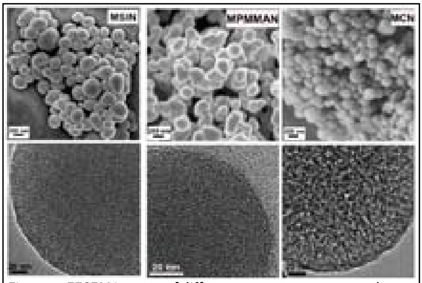


Figure 1. FESEM images of different mesoporous nanospheres (upper panel). The high magnification TEM images of the corresponding nanospheres (lower panel).

References:
[1] Hartmann , M. *Chem. Mater.* 17 (**2005**) 4577.
[2] Hoffmann, F.; Cornelius, M.; Morell, J.; Froba, M. *Angew. Chem. Int. Ed.* 45 (**2006**) 3216.
[3] Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* 13 (**2001)** 3140.
[4] Choi, M.; Kleitz, F.; Liu, D.; Lee, H. Y.; Ahn, W.-S.; Ryoo, R. *J. Am. Chem. Soc.* 127 (**2005**) 1924
[5] Zhou, H.; Zhu, S.; Hibino, M.; Honma, I.; Ichihara, M. *Adv. Mater.* 15 (**2003**) 2107.

TP33

Application of Sustainable Polymers for Oil Spill Clean Up

M.D. Teli* and Sanket P. Valia
Department of Fibres and Textile Processing Technology
Institute of Chemical Technology
Matunga (E), Mumbai-400019, India
mdt9pub@gmail.com

The aim of this study was to highlight the potential use of natural unconventional fibres for recovery of oil from the spilled area. Currently used methods (booms and skimmers, dispersants, and in situ burning) are decade's old, low-technology, manpower intensive and some with unknown environmental consequences. [1] Lignocellulosic fibres are attractive materials due to its abundance nature, sustainability and biodegradability. They are economical and have low processing energy requirements. Modification of these fibres to make them hydrophobic may allow them to be used as sorbent in oil spill. [2] In this study natural fibres have been acetylated to impart hydrophobicity and increase the oil sorption capacity. The product so formed was characterized by FT-IR, TG, SEM and its degree of acetylation was also evaluated. The extent of acetylation was measured by weight percent gain. Studies indicate that a simple squeezing operation was sufficient to remove most of the oil sorbed by the fibres so that the sorbents can be recycled several times for oil spill clean-up. The results suggest that a total or partial substitution of commercial non biodegradable synthetic oil sorbents by natural sorbent materials like modified fibres could be beneficial in the oil spill clean-up operation for improving the efficiency of oil sorption.

References:

[1] Xuepei, Y.; Mike Chung, T. C. Novel Solution to Oil Spill Recovery: Using Thermo degradable Polyolefin Oil Superabsorbent Polymer (Oil–SAP) *Energy Fuels* **2012**, 26, 4896–4902.

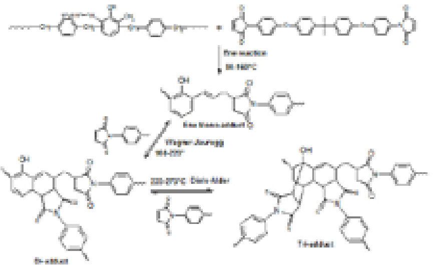
[2] Bledzki, A.K.; Mamun, A.A.; Faruk, O. *eXPRESS Polymer Letters* **2009**, *1(11)*, 755.

TP34

Novel Bismaleimide-Allyl Xylok Alder ene Blends and their Composites: Synthesis, Characterization and Structure-Property Relationships

Satheesh Chandran M*, Temina Mary Robert, Sunitha K, Dona Mathew and C P Reghunadhan Nair
Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre
Thiruvananthapuram, Kerala, India-695022
** satheeshchandran.m@gmail.com*

Allyl- functional aralkyl phenolic resin (Allyl Xylok) was synthesized and characterized. The allyl xylok resin (AX) was reactively blended with 2, 2'-bis 4-[(4'-maleimido phenoxy) phenyl] propane (BMIP) in varying proportions of maleimide and allyl groups. The cure characterization of the blends was done by DSC and the cure pattern was correlated to the composition of the blend [1]. A three stage curing pattern was manifested in the case of allyl dominated blends that converged to a two-stage pattern for maleimide rich systems. The thermal stability of the cured polymers increased systematically with increase in maleimide content [2]. The carbon fabric composites of the BMIP/AX blends exhibited high glass transition temperatures which increased in proportion to the maleimide content. The composition, incorporating highest amount of maleimide (2:1 maleimide:allyl) exhibited a Tg of 290 °C. Enhanced maleimide content increased the storage modulus also. Though increased allyl groups promoted the mechanical properties of the composites, it had a detrimental effect on the retention of the properties at high temperature. High allyl content was also conducive for better resin-reinforcement interaction as revealed in morphological analysis which resulted in high mechanical properties. Structure property co-relationship was derived [3-4] based on the composition of the blend, morphology, mechanical and thermo-mechanical properties.



Scheme 1: Alder ene cure pathway of AX and BMIP [1]

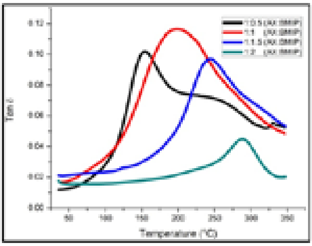


Figure 1: Dependence of Tg on the maleimide content

References

[1] Bindu R. L; Reghunadhan Nair C. P.; Ninan K. N, Journal of Applied Polymer Science, 80 **(2001)** 737.

[2] Xuhai Xiong; Ping Chen; Jinxiang Zhang; Qi Yub; Baichen Wang, Thermochimica Acta 514 **(2011)** 44.

[3] Haoyu Tang; Wanwan Li; Xinghe Fan; Xiaofang Chen; Zhihao Shen; Qifeng Zhou, Polymer 50 **(2009)** 1414.

[4] Aijuan Gu; Guozheng Liang; Llwen Lan, Journal of Applied Polymer Science, 59 **(1996)** 975.

TP35

Polymeric Ionic Liquids (PILs) possessing Substituent Asymmetry: Synthesis and Gas Permeation Studies

Sayali Shaligram, P. P. Wadgaonkar, U. K. Kharul*
Polymer Science and Engineering Division, National Chemical Laboratory, Pune – 411008 *INDIA*
Email: uk.kharul@ncl.res.in

The increase in global atmospheric CO_2 concentration and the possibility of future constraints on the greenhouse gas emissions has accelerated research on CO_2 capture and storage. Among new generation materials, ionic liquids (ILs) show high CO_2 solubility [1]. To take advantage of this property, efforts of incorporating ILs into membrane pores have been demonstrated [2]. Though they show excellent selectivity as anticipated, they suffer from usual draw-backs of supported liquid membranes such as liquid drain and poor long-term performance. It is reported that the polymers synthesized using IL-vinyl monomers show higher CO_2 absorption capacity as well as faster and reversible adsorption/desorption properties than RTILs [3]. Though this has indicated potential of PILs to be applicable as membrane materials for CO_2 separation, they are unable to be converted into membrane form, being brittle in nature. To overcome this issue, we proposed to introduce IL moieties on the main chain of a rigid polymer. This was achieved by alkylation of a rigid basic polymer, polybenzimidazole (PBI); which rendered excellent film formation ability [4]. Substitution by different bulky groups such as anthracene and pyrene is anticipated to increase free volume in the polymer matrix (to offer high diffusivity); while ionic liquid character would contribute to increase in CO_2 solubility (and thus selectivity). The asymmetry of the cations is shown to have a significant improvement in the reaction and mass transfer rates of CO_2 in the ionic liquids [5]. Picking up this thread, present work demonstrates a novel series of PILs having substitution asymmetry. Investigations of pure gas permeation properties and physical properties (that are known to affect permeation properties, e.g. thermal, solvent solubility, density, etc.) will be presented.

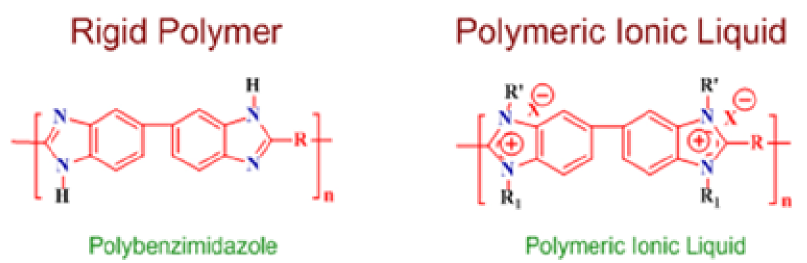


Figure 1. polymeric Ionic Liquids with substitution asymmetry

References

[1] Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Nature 1999, 399, 28–29.

[2] Baltus, R. E.; Counce, R. M.; Culbertson, B. H.; Luo, H.; DePaoli, D. W.; Dai, S.; Duckworth, D. C. Sep. Sci. Technol. 2005, 40 (1), 525–541.

[3] Tang, J. B.; Tang, H. D.; Sun, W. L.; Radosz, M.; Shen, Y. Q. Polymer 2005, 46 (26), 12460–12467.

[4] Guannan, W.; Wenlong, H.; Feng, X.; Jiao, G.; Youting, W.; Zhibing, Zhang, J. Chem. Eng. Data 2011, 56, 1125–1133.

TP36

One Pot Single Step Synthesis and Physicochemical Properties of Polyols from Renewable resources

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

Correspondence to. K.V.S.N.Raju (E-mail: kvsnraju@iict.res.in and drkvsnraju@gmail.com),
Telefax: +91-40-27193991

Renewable resource based polyols are growing in importance for the development of eco-friendly coatings, adhesives, sealants, foams etc. Castor oil and Soybean oil have been and being used for the development of polyols due to its unique backbone architecture and fatty acid compositions. This paper reports a novel methodology for the synthesis of polyol from soybean and Castor oil using a single step continuous method. The method involves epoxidation of oils and ensuing hydroxylation to synthesize polyols. The epoxidation was carried out using per acid method. The reaction time and epoxidation value were optimized by limiting the mole ratios of hydrogen peroxide and formic acid. The epoxidation was confirmed by iodine value and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The structure, average molecular weight, physiochemical and thermal properties of the synthesized polyols were studied using techniques such as ^{1}HNMR, ^{13}CNMR, FTIR, Solubility, Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and Thermo gravimetric analysis (TGA). The hydroxyl number, hydroxyl functionality, acid value, iodine value and viscosity of the synthesized polyols were also determined. The functional groups of polyol were identified using FTIR and NMR spectroscopy. This confirmed complete disappearance of the C=C double bonds, formation of the epoxy linkage following the epoxidation process, its further disappearance and incorporation of hydroxyl groups after the hydroxylation process. After modification, the polyols reached an OH-number between 230 and 270 mg KOH/g oil and their Iodine value below 1.

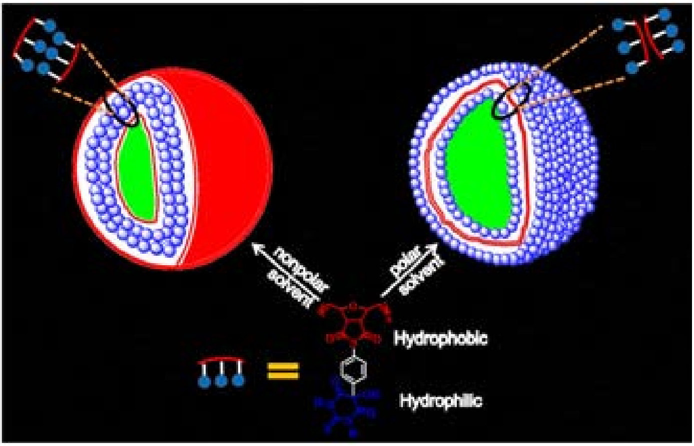
Key words: Castor oil; Soybean oil; hydroxyl number; Iodine value; Solubility; DSC;

TP37

Reversible pH- and Lipid-Sensitive Amphiphilic Homopolymer Vesicles as Unique Nano-Carriers for Cancer Therapy

Shivshankar Mane and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences,
Indian Institute of Science Education and Research Kolkata-741252, INDIA
E-mail: sraja@iiserkol.ac.in

Supramolecular architectures are known to form usually by the natural process of "self-assembly". The underlying concept of supramolecular chemistry is molecular recognition based on the bonding of complementary functional groups of low molar mass compounds or polymers that are held together using non-covalent interactions. A controlled/living polymerization technique such as Ring Opening Metathesis Polymerization (ROMP) is used as synthetic tool to make an amphiphilic, norbornene-derived thiobarbiturate homopolymer (**NTBH**). The detailed characterizations of quantitatively synthesized polymer using GPC, IR, UV and ^{1}H NMR spectroscopic techniques. Dynamic light scattering and critical aggregation concentration studies confirm the aggregate formation in solution while atomic force microscopy and transmission electron microscopy of the dried sample on the silicon substrate further confirm the vesicular morphologies of this **NTBH**. Encapsulation studies of hydrophilic doxorubicin and hydrophobic Nile red suggest the reversible nature of the **NTBH** vesicles. Release studies in acidic and lipophilic environment demonstrate the stimuli-responsive nature of the novel systems.



References:

[1]. Mane, S. R., Rao, V. N., Shunmugam, R. *ACS Macro Lett.* **2012**, *1*, 482-488.

[2]. Mane, S. R.; Rao, V. N.; Chatterjee, K.; Dinda, H.; Nag, S.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *Macromolecules*, **2012**, *45*, 8037-8042.

[3]. Mane, S. R.; Rao, V. N.; Chatterjee, K.; Dinda, H.; Nag, S.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *J. Mater. Chem.* **2012**, *22*, 19639-19642.

[4]. Rao, V. N.; Mane, S. R.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *Biomacromolecules* **2012**, *13*, 221-230.

TP38

Synthesis and characterization of flexible/stretchable Polyetherimides containing aryl/alkyl ether 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 much sacrificing the desired properties. To accomplish this goal, the incorporation of flexible bridging units as well as bulky groups into the rigid polyimide backbone, or 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) range from 200 to 280^{0}C.

At the same time there is a continuing need for elastomers capable of withstanding elevated temperatures. Within the defense industry, specific needs are associated with aircraft fuel tank sealants and elastomeric components such as O-rings and gaskets in aircraft and missile structures and engines. Silicone is the commonly used elastomeric material for these applications. However, performance limitations of these elastomers are being reached [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 having ether linkages and the prepared diamines 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 in the UTM. The optical properties will be studied using UV-Visible spectrophotometer and Refractive index and birefringence measurements will be studied using a Prism Coupler.

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

TP39

Unique Norbornene based Polymers for sensing heavy metal poisioning

Sourav Bhattacharya and Raja Shunmugam*
Polymer Research Centre, Indian Institute of Science Education and research Kolkata
Mohanpur-741252
E-mail: sraja@iiserkol.ac.in

Unique materials can be obtained with well-known polymeric properties from macromolecule architectures functionalized with electron rich moieties. The incorporation of metal-ligand interactions into macromolecules imparts them with potentially useful function. As both arsenic (III) and mercury (II) are having specific affinity towards thiol group, synthesis of thiol based copolymer via ROMP is employed for the application of sensing Arsenic(III) and mercury (II) in drinking water. This novel polymer is throughly charecterised by NMR, IR and gel permeation chromatography (GPC). Fluorscence and Uv-Visible spectroscopy methods are used to monitor the sensing event of the newly designed polymer, both by fluorometrically as well as colorimetrically in it's very low concentration (standardized by WHO, 10µg/L).

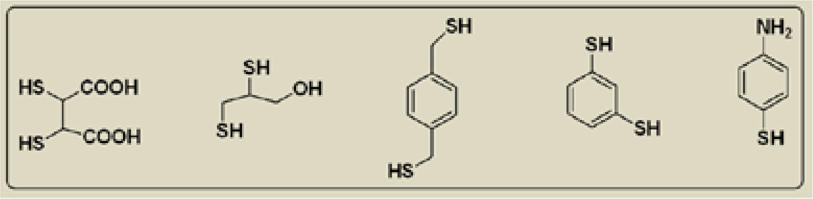


Figure1. Thiol functionlized ligand expected to bind As (III) and Hg (II).

References:

[1]. Vickaryous, W. J.; Herges, R.; Johnson, D.W. *Angew.Chem. Int. Ed.* 116 (**2004**) 5955

[2]. Bhattacharya , S.; Rao, V.; Sarkar, S.; Shunmugam, R. *Nanoscale* 4 (**2012**) 6962

TP40

POSS tethered Poly(methyl methacrylate), Synthesis and Characterization

Souvik Ata, Dhruba J. Haloi and Nikhil K. Singha*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur
Kharagpur-721302 INDIA

The development in the area of inorganic-organic hybrid materials has led to growing attention and to one example of such material is polyhedral oligomeric silsesquioxane (POSS), represented as $(RSiO_{1.5})_{n.}$ POSS consists of an inner inorganic framework of silicon and oxygen atoms and an outer shell of organic moieties[1-3]. Such materials significantly enhance the engineering properties of the polymers, such as mechanical, chemical, and physical characteristics[4-6]. A variety of polymerization techniques has been used to prepare POSS-polymer and POSS-block copolymer composite materials[7]. There has been report on the preparation of POSS-polymer hybrid material with different architectures, topologies of polymers via atom transfer radical polymerization (ATRP).[8-9] In this investigation POSS containing poly (methylmethacrylate) was prepared via thiol-ene addition reaction followed by atom transfer radical polymerization (ATRP). The polymerization reaction was carried out using CuBr as catalyst in combination with different ligands and POSS-Br as macro initiator. Molecular weights were calculated by gel permeation chromatography (GPC) as well as by ^{1}H NMR. Morphological studies were done using transmission electron microscopy (TEM), X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) (Figure 2). Thermal properties were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

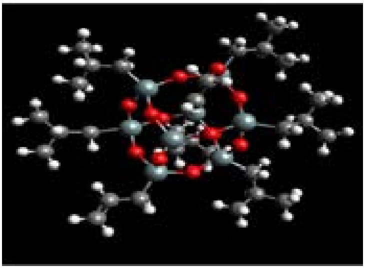


Figure 1. Three dimensional image of allyl POSS

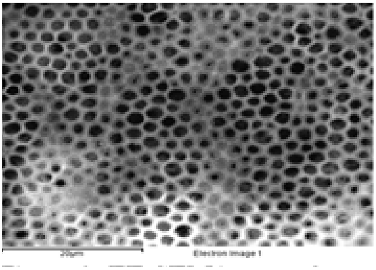


Figure 2. FE-SEM image of POSS-PMMA polymer hybrid

References:

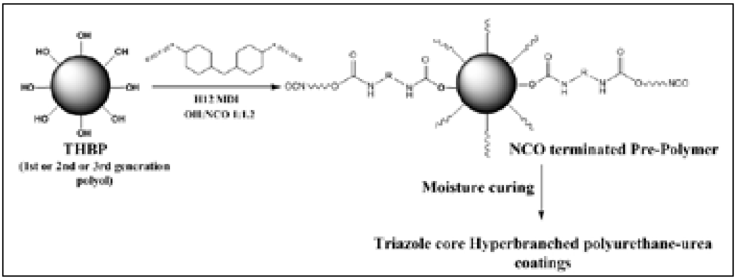
[1]. Tanaka, K., Inafuku, K., Adachi, S., Chujo, Y., *Macromolecules* 42 (**2009**) 3489.
[2]. Tanaka, K., Chujo, Y., *J. Mater. Chem* , (**2012**), 22, 1733.
[3]. Xue, Y. H., Wang, H. X., Yu, D. S., Feng, L. F., Dai, L. M., Wang, X. G., Lin, T., *Chem. Commun*. (**2009**) 6418.
[4]. Ghanbari, H., Mel, A. de., Seifalian, A. M., *Int. J. Nano. Med.* (**2011**), 6, 775.
[5]. Pielichowski, K., Njugna, J., Janowski, B., Pielichowski, J., *Adv.Polym.Sci.*, (**2006**), 201, 225.
[6]. Phillips, S.H., Haddad, T.S., Tomczak, S.J., *Curr.Opin.Colloid.Interface Sci.*, (**2004**), 8, 21.
[7]. Fei, M., Jin, B., Wang, W., Liu, L., *J. Polym. Res.* 17 (**2010**) 19.
[8]. Costa, R. O. R., Vasconcelos, W. L., Tamaki, R., Laine, R. M., *Macromolecules* 34 (**2001**) 5398.
[9]. Pyun, J., Matyjaszewski, K., *Macromolecules* 33 (**2000**) 217.

TP41

Click Chemistry approach for the synthesis of 1, 2, 3-Triazole rich Hyperbranched polyether-polyols and their application as Anti-microbial polymers

K.Sasidhar, Srinivasarao Pilla, Ramanuj Narayan, KVSN Raju*
Polymers & Functional Materials Division, Indian Institute of Chemical Technology,
Hyderabad-500007, India
*Correspondence to. K.V.S.N.Raju (E-mail: kvsnraju@iict.res.in and
drkvsnraju@gmail.com), Telefax: +91-40-27193991

Abstract:
The click chemistry is becoming one of the important tools for the modification of polymer backbone and/or to synthesize the starting materials for the formation of polymer. 1,2,3-Triazoles are becoming a materials of choice for the development of polymer due to its properties such as quantitative yield, regio-selectivity, ease of product isolation, chemical inertness of the ring, etc to impart functional properties such as antimicrobial, anticorrosive to the finished products.



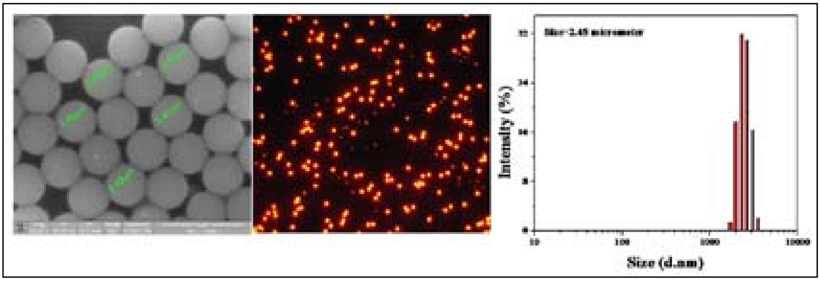
In the present study three generations of hyperbranched polyether polyols were prepared by using copper (I) catalyzed azide-alkyne click reaction. These polyols were characterized by using H^1-NMR, C^{13}-NMR, FT-IR and GPC techniques. These polyols were treated with a diisocyanate in OH: NCO ratio 1:1.2 to form –NCO terminated prepolymers. The cast of prepolymers were cured under atmospheric moisture to get the eco-friendly triazole rich polyurethane urea. The polyurethane-ureas coating films were characterized by techniques such as TGA, DMTA, UTM to understand the structure property relationship. The coating films on supported substrates were evaluated for the anti-microbial and corrosion resistance properties. All the three generation coating films show excellent antimicrobial activity with good corrosion resistance. The increase in generation of hyperbranched architecture has been resulted in increase of antimicrobial, corrosion resistance and thermo-mechanical properties. These types of coatings can be a suitable candidate for multifunctional applications in marine and moist environment

TP42

Highly Fluorescent Monodisperse, Cross-linked Polymer Microbeads

Swapnil L. Sonawane and S. K. Asha*
Polymer Science and Engineering Division, National Chemical Laboratory,
Pune - 411008. INDIA

Fluorescent cross-linked polymer microspheres with controlled structure (monodisperse), thermal stability, bright and uniform emission are in great demand in many fields such as biolabelling, bioimaging, sensing, optoelectronics etc. Perylene bisimide (PBI), which has high absorption coefficient in the visible region, high quantum yield, good photo and thermal stability, was used as a fluorescent material for the preparation of polystyrene-PBIX fluorescent microspheres. A Perylene bisimide cross-linker (PBIX) was designed and synthesized, where the chromophore played a dual role of cross-linker and fluorophore. The PBI cross-linker was introduced into polystyrene backbone through two-stage dispersion polymerization. The fluorescent polymer beads exhibited bright orange-red emission in the solid state also as observed under hand-held UV–lamp. The microspheres were characterized using dynamic light scattering, scanning electron microscopy, transmission electron microscopy, and fluorescence microscopy. This work provides a good platform for the preparation of monodisperse cross-linked fluorescent microspheres. The approach is very facile and can be extended to other fluorescent cross-linkers also thereby enabling the fine-tuning of emission colours.



References:
[1] R. Wilson, A. R. Cossins D. G. Spiller. *Angew. Chem. Int. Ed*. **2006**, *45*, 6104.
[2] J. S. Song; F. Tronc; M. A. Winnik. *J. Am. Chem. Soc.* **2004**, *126*, 6562.
[3] B. I. Chan; J. P. Zimmer; M. Stroh; J. S. Steckel; R. K. Jain; M.G. Bawendi. *Adv.Mate*, **2004** *16*, 23.

TP43

One Step Synthesis Of Novel Linear Water-Soluble β-Cyclodextrin Based Polymers For Drug Delivery Applications

T. Gangadhar and C. N. Murthy*
*Applied Chemistry Department, Faculty of Technology and Engineering,
The M. S. University of Baroda, Vadodara-390001, INDIA.

Linear cyclodextrins based polymers have several advantages, such as higher water-solubility, inclusion ability and moderate cavity size. Controlling the degree of substitution and reactivity is an important phenomenon in balancing the water-solubility of the β-cyclodextrin based polymers. For this purpose, it is necessary to design the synthetic methods which have controlled the reactivity with no crosslinking. Thus, in order to avoid crosslinking we had taken the 4, 4'-disulfonyl bridged β-cyclodextrin as a monomer and urea as a linking agent to design the synthesis of highly water-soluble β-cyclodextrin polymers consisting β-cyclodextrin in the main chain of the polymers. Thus, the cyclodextrin based polymers synthesized were used as carriers for the poorly water-soluble antibiotic drug Cefpodoxime Proxetil (CPDX-PR), with the intention that these synthesized cyclodextrin based polymers can change the solubility of CPDX-PR and alter the stability of the drug CPDX-PR/cyclodextrin polymers inclusion complex with better release performance [3]. The physicochemical properties of the synthesized polymers were characterized by FT-IR, XRD, TGA, and NMR. The formation of 1:1 inclusion complex of Cefpodoxime Proxetil (CPDX-PR) with the prepared polymers was confirmed from FT-IR, UV-VIS and phase solubility studies. The release performance was investigated through phase solubility Fig. 1 and dissolution studies Fig.2. It was found that these polymers showed improved drug dissolution abilities.

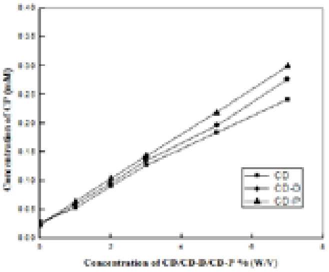


Figure 1 Phase solubility diagram of CPDX-PR with CD, CD-Dimer, CD-Polymer

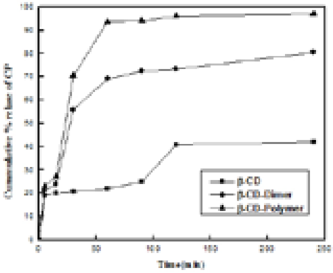


Figure 2 Dissolution curves of CPDX-PR with CD, CD-Dimer, CD-Polymer

References

[1] Shown, I.; Murthy, C. N. *Macromol. Symp*. 287 (**2010)** 59.
[2] Gangadhar, T.; Murthy, C. N. *Trends in carbohydrate research* 4 (**2012**) 7.
[3] Challa, R.; Ahuja, A.; Khar, R.K. *AAPS Pharm. Sci. Tech.* 6 (**2005**) 319.

TP44

Intra-Chain H-Bonding and Vesicular Assembly by Amphiphilic Polyurethane

Tathagata Mondal [a], Krishna Dan [a], Jolly Deb [b], Siddhartha S. Jana [b] and Suhrit Ghosh*[a]
[a] Polymer Science Unit, [b] Biological Chemistry Department
Indian Association for the Cultivation of Science
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata-700032
** Corresponding author's email id.: psusg2@iacs.res.in*

Polyurethanes have been known since long as good candidates for bio-medical applications due to their excellent physical properties and bio-compatibility. We are revisiting this classical family of macromolecules to explore H-bonding interaction among the self-complementary urethane functionality present in the polymer backbone to dictate self-assembly of custom designed amphiphilic polyurethanes in aqueous medium.

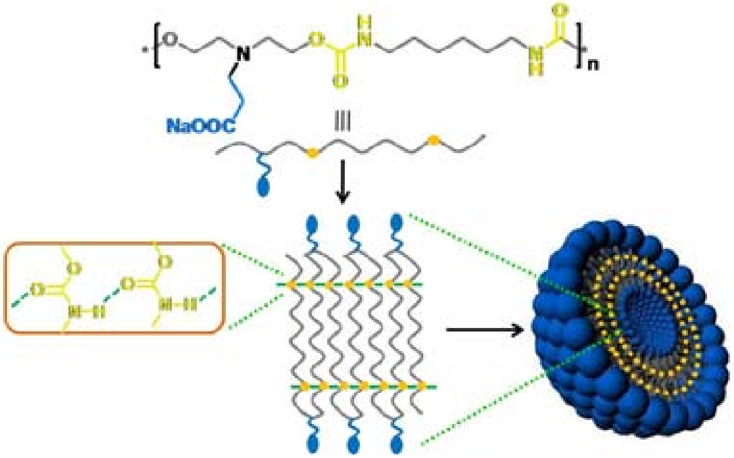


Fig: Vesicular Assembly by Amphiphilic Polyurethane

We have synthesized amphiphilic polyurethane where urethane linkages were placed periodically and pendant carboxylate group was attached with hydrophobic backbone. In aqueous medium (pH ~ 8.0) it shows vesicular assembly even at very dilute condition which was characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS) and atomic force microscopy (AFM) studies. Such vesicular aggregation could encapsulate a hydrophilic dye (Calcein) which was probed by fluorescence studies. It was proposed that the vesicular membrane was formed by folding of the polyurethane chain induced by intra-chain H-bonding interaction among the urethane functional groups. This was also supported by urea addition experiment, solvent dependent FT-IR study and concentration dependent FT-IR and DLS experiments. Further XRD of that sample also established the H-bonded folded structure of the vesicle. This vesicle is kinetically very stable and it is also zwitterionic in nature. MTT assay assured structural engineering in this case did not affect inherent biocompatibility of polyurethane.

TP45

Sulfone linkage containing Polyhydrazides: Synthesis and Characterisation

V. P. Ubale[1]; R. A. Patil[1]; S. S. Kumbhare[1]; P. H. Basutkar[1]; A. A. Ghanwat[2] and N. N. Maldar[2]
1. D.B.F. Dayanand College of Arts and Science, Solapur – 413002 (India).
2. School of chemical sciences, Solapur University, Solapur – 413255(India).
vpubale@yahoo.co.in; maldar_nn@rediffmail.com

Wholly aromatic (amide-hydrazide)s exhibit some interesting and potentially useful characteristics and have enormous technical and economic importance[1]. These polymers are heat resistance materials [2, 3], thermally stable due to their chemical structure containing amide groups, aromatic moieties; considerable crystallinity and because of strong hydrogen bonding between the amide groups of the neighbouring chain segments [4]. Polyhydrazides on heating undergo cyclodehydration to form polyoxadiazoles. Siloxane-containing poly (oxadiazole-imide)s were prepared by polycondensation reaction of aromatic oxadiazole-diamines with dianhydride containing tetramethylsiloxane moiety. Free-standing flexible films having good mechanical properties were made therefrom [5].

The present investigation is directed toward the evaluation of the influence on thermal behavior and processability exerted due to incorporation of various structural variations into polyhydrazides. A new dihydrazide having sulphone linkage was synthesized, in multiple steps, from 4, 4'–dicarboxydiphenylsulphone [6], which was subjected to esterification followed by reaction with hydrazine hydrate to get dihydrazide (DSDH). Monomer DSDH was characterised by spectroscopic methods. A series of polyhydrazide having sulphone linkage was synthesized from (DSDH), isophthaloyl dihydrazide (IDH) or terephthaloyl dihydrazide (TDH) and terephthalic / isophthalic acid by Yamazaki's phosphorylation method using triphenylphosphite as condensing agent. All the polymers were obtained in quantitative yields and were characterized by spectroscopic techniques, solubility, inherent viscosity, thermogravimetric analysis and X-ray diffraction studies.

Structure property relationship was evaluated. Due to incorporation of sulphone unit in the polymer backbone, the solubility of polyhydrazide was good in comparison with polyhydrazide which do not have sulphone linkage.

References:

[1] Abdolmaleki, A. *Polym. Degrad. Stab.* 92 **(2007**) 292.
[2] Gervasi, P. G.; Petris, S.D.; Lupinacci, D. *Eur. Polym. J.* 11 (**1975)** 233.
[3] Mohamed, N. A.; Hamad, A.O.; Al-Dossary. *Polym. Degrad. Stab*. 79 (**2003**) 61.
[4] Frazer, A.H.; Sweeny, W.; Wallenberger, F.T. *J. Polym.Sci.A* 2 **(1964)** 1157.
[5] Damaceanu, M. D.; Musteata, V. E.; Cristea, M.; Bruma, M. *Eur. Polym. J.* 46 **(2010)** 1049.
[6] Hsiao, S. H.; Yang, C.P. *J. Polym.Sci.A* 28 **(1990)** 2501.

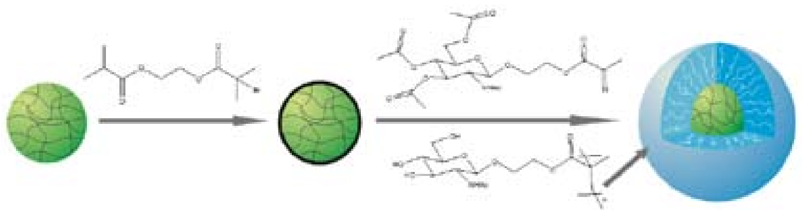
TP46

Sugar-containing Polymer Brushes

Vaishali Shinde*
Vaishali Shinde,[a] *André Pfaff,[b] Yan Lu,[c] Matthias *Ballauff*[c] *and* Axel H. E. Müller[b]
[a]Department of Chemistry, University of Pune,
Pune-411007 INDIA
[b]Makromolekulare Chemie II, [c]Physikalische Chemie I,
Universität Bayreuth, 95440 Bayreuth, Germany
** email i.d:.vsshinde@chem.unipune.ac.in*

Glycopolymers, synthetic sugar-containing macromolecules, which display complex functionalities similar to those found in natural glycoconjugates are attracting ever-increasing interest from the chemistry community due to their role as biomimetic analogues and their potential for commercial applications[1, 2]. controlled/"living" radical polymerizations of carbohydrate-modified vinyl monomers have been reported as a very facile approach for well-defined and controlled synthesis of Glycopolymers [3].

The synthesis and characterization of spherical sugar-containing polymer brushes consisting of PS cores onto which chains of sugar-containing polymers have been grafted via two different techniques are described (Scheme 1). Spherical glycopolymer brushes were prepared in aqueous dispersion by photopolymerization using the functional monomer 3-*O*-methacryloyl-*D*-glucose (MAGlc) and cross-linked or non-cross-linked polystyrene (PS) particles covered with a thin layer of photo-initiator. Dynamic light scattering (DLS) measurements and cryo-TEM images show that homogeneous glycopolymer brushes are affixed on the spherical PS cores. As an alternative, ATRP was performed to graft poly-(*N*-acetyl-glucosamine) arms from cross-linked PS cores, which were functionalized with an ATRP initiator. Using the "grafting from" approach, protected poly-(*N*-acetyl-glucosamine) chains were densely grown from the nanospheres. Deprotection of the grafted brushes led to water soluble particles that act as carriers for catalytically active gold nanoparticles [4]. Additionally we demonstrate that these glycopolymer chains show a high affinity to adsorb wheat germ agglutinin (WGA) whereas no binding to bovine serum albumin (BSA) or peanut agglutinin (PNA) could be detected [5, 6].



Scheme 1. Synthesis of the sugar-containing polymer brush

References:

[1] Ladmiral, V.; Melia, E.; Haddleton, D. V., *European Polymer Journal,* (**2004),** 40, 431.
[2] Wang, Q.; Dordick, J. S.; Linhardt, R. L., *Chem. Mater.* (**2002),** 14, 3232.
[3] Albertin, L.; Stenzel, M. H.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P., *Macromolecules* (**2004**), 37, 7530.
[4] Mei, Y.; Sharma, G.; Lu, Y.; Ballauf, M., *Langmuir* (**2005),** 21, 12229.
[5] Duverger, E.; Frison, N.; Roche, A.-C.; Monsigny, M., *Biochimie* (**2003),** 85, 167.
[6] Andre Pfaff; Vaishali Shinde ; Yan Lu,.; Alexander Wittemann, Matthias Ballauff, and Axel Müller *Macromol. Biosci.*, 11, (**2011**), 199.

TP47

Synthesis and Characterization of Glycerol based Hyperbranched Polyurethane-Urea Coatings

Varaprasad S, Shaik Allauddin, Ramanuj Narayan and KVSN Raju*
Polymers & Functional Materials Division, Indian Institute of Chemical Technology,
Hyderabad-500007, India
Correspondence to. K.V.S.N.Raju (E-mail*:* kvsnraju@iict.res.in and drkvsnraju@gmail.com),
Telefax: +91-40-27193991

In recent years, there has been exponential growth on the use of Polyurethane (PU) for the development of coatings for different applications due to wide array of raw materials available for its synthesis and versatile chemistry. Eco-friendly moisture cure Polyurethane Urea coatings is emerging as a potential candidate for protective coating segment. This paper reports the development of polyurethane urea coating using glycerol core based green hyperbranched polyester (HBP). The HBP has been prepared by an A+B3 approach by reacting Succinic anhydride and glycerol without any solvent. The obtained HBP was characterized by Nuclear Magnetic Resonance (NMR) spectroscopy and Fourier transform-infrared (FTIR) spectroscopy. NMR was also used for the calculation of the degree of branching of HBP. The HBP has been reacted with isophorone diisocyanate (IPDI) at different NCO/OH ratio of 2: 1, 1.6: 1, 1.4: 1 and 1.2: 1 to get a series of isocyanate terminated PU pre-polymers. These pre-polymers were casted on substrate and cured under atmospheric moisture to get the Hyperbranched polyurethane (HBPU) urea coatings. FT-IR spectroscopy has been used for the quantitative evaluation of the extent of urethane and urea bonds and the others structural investigation of the coating films. The Dynamic Mechanical Thermal Analyzer (DMTA) and Thermogravimetric Analyzer (TGA) have been used to study the visco-elastic and thermal stability of the coating films respectively. The combined FTIR, DMTA and TGA analysis infer the importance of NCO/OH ratio in understanding the network formation and stability of HBPU-Urea network. The glass transition temperature and thermal stability of the HBPU–urea coatings were found to be increased with increasing NCO: OH ratio.

Key words: Coatings, Polyurethane Urea, Hyperbranched Polyester, Moisture Cure

TP48

Synthesis of Aromatic Poly(thioether)s by Oxygen-Oxidative Polymerization

Yohei Takatori, Kenichi Oyaizu, and Hiroyuki Nishide*
Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
E-mail : applied-science@akane.waseda.jp

Oxidative polymerization utilizing the abundant and cheap oxidant oxygen renders the synthesis of aromatic polymers clean and more convenient. Poly(phenylene sulfide) (PPS) possesses high chemical resistance, thermal stability, and good moldability. Commercially available PPS is prepared by the high-pressure and high-temperature polycondensation process, and obtained polymer has salt contamination. However, using oxidative polymerization of disulfide, highly pure PPS can be easily synthesized under atmospheric pressure producing only water as a by-product (**Scheme**) [1]. Herein, we report the establishment of the synthesizing process of a high molecular weight PPS using oxidative polymerization.

Scheme Oxidative polymerization of diphenyldisulfide.

Generally, direct electron transfer between a disulfide and oxygen is very slow, and $V^{IV}O$ catalyst acts as the electron mediator between the disulfide and oxygen. In acidic condition, V^{IV}-O-V^{IV} dinuclear complex is formed and disproportionate to the vanadium(III) and vanadium(V) species. Vanadium(V) oxidize the disulfide to form the sulfonium cation as the active species, and vanadium(III) is reoxidized by oxygen to regenerate the vanadium(V) species. Thus, the catalytic crycle is established as illustrated in the Figure [2].

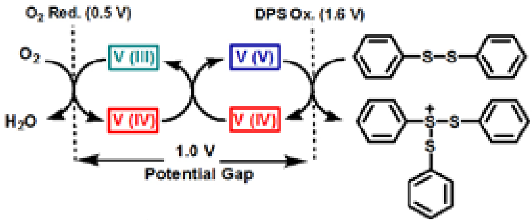


Figure Electron transfer between the monomer and oxygen by vanadyl catalyst.

PPS was synthesized by solvent free oxidative polymerization of diphenyl disulfide. IR spectra of the obtained PPS showed the IR absorption band at 820 cm^{-1} attributed to the C-H out-of-plane vibration of the 1,4-substituted benzene unit and no absorption band attributed to the branched structure was detected. Solid state NMR showed only two peaks, according to the highly symmetric structure. These results indicated that the PPS was linear. In addition, oxidative polymerization allowed the synthesis of many substituted PPS derivatives. In this presentation, we also report the synthesis, characterization and properties of alkyl-substituted PPS derivatives.

References:

[1] Hiroyuki, H., et al., *Macromolecules*, 26 (**1993**) 3432.
[2] Kenichi, O., et al., *Inorg. Chem*, 33 (**1994**) 1056.

Block copolymer and nanostructured films

Invited Talk

Nanoscale Patterning of Block Copolymer Thin Films: Toward Energy Conversion and Storage Applications

Soojin Park*
[a]*Interdisciplinary School of Green Energy, UNIST, Ulsan 689-798, South Korea*
** spark@unist.ac.kr*

Nano- and micro-scale patterning of polymer thin films is essential to their use as templates or masks for the fabrication of secondary nano- and micro-structured materials. In particular, these patterning techniques can be extended to energy conversion and storage applications, including organic polymer solar cells and lithium-ion batteries [1].

Herein, we describe that block copolymer templates were used to make arrays of metal nanoparticles (e.g., Au, Cu, Au-Cu alloy). We found that bimetallic nanostructures as well as pure metal nanoparticles induced the surface plasmon resonance effect in the optoelectronic devices. Increased light absorption of the polymer thin layer with the incorporation of metallic nanostructures was demonstrated, resulting in higher efficiency compared to conventional optoelectronic devices [2]. Moreover, metal patterned arrays were used as catalyst to etch silicon materials via metal-assisted chemical etching (MACE) process. Silicon nanostructured materials have been widely used as lithium-ion battery electrodes, due to its effective cost, abundance and high storage capacity [3]. The MACE process has several advantages for preparing nonporous and porous silicon nanowires (SiNWs) at the mild etching condition. We demonstrate a simple, massive production of diameter-controlled SiNWs by combining copolymer patterning and chemical etching. Nonporous and porous SiNW arrays having diameter of 80-100 nm were prepared by controlling resistivity of silicon wafer, and the electrochemical properties of both SiNWs were compared. Porous SiNWs exhibited a highly stable cycling retention over 50 cycles at high lithium storage capacity of 1500 $mAhg^{-1}$ compared to nonporous SiNWs. The advantage of porous SiNWs to alleviate a large volume expansion during lithiation/delithiation may open a new avenue for the use as excellent anode materials in lithium ion batteries [4].

References

[1] S. Park, T. P. Russell, "Nanopatterning and functionality of block-copolymer thin films" *Functional Polymer Films* 1 **(2011)**, 403-473. Publisher: Wiley-VCH

[2] M. Heo, H. Cho, J.-W. Jung, J.-R. Jeong, S. Park, J. Y. Kim, Adv. Mater.23 **(2011)** 5689.

[3] Z. Huang, N. Geyer, P. Werner, J. de Boor, U. Gösele, *Adv. Mater.* 23 **(2011)** 285.

[4] H. Yoo, J.-I. Lee, H. Kim, J.-P. Lee, J. Cho, S. Park, *Nano Lett.* 11 **(2011)** 4324.

New Directions in Hierarchical Self Assembly of Liquid Crystalline Random and Block Copolymers

Rajeswari Kasi
Polymer Program, Institute of Materials Science & Chemistry Department
University of Connecticut
Storrs, CT 06269, USA

E-mail: kasi@mail.ims.uconn.edu

We are interested in developing general molecular engineering approaches to liquid crystalline and semicrystalline brush random and block copolymers. These polymers self-assemble into hierarchical supramolecular nano structures with organization over several length scales that allows for evolution for unique property and function. In these polymeric libraries, we exploit liquid crystalline units for its responsive optical and mechanical features and semicrystalline brush units for its mechanical and thermal features. These materials are useful for applications in 1D photonic band gap materials as well as templates for preparation of nanoporous scaffolds.

Tailor-made Polyfluoroacrylate and its Block Copolymer by RAFT Polymerization in Miniemulsion; Enhanced Hydrophobicity in the Core-shell Block Copolymer

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

Controlled/living radical polymerization (CRP) of a fluoroacrylate was successfully carried out in miniemulsion by Reversible Addition-Fragmentation chain Transfer (RAFT) process [1]. In this case 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) was polymerized in miniemulsion [2] using 2-cyanopropyl dodecyl trithiocarbonate (CPDTC) as RAFT agent, TritonX-405 and sodium dodecyl sulfonate (SDS) as surfactant and potassium persulphate (KPS) as the initiator. The miniemulsion was stable without any costabilizer. The long chain dodecyl group ($-C_{12}H_{25}$) in the RAFT agent had beneficial effect in stabilizing the miniemulsion. Block copolymerization with butyl acrylate (BA) using PHFBA as macro-RAFT agent showed core-shell morphology. The PBA was in the core and the shell was formed by the aggregation of PHFBA segment. This was confirmed by TEM analysis as well as by EDX analysis of the shell. The block copolymer with nano phase separated morphology showed higher hydrophobicity compared to PHFBA alone, as determined by Goniometer. The molecular weight (M_n) and polydispersity index (PDI) were determined by GPC analysis.

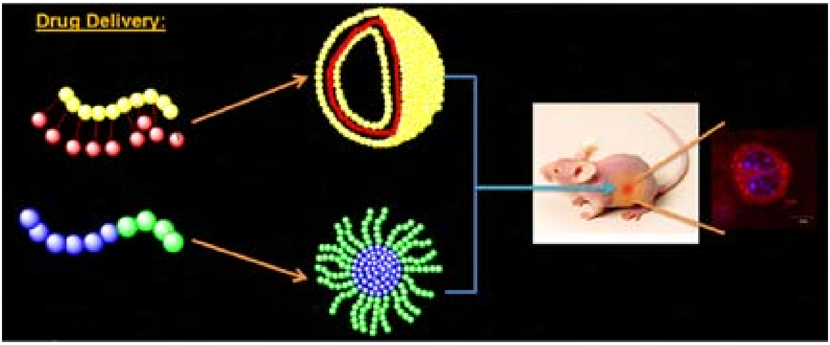
References

[1] Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R.; Meijs, G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules,* 31 (**1998**) 5559
[2] McLeary, J. B.; Klumperman, B. *Soft Matt*er, 2 (**2006)** 45

Polynorbornene Based Nonocarriers for Biomedicinal Application

Raja Shunmugam
Polymer Research Centre, Department of Chemical Sciences
Indian Institute of Science Education and Research, Kolkata, India.
sraja@iiserkol.ac.in

Polymers that have potential application in the field of drug delivery with anti tumor prodrugs are being developed. Controlled/living polymerization techniques such as ROMP will be used to synthesize random and block copolymers where the composition of the copolymer length that contain drugs can be controlled. The advantage of ongoing work in designing prodrugs is that one block is linked to the nanoparticle so the drug-carrier's path can be influenced by external stimuli like magnetic force, thus drug delivery can be targeted. Preliminary enzymatic cleavage of drug from the polymer is studied using spectroscopic and chromatographic techniques. The preliminary results on monomer synthesis are shown here. We also develop CdSe nanoparticles and carbon nano tube (CNT) containing polymers that are used to sense heavy metals such as arsenic and mercury.



References:

[1] Grubbs R. H. (ed) Handbook of Metathesis, 2003, Vol 3 (Wiley-VCH, Weinheim); b) Grubbs, R. H. *Angew. Chem. Int. Edn.,* 2006, 45, 3760; Maynard, H. D.; Grubbs R. H. *Macromolecules* 1999, 32, 6917.
[2] Shunmugam, R.; Tew, G. N. *J. Polym. Sci., Part A: Polym. Chem.* 2005, 43, 5831.; b) Shunmugam, R.; Tew, G. N. 2008, *Chem. Eur. J.* 14, 5409-5412; Shunmugam, R.; Gabriel, G. J.; Smith, C. E.; Aamer, K. A.; Tew, G. N. *Chem. Eur. J.* 2008, 14, 3904-3907.
[3] Shivshankar, M; Vijaykameswara Rao, N.; Koushik, C.; Himadri, D.; Soma, N.; Abhinoy, K.; Das Sarma, J*.; *Shunmugam, R.** Macromolecules, 45(19), 8037-8042, 2012.
[4] Vijaykameswara Rao, N.; Abhinoy, K.; Sarkar, S.; Das Sarma, J*.; Shunmugam, R.* *Biomacromolecules* 2012, *13* (9), 2933–2944.
[5] Shivshankar, M; Vijaykameswara Rao, N.; Koushik, C.; Himadri, D.; Soma, N.; Das Sarma, J*.; *Shunmugam, R.* J. Mater. Chem.,* 2012, 22, 19639-19642.
[6] Shivshankar, M; Vijaykameswara Rao, N.; Shunmugam, R.* *ACS Macro Letters*, 2012, 1(4), 482-488.
[7] Sarkar S., Mondal, A., Tiwari, A. K. and Shunmugam, R* *Chem. Comm***.** 2012, 48, 4223-4225.
[8] Vijaykameswara Rao, N.; Shivshankar, M.; Abhinoy, K.; Das Sarma, J*.; Shunmugam, R* *Biomacromolecules,* 2012, 13 (1), 221-230.

Phase behavior in copolymers with poly(ethylene glycol) blocks: Implications for biomaterial applications

N. Sanjeeva Murthy*
New Jersey Center for Biomaterials, Rutgers University, Piscataway, NJ 08854, USA

Poly(ethylene glycol) (PEG) is widely used as a biomaterial by either incorporating it into the polymer backbone, or by immobilizing it on surfaces [1]. PEG's unique properties include low-protein adsorption, low-toxicity, and absence of cell attachment. Therefore, cellular response of PEGylated surfaces can be precisely controlled by tagging the polymer with desired functional groups. The distribution of PEG domains in the matrix influences the properties such as mechanical behavior, permeability and cellular response in PEG-containing polymers. Studies of phase behavior in these polymers provide insight into how PEG modulates the polymer properties.

Thermal analysis, imaging and scattering techniques (small-angle x-ray, neutron and wide-angle x-ray) have provided important insights into the phase behavior of copolymers with PEG. We have been investigating this phase behavior in amorphous copolymers containing hydrophobic segments (desaminotyrosyl-tyrosine ethyl ester) and hydrophilic blocks of PEG. PEG blocks crystallize when the block size is at least 2000 Da and present at ~ 40 wt%. The PEG blocks in dry polymers with up to 50 wt% PEG are uniformly distributed with no evidence of phase separation at ~10 nm length scales. Irrespective of whether PEG was crystalline or not, hydration induces PEG to separate into 15 nm hydrated domains (Figure 1) [2]. A sequence of distinct regimes of hydration were observed: homogeneous distribution (~10 Å length scales) at <13 wt.% PEG (~1 water per EG), clusters of hydrated domains (~50 Å radius) separated at 24 wt.% PEG (1–2 water per EG), uniformly distributed hydrated domains at 41 wt.% PEG (~4 water per EG) and phase inversion at >50 wt.% PEG (>6 water per EG).

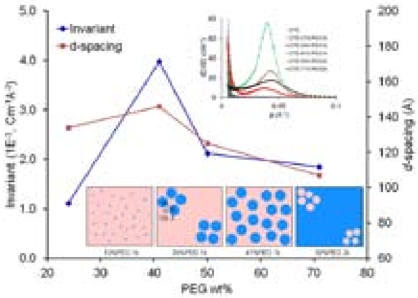


Figure 1. Small-angle x-ray scattering data in the form of invariant and *d*-spacings of the interference peak observed in polymers with different amount of PEG. The schematic shows the distribution of the hydrated PEG domains (blue/dark in gray scale) in the hydrophobic matrix (pink/light in gray scale).

Some of the consequences phase separation will be discussed. First, these phase-separated domains evolve into micrometer-size channels that form during hydrolytic erosion. Second, phase separation was found to unexpectedly increase the Young's modulus of the copolymer by as much as 15-fold upon hydration with 30 to 60 vol% of PEG [3]. This stiffening effect is attributed to the phase-separated PEG segments in the hydrated domains that no longer participate in the transfer of stress through the polymer matrix as they do when they are molecularly dispersed along the polymer chain in the dry state. Finally, these hydration-induced morphological changes were found to influence the release profile of drug molecules such as voclosporin [4].

References

[1] Tessmar, J.K.; G~ pferich, A.M. *Macromol. Biosci*. 7 **(2007)** 23.
[2] Luk, A.; Murthy, N.S.; Wang, W.;R. Rojas, R.; Kohn, J. *Acta Biomaterialia* 8 **(2012)** 1459.
[3] Bedoui, F.; Widjaja, L.K.; Luk, A.; Bolikal, D.; Murthy N. S.; Kohn, J. *Soft Matter* 8 **(2012)** 2230.
[4] Khan, I. J.; Murthy, N. S.; Kohn, J. *J. Funct. Biomater.* 3 (2012) 745.

Photoresponsive Soft Materials from Block Copolymers

Suresh Das
Photosciences and Photonics Section, Chemical Sciences and Technology Division
National Institute for Interdisciplinary Science and Technology (NIIST), CSIR
Trivandrum – 695 019
E-mail: sureshdas55@gmail.com

Self-assembly of amphiphilic block copolymers (BCPs) in selected solvents has provided a simple route to prepare polymeric assemblies with various morphologies including spherical micelles, vesicles, and nanotubes. Compared to low molecular weight molecules, block copolymer aggregates offer advantages and broaden their potential for technological applications in a variety of areas such as in biology, colloid science, and encapsulation technology. There has recently been growing interest in developing light-responsive BCP micelles whose aggregation state in solution can be disrupted by illumination. Here we synthesized different types of light responsive amphiphilic BCPs synthesized via atom transfer radical polymerization. These BCPs comprise of a water soluble block and a water insoluble photoresponsive block consisting of spiropyran (see Figure 1), azobenzene, stilbene or pyrenylmethyl methacrylate. All these BCPs form well defined aggregates in water which can act as carriers of hydrophobic molecules in aqueous environment. The aggregation properties and the release kinetics of the encapsulated guest molecule in response to light for these polymeric aggregates have been investigated.

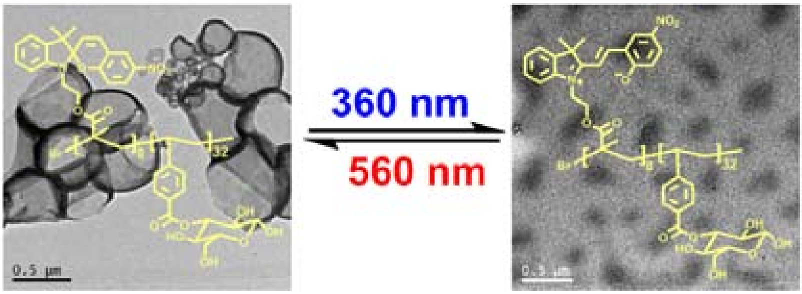


Figure 1. Vesicular aggregates formed by a spiropyran containing glycopolymer in water were reversibly dissociated using light making them suitable as control release systems

References:
[1] Menon, S.; Ongungal, R.M.; Das, S. *Polym. Chem.* 4 (**2013**) 623.
[2] Menon, S.; Das, S. *Polym. Chem.* 3 (**2012**) 2619.

Cylindrical Nanostructure from Rigid-rod POSS containing Star-branched Block Copolymer

RaitaGoseki, Takashi Ishizone, Akira Hirao, and Teruaki Hayakawa*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S8-36
O-okayama, Meguro-ku, Tokyo 152-8552, Japan
*Teruaki Hayakawa:hayakawa.t.ac@m.titech.ac.jp

It is well known that block copolymers self-assemble into nanoscale periodic domains due to repulsion between the covalently connected blocks. Particularly, these well-defined morphologies from bulk as well as in thin film are intense current interest for applications including porous membrane, lithographic templates and photonic band-gap materials[1]. Therefore, to investigate the correlation between the morphologies of the nanostructures and their functionalities is promising way to establish unique self-assembly materials. Recently, we had reported the development and self-assembly of a series of polyhedral oligomericsilsesquioxnes (POSS)-containing polymethacrylate (PMA)-based diblock copolymers. We had found that the well-defined microphase separated nanostructures from the bulk as well as in thin film and also excellent performance such as high resistance to oxidation[2]. However, the cylindrical structures that comprise the minor domains of the POSS segments were not observed. This type of phase-separation behavior is often observed in the so-called "rod-coil" block copolymers as well. Indeed, since the POSS molecule itself is bulky and crystalline, it may be said that its size causes the distinct phase-separation behavior. In this study, we devised a new approach for designing polymer structures to obtain POSS with a cylindrical microphase-separated structure having a volume fraction unobtainable using diblock copolymers. To do so, we employed copolymers with A2Bwell-defined star-branched structures, because the branched arms of these copolymers allow for greater curvature at the A-B interface. Herein, we describe the procedure for synthesizing a POSS-containing A2B-shaped polymer in which polystyrene (PS) was the A segment and PMAPOSS was the B segment. The self-assembled structures obtained using PMAPOSS in the A2B-shaped polymer in various volumetric concentrations were also investigated.

Star-branched PS2-PMAPOSS was prepared by linking reaction of benzyl bromide (BnBr)-difunctionalized PMAPOSS and living polystyrene end-cappdedwith 1,1-diphenylethylene anion. The chemical structures of the star-branched PS2-PMAPOSS polymers were determined using 1H, 13C, and 29Si NMR spectroscopy and infrared (IR) spectroscopy. The obtained star-branched PS2-PMAPOSSs investigated in the present study had overall PS-to-PMAPOSS volume fractions ranging from 26 to 70 vol.%. The morphologies of the samples were characterized using small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and transmission electron microscopy (TEM), which were performed on samples subjected to thermal annealing at 180 °C for 24 h in a vacuum oven.

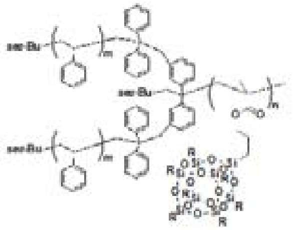


Figure 1. Chemical structure of star-branched PS_2-PMAPOSS.

In the TEM measurements, all the polymers exhibited well-defined morphologies, which resulted from the microphase separation. The TEM images of the star-branched PS2-PMAPOSSs (φPS = 24 and 56 vol.%) are shown in Figures 2 (a) and (b), respectively, along with the corresponding SAXS profiles. On the other hand, in the case of the high-coil-fraction star-branched PS2-PMAPOSS (φPS = 70 vol.%), self-assembly into hexagonal structures, the type has not seen in the case of PS-b-PMAPOSS diblock copolymers with similar volume fractions, was observed (Figure 2(c)).

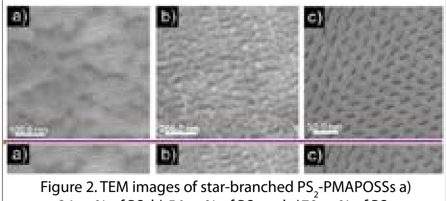


Figure 2. TEM images of star-branched PS_2-PMAPOSSs a) 24 wt% of PS, b) 56 wt% of PS, and c)70 wt% of PS.

To summarize, we successfully synthesizaed star-branched PS2-PMAPOSSs and studied their copolymers could be made to self assemble into cylinder-like nanostructure by using an architectural approach.

References

[1] Park, C.; Yoon. J; Thomas, E. L. *Polymer*, 44 (**2003)** 6725.
[2] Goseki, R.; Hirai. T.; Ishida, Y.; Kakimoto, M.; Hayakawa, T. *Polymer Journal*, 44 (**2012)** 658.

Oral

Crystallinity and Crystallographic Orientation of Biodegradable Poly[(R)-3-hydroxybutyrate] Thin Films blended with Biodegradable Poly(lactic acid)
-An Effective Use of Novel Confinement Effects-

Isao Takahashi*[a], Harumi Sato[a], Yukihiro Ozaki[a], Xiaoli Sun[b] and Shouke Yan[b]
[a] *Faculty of Science and Technology, Kwansei Gakuin University, Sanda 6691337, Japan*
[b] *State Key Laboratory of Chemical Resource Engineering,*
Beijing University of Chemical Technology, Beijing 100029, China.
suikyo@kwansei.ac.jp

Poly[(R)-3-hydroxybutyrate] (PHB) is an environmentally benign biodegradable thermoplastic. However, there are several inherent drawbacks in PHB, i.e., poor processing properties and brittleness due to its high crystallinity. To overcome such problems, many smart processes including copolymerization, nanocomposites and blending have been proposed. Of these, creating a polymer blend of PHB and Poly(lactic acid) (PLA) is the most appealing, since miscibility of PLA with PHB is known to be dependent on the molecular weight of PLA.

In the present study, we performed surface X-ray diffraction and infrared reflection absorption spectroscopy (IRRAS) measurements so as to investigate the PLA-molecular-weight dependence of PHB crystallization and crystallographic orientation, and surface morphology of the ultrathin blend films [1]. Two types of PHB/PLA blend thin films were prepared: PHB/high-molecular-weight PLA (H-PLA) (MW = 13,000 g/mol) and PHB/low-molecular-weight PLA (L-PLA) (MW = 720 g/mol) with thicknesses of 50 nm and 100 nm. Grazing incident X-ray diffraction (GIXD) revealed that only 20% of H-PLA (weight ratio of PHB = 0.8) completely inhibits crystallization of PHB, although PHB crystallites in thin films can survive even under the presence of 75% of L-PLA (weight ratio of PHB = 0.25). IRRAS data strongly suggested that PHB molecules in ultrathin PHB/H-PLA blend films are in an intermediate state between amorphous and crystalline states. Interaction between PHB and H-PLA and confinement effect peculiar to thin films should be responsible for the formation of intermediate structure of PHB. Since the degree of crystallinity of PHB thin films is now controllable by adding small amount of L-PLA, we have tried to control the crystallographic orientation of PHB crystallites dispersed in thin films [2]. Figure 1 indicates an out-of-plane GIXD profile of a 100 nm-thick PHB thin film in which only (020) Bragg reflection is seen. It shows a distinct contrast with the diffraction profile of a cast PHB film with thickness ca 0.1 mm (Figure 2). Figure 1 clearly indicates a surface-induced preferred orientation of PHB crystallites in which the *b*-axis strongly tends to align along the surface normal direction by forming the so-called edge-on lamellae. Forming the flat-on-lamellae-dominant thin films is revealed to be possible under the choice of different thermal annealing conditions and different substrates.

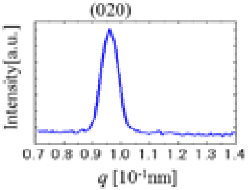


Fig. 1 GIXD profile of PHB film with thickness of100nm

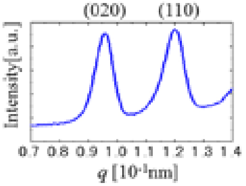


Fig. 2 Diffraction profile of cast PHB film

References

[1] Xiaoli Sun, Akihisa Tokuda, Yusuke Oji, Takashi Nakatani, Hideto Tsuji, Yukihiro Ozaki, Shouke Yan, and Isao Takahashi, *Macromolecules*, 45 (**2012**) 2485.

[2] Xiaoli Sun, Zhen Chen, Feng Wang, Shouke Yan and Isao Takahashi, *Macromolecules*, 46 (**2013**) 1573.

Characterization of Detached Polymer Brush Membranes

M. Elizabeth Welch[a], Christopher K. Ober[a*]
[a] *Department of Materials Science and Engineering*
Cornell University, Itahca, NY, USA
** cko3@cornell.edu*

Polymer brushes have attracted much attention in the past decade due to their ability to change the properties of a surface on a scale of just a few nanometers. Analysis of polymer brush films is often limited to surface techniques that average over a large area such as water contact angle, ellipsometry, and FTIR. The bottom side of these membranes can provide valuable information as well; however, because brushes are covalently tethered to the surface, such characterization becomes difficult. Therefore we have developed a method of detaching polymer brush films for further exploration by transmission electron microscopy (TEM).

To remove the films, a thick silicon oxide layer is first thermally grown on a wafer before brush polymerization via atom transfer polymerization (ATRP).[1] The oxide layer provides a surface identical to a conventional silicon wafer used in polymer brush growth, and thus we are not limited to the type of brushes that can be grown. Polymer brushes can be easily patterned by conventional lithographic process to provide reference points in the membranes for microscopy purposes. Applying an HF solution etches away the oxide layer allowing the polymer brush film to lift off undamaged.

Polystyrene (PS) and poly(glycidyl methacrylate) (PGMA) polymer brushes have been explored with this technique and the resulting membranes have proven quite robust. For additional strength, lithographic and chemical crosslinking methods were investigated and compared to the uncrosslinked films. Results indicated that application of a crosslinking process produced films that retained shapes closer to that of the original pattern dimensions. This also provides insight into the properties of polymer brushes as stretched chains and their associated strains as compared to detached membranes.

Additionally this technique can provide information regarding the initiator immobilization and brush polymerization process. Results show initiator immobilized at low concentrations produces lower density, patchy brushes whereas initiator immobilized at high concentrations generates high density, homogeneous brushes. Overall, detached membranes can be characterized to test initiator quality, immobilization conditions, optimization parameters, and answer questions about the nature of polymer films.

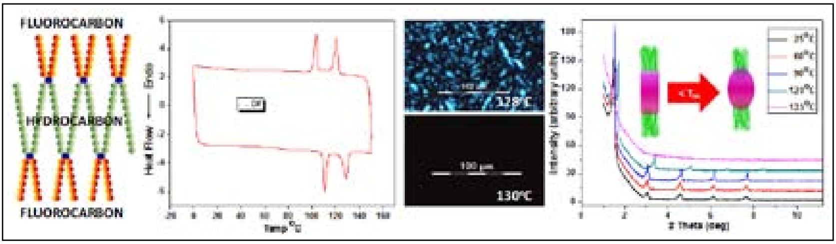
References

[1] Welch, M. E.; Ober, C. K. *Macro Lett.*, (**2013) ASAP**.

Single-chain nanostructuring in periodically grafted polyesters

Joydeb Mandal, Dr. S. Krishna Prasad#, Dr. D. S. Shankar Rao# and S. Ramakrishnan*
Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore-560012 INDIA
#*Center for Soft Matter Research, Bangalore - 560013*

One of the important challenges in polymer science is to control the solution conformation of polymer chains, their self-assembly and, finally, their organization in the solid state by tailoring their architecture. Wagner and co-workers showed that precise placement of substituents, like a Cl atom, along a polyethylene backbone changes the crystal thickness; this can be tuned by varying the distance between two adjacent Cl atoms [1]. Recently, we demonstrated that a polymer with pendant hexaethylene glycol (HEG) units placed periodically along a hydrophobic a polyester backbone containing long alkylene segments adopts a folded zigzag conformation due to the mutual segment immiscibility that is reinforced by the strong crystallization tendency of the alkylene segments [2]. In this previous study the pendant HEG segments do not crystallize and therefore permits the alkylene segments to organize freely; thus, an interesting question would be: *What would happen if one were to replace the HEG by another immiscible but crystallizable unit, such as a fluorocarbon (FC)?*



In order to prepare such periodically grafted polymers, we developed a strategy that permits us to place *clickable* units at periodic intervals using a suitable combination of monomers, one that carries the clickable groups; this allowed us to access polyesters carrying long alkylene segments along the backbone and fluoroalkyl (FC) pendant segments. The DSC thermograms of these FC derivatives exhibit two sharp melting transitions; one due to hydrocarbon (HC) and the other due to FC melting, which were consistent with earlier observations in similar amphipathetic polymers [3]. It is interesting that these polymers exhibit a mesophase in the temperature region between the two melting transitions, as evident from the PLOM observations. SAXS studies also confirmed the formation of a lamellar morphology and the formation of a smectic mesophase; a clear decrease in the spacing is evident when the material transitions from the crystalline to the smectic mesophase.

References

[1] Alamo, R. G.; Jeon, K.; Smith, R. L.; Boz, E.; K. B. Wagener, K. B.; Bockstaller, M. R. *Macromolecules* **2008**,*41*, 7141
[2] Roy, R. K.; Gowd, E. B.; Ramakrishnan, S. *Macromolecules* **2012**, *45*, 3063
[3] Wilson, L. M.; Griffin*, A. C. Macromolecules* **1994***, 27,* 4611

Temperature Induced Structural Changes in Biodegradable Poly(lactide) Stereocomplex Ultrathin films as Viewed from the Combination of IR-RAS and GIXD

Kummetha Raghunatha Reddy*, Takashi Nakatani, Isao Takahashi, Yukihiro Ozaki
Faculty of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan
kr_raghunath@yahoo.com

Polylactide (PLA) (-[CH(CH$_3$)-COO)]$_n$-), biodegradable linear aliphatic polyester, has been investigated extensively because it can be produced from renewable sources. Two enantiomers of PLA, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), can be synthesized due to the presence of chiral carbon in the main chain. The PLA stereocomplex is formed by blending between PLLA and PDLA in equimolar ratio either in the solution or the melt.[1] The PLA stereocomplex has been attracted attention mainly because of its better physical properties and higher melting point (≥50 °C) than that of the homopolymer. Recently crystallization of polymer thin films has been gained much attention.[2,3] To the best of our knowledge there has been no previous study on the temperature-induced structural changes (in the crystallization process) of the stereocomplex in the ultrathin films state. In the present study, we investigated the thermal behaviour of the ultrathin films by the combination of surface-sensitive grazing incidence X-ray diffraction (GIXD) and infrared reflection-absorption spectroscopy (IR-RAS).

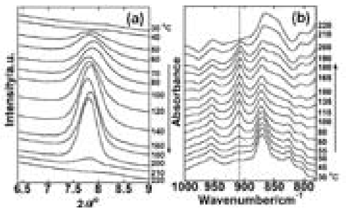


Figure 1. Temperature-dependent of (a)(110) Bragg reflection under out-of-plane condition (b) RAIR spectra obtained in the 1000-800 cm^{-1} region.

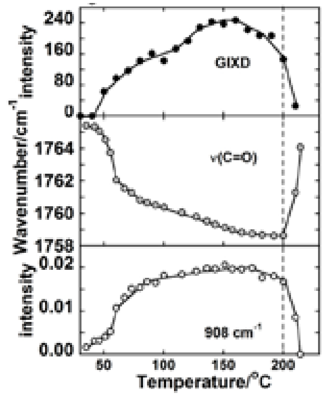


Figure 2. Temperature-dependent of (110) reflection intensity, ν(C=O) frequency and integrated intensity of 908 cm^{-1} band.

The PLA stereocomplex thin films with 30 nm (1 wt% of PLLA and PDLA in 1:1 mole ratio) on silicon wafers were spin coated. Figure 1 (a), shows GIXD out-of plane profiles of stereocomplex thin films measured using synchrotron radiation (Wavelength = 1Å, incident angle = 0.11°, SPring-8, Japan) as function of temperature in the heating process. It should be noted that, at room temperature absence crystalline peak in both the out-of-plane and in-plane (profiles not shown here) mode profiles indicate that as spun-cast films are in amorphous state. In the X-ray profiles, as the temperature increased to ca. 50 °C, a crystalline peak at $2\theta = 7.8°$ of 110 Bragg reflection is detected. As the temperature increased further, the peak increased in the intensity up to 200 °C followed by melting at 220 °C. Figure 1(b) shows the IR-RAS spectral profiles collected in the region of 1000-800 cm^{-1} during the heating process. The appearance of infrared band at 908 cm^{-1} at ca. 50 °C indicate the formation of 3/1 helices in the crystallization process. Thus structural changes occurred both in IR-RAS (frequency of ν(C=O) and integrated intensity of 908 cm^{-1} band) and GIXD ((110) reflection intensity) are plotted against temperature in Figure 2. The intensity of 908 cm^{-1} band and the frequency of the ν(C=O) changed gradually with temperature. The *helical conformation stability* is higher in the ultrathin films as compare to the bulk films during the heating process of PLA stereocomplex.

References

[1] Tsuji, H. *Macromolecular Bioscience*, 5 (**2005)** 569.
[2] Frank, C.W.; Rao, V.; Despotopoulou, M.M. et al. *Science*, 273 (**1996)** 912.
[3] Sun, X.; Tokuda, A. et al. *Macromolecules*, 45 (**2012)** 2485.

High Performance Laboratory SAXS/WAXS Instrument for Polymer and Nanomaterials Research

*S. Rodrigues, P. Panine, M. Fernandez-Martinez, B. Lantz, R. Mahe, N. Galatanu, P. Høghøj and F. Bossan**
Xenocs S.A., Sassenage, France
E-mail: frederic.bossan@xenocs.com

Small Angle X-Ray Scattering (SAXS) is a technique well suited for investigating nanomaterials and nano-structures. The technique gives information 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. In combination with Wide Angle X-ray Scattering (WAXS), the technique can provide information on length-scales down to 0.1 nm, thus allowing to measure both crystalline and nano-structure properties.

Little sample preparation is needed, as the x-ray beam probes the sample in volume. The x-ray beam typically probes a sample volume from 0.1-1 mm^3, and the measurement gives data which is statistically representative of this macroscopic volume. This is a major difference to local probe techniques such as microscopy.

New developments in x-ray techniques now allow for high performance SAXS, GISAXS and WAXS measurements in the laboratory. A micro-focus x-ray source together with a single reflection multilayer coated collimating optic provide a high brilliance x-ray beam previously only attainable with rotating anode sources, but with high reliability and low facilities requirements. A new generation of collimation system with adjustable scatterless slits enables the generation of an extremely well defined beam and the detection of scattered intensity at very small angles and thus the ability to extend the range of dimensions measured to beyond 100 nm. The latest generation of hybrid-pixel photon counting detectors has virtually zero background and read-out noise, giving the user the possibility to use very long exposure times or to conduct dynamic studies as a function of changing sample environment parameters.

In the Xeuss instrument all of these features are integrated into a flexible, reliable and high performance SAXS/GISAXS/WAXS platform. With plenty options and space for sample environment, we will show how the instrument addresses a wide range of topics in polymer and nanomaterials research.

Poster

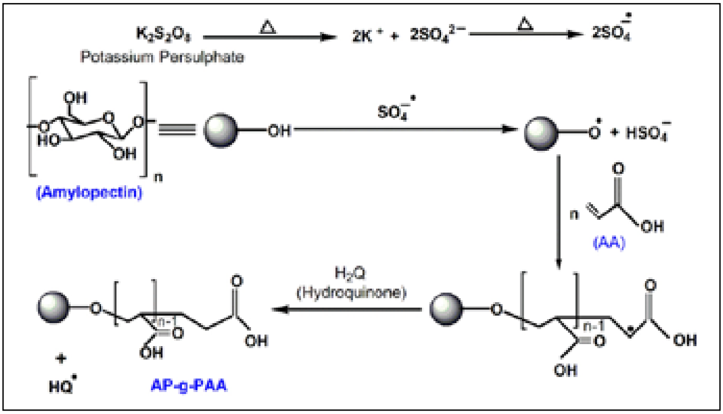
BC1

Amylopectin-*graft*-poly (acrylic acid): An efficient flocculant

Amit Kumar Sarkar and Sagar Pal*
Polymer chemistry Laboratory, Department of Applied Chemistry, Indian School of Mines
Dhanbad- 826004, INDIA

Industrial development and growing population lead to creating a paramount problem in potable water. To protect the environment and aquatic bodies from oblivious disposal of wastewater, it is essential to treat wastewater and its possible reuse.

Out of different techniques for wastewater treatment, flocculation is an ecofriendly and one of the most efficient techniques. Flocculation is a process of bringing together smaller particle to form larger flocs, so as to be settled and separated from wastewater [1]. To overcome the untoward effect of inorganic coagulants, it is essential to develop high performance organic flocculant, which produces less sludge and more efficient at low dosage. The present study introduces the development of a natural polymer based flocculant [amylopectin-graft-poly (acrylic acid)] by free radical polymerization technique (Scheme 1) for treatment of synthetic effluents and mining industry wastewater [2]. The flocculation characteristics were evaluated in three different synthetic effluents, namely kaolin, manganese ore and iron-ore suspensions by means of floc size measurement as well as traditional turbidity and settling rate measurement. The flocculation kinetics demonstrates that it is in accordance with the aggregation of particle and particle collision model concurrently. Moreover, raw mining industry wastewater was used for further investigation of the flocculation properties of AP-g-PAA. It has been observed that AP-g-PAA shows excellent potential as flocculant for treatment of industrial wastewater, in particular for removal of TS, TSS, and COD. Further, the colour profile (absorbance vs. wavelength) of supernatants drawn from the treated wastewater revealed impressive performance in removal of colour using AP-g-PAA based flocculants.



References:
[1] Brostow, W.; Pal, S.; Singh, R.P. *Materials Letters* 61 (**2007**) 4381.
[2] Sarkar, A. K.; Mandre, N. M.; Panda, A. B.; Pal, S. *Carbohydrate Polymers;* In Press, DOI: 10.1016/j.carbpol.2013.03.025, **2013.**

BC2

Synthesis and Characterisation of Self Assembling Hybrid Copolymer Templates Based on *Aminopropyl Tri–(2-Carboxy-3-(Pentadeca-8,11,14-Trienyl)Phenoxy Silane Modified Layered Silicate* for Micromolding of Poly(lactic caid) Vesicles

Asha Susan Chacko and V. S.Prasad*
Functional Materials, Material Science and Technology Division, CSIR-NIIST,
Thiruvananthapuram 695019, INDIA
vsprasad@niist.res.in

Synthesis of micro morphologies of defined dimensions in the micrometer range is of great interest as functional materials for biomedical applications for controlled delivery of drugs and bioactive materials [1]. Amphiphilic systems such as hybrid copolymers incorporating organo modified layered silicates which can self assemble into defined morphologies received great attention in this regard [2]. A natural renewable bioactive material of plant origin, Anacardic Acid based novel reactive cations of aminopropyl, tri–(2-carboxy-3-(pentadeca-8,11,14-trienyl)phenoxysilanes were synthesised and used for organo modification of layered silicate, MMT and characterised by FTIR & NMR spectroscopy and XRD measurements. The modified reactive MMT was further copolymerised with styrene by radical polymerisation at 80±5 °C by using AIBN and characterised by MALDI-TOF mass spectra, XRD and by TGA/DSC analysis. The self assembling characteristics of the system were studied by OLM, SEM and TEM and the particle size by DLS. XRD of the modified clay showed disappearance of peaks correspond to d_{001} in the clay corresponds to 11.7 A° indicating the extent of exfoliation. The copolymer showed an m/z value of 1.4 lakhs under MALDI-TOF and the FTIR results showed the corresponding peaks confirming the composition. The TGA of the system showed thermal stability above 300°C. The hybrid system self assembled into uniform vesicular morphology with an outer diameter of 5-6μm and PLA vesicles of 600nm were further synthesised using these reusable templates (figures 1&2). The formation of the vesicular morphology was further confirmed by DLS and fluorescent microscopic studies.

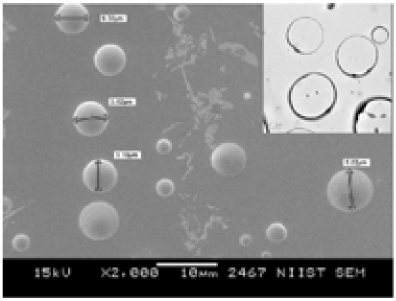


Figure 1. SEM of Hybrid Vesicles with TEM Image (inset)

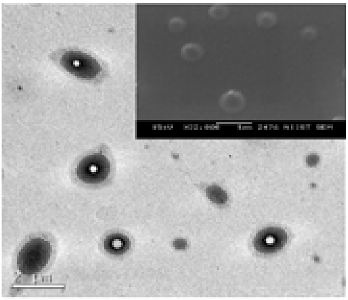


Figure 2. TEM Image of the PLA Vesicles with SEM Micrograph (Inset).

References

[1] Du, J.; O'Reilly, R. K. *Soft Matter*, 5 (**2009**), 3544.

[2] Nair, B.P.; Pavithran, C.; Sudha, J.D.; Prasad, V.S. *Langmuir,* 26 **(2010**), 1431.

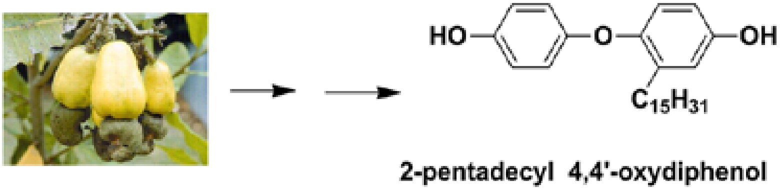
BC3

Synthesis and Characterization of New Polyesters Containing Pendent Pentadecyl Chains

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

A new bisphenol *viz*., 2-pentadecyl 4,4′-oxydiphenol was synthesized starting from cashew nut shell liquid (CNSL) – a by-product of the cashew processing industry. [1]

A series of new aromatic polyesters containing pendant pentadecyl chains was synthesized by interfacial polycondensation of 2-pentadecyl 4,4′-oxydiphenol with terephthalic acid chloride (TPC), isophthalic acid chloride (IPC) and a mixture of TPC and IPC (50:50 mol %). A series of copolyesters was synthesized from varying mixture of 4,4′-isopropylidenediphenol and 2-pentadecyl 4,4′-oxydiphenol with TPC. Inherent viscosities of polyesters and copolyesters were in the range 0.70–1.21 dL g^{-1} and number-average molecular weights were in the range 16,000–48,200. Polyesters containing pendant pentadecyl chains dissolved readily in organic solvents such as chloroform, dichloromethane, pyridine and *m*-cresol and could be cast into transparent, flexible and tough films from chloroform solution. Wide-angle X-ray diffraction data revealed amorphous nature of the polyesters containing pendent pentadecyl chains. The formation of loosely developed layered structure was observed due to the packing of pendant pentadecyl chains. The temperature at 10% weight loss (T_{10}), determined using thermogravimetric analysis in nitrogen atmosphere, of the polyesters containing pendant pentadecyl chains was in the range 430–460°C indicating their good thermal stability. Polyesters and copolyesters exhibited glass transition temperatures (Tg) in the range 29–47°C and 147–202°C, respectively. A large difference between glass transition (29–202°C) and T_{10} (430-460°C) values of aromatic polyesters containing pendent pentadecyl chains offers a wide processing window. [2]



2-pentadecyl 4,4'-oxydiphenol

References :

[1] Balachandran V. S., Swapnil Rohidas Jadhav S. R., Praveen Kumar Vemula P. K., John G.; *Chem Soc Rev*. **2013**, 42, 427-38.

[2] Arroyo. M. in *Handbook of Thermoplastics*, Olabisi,O., Ed., Marcel Dekker Inc.: New York, **1997**, 599.

BC4

Block copolymer–small molecule supramolecular assembly: tuning block copolymer morphology, adjusting small molecule properties and surface patterning of nanomaterials

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

Supramolecular approach to block copolymer has generated widespread research attention in the areas of nanoscience and nanotechnology due to their formation of wide range of periodic structures in nanoscopic length scale [1]. In this approach, a low molar mass additive is associated with one of the blocks by noncovalent interactions such as metal coordination, hydrogen bonding, Van der Waals forces, π-π interactions and electrostatic effects [2]. These supramolecular assemblies offer advantages over the covalently linked analogues, since different functionalities can be incorporated into the assemblies simply by substituting the small molecules. A number of tunable morphologies are readily accessible using a single block copolymer either by varying the stoichiometry between the small molecules and block copolymer or by redistributing the small molecules between the two microdomains using external stimulus, such as heat. After forming ordered structure from these supramolecular assemblies, the small molecules can be easily removed to obtain highly order nanoporous template which can be further used for nanofabrication to create nanopatterns [3] (Fig-1). Instead of removing the small molecules, organometallic compounds can be used as small molecule additive and the periodic structure created by one of the block copolymer and the organometalic compounds can be easily transformed into metal nanostructures[4]. The shape, size and periodicity of the nanomaterials can be tailored by playing with block copolymer composition, stoichiometry of the small molecules, thickness of the film etc. The well-defined microphase separation of the block copolymers can also induce controlled and ordered assembly of the small additive molecules into nanoscopic length scale resulting structure-within-structure pattern characterized by two length scales from phase separation of block copolymer and the comb block. So, block copolymer supramolecular strategies can be effectively used to tailor the physical properties (like optical, luminescence, electronic etc.) of the functional small molecules by controlling their aggregation, as these properties highly depend on their nanostructured morphology. We have studied a synergistic co-assembly of block copolymer and a fluorescent probe in thin film where we can simultaneously tune the block copolymer morphology by varying composition of the probe molecule and adjust the luminescence property of the probe molecules by its controlled assembly induced by block copolymer microphase separation. Here we will discuss such recent developments in the area of block copolymer supramolecular assembly carried out in our group.

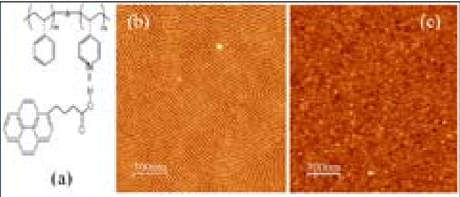


Figure.1 (a) Chemical drawing of the SMA formation through hydrogen bonding between P4VP block of PS-b-P4VP copolymer and PBA. (b) AFM images of PS- b -P4VP (PBA) (1 mol of FAA to 1 mol of 4-vinyl pyridine monomer unit) supramolecular thin films annealed in 1,4-dioxane. (c) AFM image of that thin film after immobilizing with quantum dots.

References

[1] `(a) Hamely, I. W. *The Physics of Block Copolymers; Oxford University Press: New York, (***1998**).(b) Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. *J. Am. Chem. Soc.* 125 (**2003**) 12211.
[2] (a) Ikkala, O.; ten Brinke, G. *Science*, 295 (**2002**) 2407. (b) Kuila, B. K.; Gowd, E. B.; Stamm, M.; *Macromolecules,* 43 (**2010**) 7713.
[3] Kuila, B. K.; Stamm, M. *J. Mater. Chem,*. 21 (**2011)** 141271.
[4] Kuila, B. K.; Rama, M. S.; Stamm, M. *Adv. Mater.,* 23 **(2011)** 1797.

BC5

Crystallization of Diblock Copolymer Studied by Dynamic Monte Carlo Simulation

Chitrita Kundu* and Ashok Kumar Dasmahapatra
Department of Chemical Engineering, Indian Institute of Technology Guwahati,
Guwahati – 781 039, Assam, INDIA (Email: chitrita@iitg.ernet.in)

Diblock copolymers consist of two chemically different blocks of repeat units, which are in most of the cases, incompatible (viz. immiscible) [1]. This mutual immiscibility leads to the formation of respective domain via microphase separation producing a large variety of morphologies, which are significant in developing nano-materials [2]. In the presence of crystalline blocks, microphase separation competes with crystallization. Usually, the block with higher melting point or longer block length crystallizes first followed by the crystallization of the block with lower melting point or shorter block length. The first crystallizing block creates a confinement for the crystallization of the second block [3-5]. As a result, the crystallization of the second block is slowed down and it influences the overall crystal morphology.

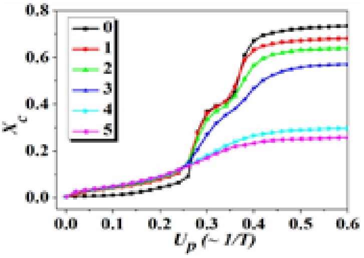


Figure 1: Change in Crystallinity with U_p (~ 1/T) for $x_B = 0.5$; $\lambda = 0, 1, 2, 3, 4$, and 5.

We employ dynamic Monte Carlo simulation to study the crystallization behaviour of double crystalline diblock copolymers. The block immiscibility has been modelled by a parameter, λ, which represents the strength of microphase separation and the crystallization driving force has been modelled by the parallel bond interaction energies, U_p (normalized by kT). Increase in the value of U_p (from 0 to 0.6) represents the transition from melt to crystal. We study the crystallization behaviour for a series of λ and compositions (x_B). For a given composition, with increasing the value of λ, we observe a gradual decrease in crystallinity (Figure 1 for $x_B = 0.5$) accompanying with smaller and thinner crystals. On the other hand, for a given value of λ, with increase in the composition of the second block (decreasing the composition of first block) we observe a gradual decrease in the overall crystallinity with smaller and thinner crystals. The onset of microphase separation has been detected by measuring mean square radius of gyration, which shows an increased value in comparison with its value at the homogeneous melt state. Isothermal crystallization reveals that the transition kinetics follows a pathway with the variation of the magnitude of λ.

Acknowledgement: SERC-DST for research funding.

References:

[1] Bates, F.S.; *Annu. Rev. Phys. Chem.* 41 (**1990**) 525
[2] Darling, S. B.; *Prog. Polym. Sci.* 32 (**2007**) 1152
[3] Muller, A. J.; Albuerne, J.; Marquez, L.; Raquez, J.M.; Degee, P.; Dubois, P.; Hobbs, J.; Hamley, I.W.; *Faraday Discuss* 128 (**2005**) 231
[4] Castillo, R. V.; Muller, A. J.; Lin, M.C. ; Chen, H.L.; Jeng, U.S.; Hillmyer, M. A.; *Macromolecules* 41(**2008**) 6154
[5] Li, Y.; Ma, Y.; Li, J.; Jiang, X.; Hu, W.; *J. Chem. Phy.* 136 (**2012**) 104906

BC6

Thermal Analysis and Characterization of Cellulose acetate grafted with Acrylic Monomers

Chittaranjan Routray and Biranchinarayan Tosh*
Department of Chemistry, Orissa Engineering College, 36 A, Sahid Narag,
Bhubaneswar – 751 007, Odisha, India
** bntosh@yahoo.com*

The graft copolymerization of methyl methacrylate (MMA), acrylic acid (AA) and acrylonitrile (AN) onto cellulose acetate (CA) was carried out homogeneously in different solvents like N, N – dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), 1, 4 – dioxane and acetone taking benzoyl peroxide (BPO), ceric ammonium nitrate (CAN) and tin (II) 2-ethyl hexanoate [$Sn(Oct)_2$] as catalysts. The molecular weight of the grafted homopolymer was evaluated as a function of reaction time and temperature, amount of initiator and monomer. The grafted products were characterized by infrared spectroscopy. Thermal decomposition of the optimized grafted products of CA was studied using thermo-gravimetric analysis (TG), differential thermo-gravimetry (DTG) at four heating rates, 5, 10, 20 and 30 °C and also by differential scanning calorimetry (DSC). Almost all the thermograms showed three major decomposition steps and the kinetic parameters for the three decomposition steps were estimated with the help of three well known methods; Coats and Redfern, Horowitz and Metzger, and Broido method.

Thermal stability of the grafted products was found to be decreased with the increase in the molecular weight of the grafted homopolymer. The initial temperature of active decomposition was found to be increased with increase in the heating rate of the thermal analysis. Acrylic acid and acrylonitrile grafted CA products were found to be thermally more stable that methyl methacrylate grafted products which may be due to the branching in the grafted homopolymers in the latter case.

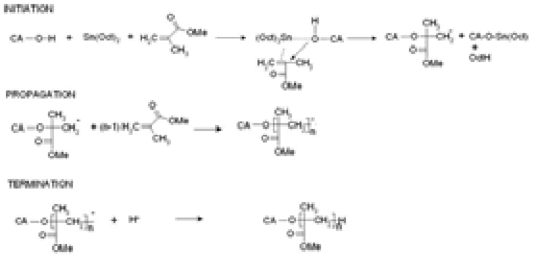


Figure 1. Mechanism of grafting of PMMA onto CA using Sn(Oct)2 as the initiator

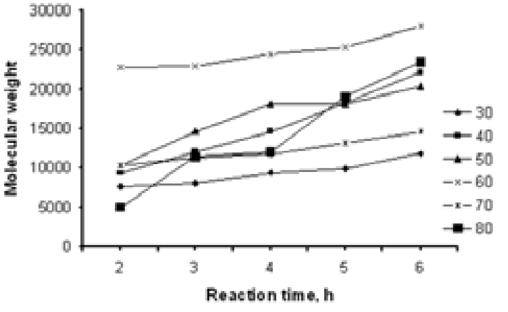


Figure 2. Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of CAN at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; CAN, 0.91 mmol

BC7

pH Responsive Self-assembly of Amphiphilic Block copolymer with Custom Designed Hydrophobic Block

Dr. Dipankar Basak[a], and Dr. Suhrit Ghosh[a]*
[a]*Polymer Scienece Unit, Indian Association for the Cultivation of Science, Kolkata-700032, India*

Stimuli responsive amphiphilic copolymers that self-assemble into micelles or vesicles have great potential for use as drug-carriers [1]. In this context, extensive efforts have been devoted over the past decades in studying assembly/disassembly of these polymers in presence of various external stimuli such as pH [2], redox [3] or light [4]. The key challenge, however, lies in designing and developing a cargo that exhibits stimuli-responsive tunable assembly/disassembly kinetics to achieve drug release at desirable rate. In this study we designed and developed a series of pH-responsive amphiphilic block copolymers based on poly(ethylene glycol)monomethyl ether-*b*-poly(methyl methacrylate-*co*-methacryloxypropanoic acid) (PEO-*b*-PMMA-*co*-PMAPA) where the pH-responsive carboxylic acid groups are randomly oriented in the hydrophobic block of PMMA. We hypothesize that such indiscriminate spreading of the pH responsive unit would help in controlling the release of the encapsulated hydrophobic moieties at certain pH. We also varied the percentage of acid/PMMA to investigate the extent of swelling/de-swelling of the aggregate as a function of pH.

First, a series of polymers based on PEO-*b*-PMMA-*co*-PMASI (polymethacryloxysuccinimide) were synthesized using atom transfer radial polymerization (ATRP) technique. Post polymerization functionalization of the reactive unit (MASI) with β-alanine furnished the final amphiphilic polymer with free $-CO_2H$ group as the pH responsive unit. In aqueous medium, the polymers self-assembled into micelle-type aggregates and the size of the aggregates were found to be sensitive to the solution pH. For example, at neutral or acidic pH (pH = 7 or less) TEM study exhibited uniform, compact micelle-type aggregates with an average size of 25 nm, which corroborated very well with the size found in dynamic light scattering study (21 nm) at these pHs. In contrast, at basic pH (pH$\geq$ 8) the size of the aggregates increased from 21 nm to 142 nm, presumably due to the electrostatic repulsion between charged carboxylate groups. This observation was further supported by TEM study that showed swollen aggregates of the size of 120 nm. The micellar aggregates were able to encapsulate hydrophobic dyes such as pyrene at their interior. Further, the release kinetics was investigated as a function of pH by using pyrene as a spectroscopic probe.

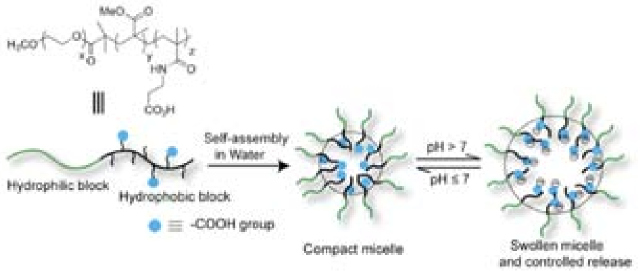


Figure 1. Schematic representation of micellization and pH dependent swelling/de-swelling of the aggregates

References

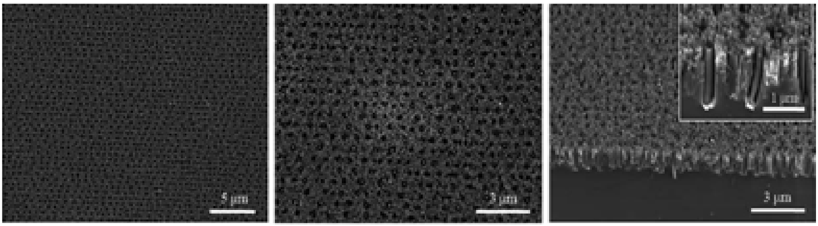
[1] O'Reilly, R. K.; Hawker, C. J.; Wooley, K, L. *Chem. Soc. Rev.*, 35 (**2006)** 1068.
[2] Dan, K.; Ghosh, S. *Langmuir*, 27 (**2011)** 612.
[3] Abbott, N. L.; Jewell, C. M.; Hays, M. E.; Kondo, Y.; Lynn, D. M. *J. Am. Chem. Soc.*, 127 (**2005**) 11576.
[4] Goodwin, A. P.; Mynar, J. L.; Ma, Y.; Fleming, G. R.; Fréchet, J. M. J. *J. Am. Chem. Soc.*, 127, (**2005**) 9952.

BC8

Fabrication of Periodic Nanostructures from Self-Assembly of Polymers

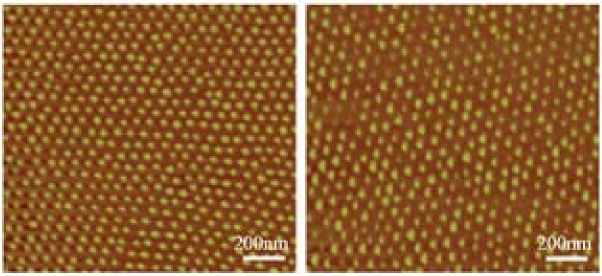
Hyungmin Park and Soojin Park*
Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology(UNIST),
Ulsan, KOREA
e-mail: spark@unist.ac.kr

Nanostructures with 2-dimensional and/or 3-dimensional arrays have been explored due to their own special properties for applications in electronic, biosensor, and photonics.[1-2] Recently, we reported the fabrication of polymer dot arrays using chemical instability phenomena between Teflon AF films and PDMS pattern.[3] We go even further and demonstrate that the silicon pin-in-a-hole can be fabricated combining this idea with metal-assisted chemical etching process. Through this process, we fabricated the novel structures that are periodic over large areas.



<Silicon pin-in-a-hole structures prepared by combining polymer mask pattern and chemical etching>

Moreover, one of the most representative ways of bottom-up fabrication technique, block copolymer was used for fabricating metal and metal oxide nano-dot arrays. Block copolymer films were controlled thermal annealing and solvent annealing for precise metal deposition.[4] Finally, block copolymer template films were removed by oxygen plasma. These arrayed patterns can be transfer other certain substrate and more can be applied various application area like data storage device, optoelectronic device and so on.[5]



<Gold dotted arrays prepared by solvent annealed block copolymer thin films>

References:
[1] M. C. P. Wang and B. D. Gates, Mater. Today, 12 **(2009)** 34
[2] G. Yu, A. Cao and C. M. Lieber, Nat. Nanotechnol., 2 **(2007)** 372
[3] H. Park, T. P. Russell, S. Park, *journal of colloid and interface science 348* **(2010)** 416
[4] Y. Xuan, J. Peng, L. Cui, H. Wang, B. Li and Y. Han,Macromolecules, 37 **(2004)** 7301
[5] Y. Cui, M. J. Bjork, J. A. Liddle, C. Sonnichsen, B. Boussert and A. P. Alivisators, Nano Lett., 4 **(2004)** 1093

BC9

Forward Osmosis of Composite Membranes Containing Ultrathin Hydrophobic Active Layer of Tri-block Copolymers Blends for the Removal of Organic Micro-pollutants from Water

M. Ravikumar[a], T. Rajasekhar[b], M. G. Ravindra[a], M. Trinadh[b], J. Gopinath[b],
S. K. Jewrajka[a], A. V. Sesha Sainath[b*], A.V.R. Reddy[a*]

[a]Reverse Osmosis Membrane Division, CSIR-Central Salt & Marine Chemicals Research Institute,
Bhavnagar- 364002, Gujarat, India. E-mail: avreddy@csmcri.org
[b]Polymers and Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007,
Andhra Pradesh, India. E-mail: avssainath@yahoo.com; avss@iict.res.in

Waste waters are increasingly contaminated with different types of organic micro-pollutants such as pharmaceutical substances, personal care products, biocides, etc. Removal of these organic substances from water is essential because they are harmful for aquatic ecosystems and human health. Forward osmosis (FO) membrane process is widely recognized as the promising membrane based separation process for desalination and water purification. We developed composite membranes by solution coating of blends of well defined tri-block copolymers such as poly(*n*-butyl acrylate)-*b*-polydimethylsiloxane-*b*-poly(*n*-butyl acrylate) [PBA-*b*-PDMS-*b*-PBA] prepared by atom transfer radical polymerization and poly(acryloyloxybenzoic acid)-*b*-polystyrene-*b*-poly(acryloyloxybenzoic acid) [PABA-*b*-PS-*b*-PABA] prepared by reversible addition-fragmentation chain transfer polymerization, from acetone-methanol mixture on the top of polysulfone (PS) microfiltration membrane as ultrathin active layer. The membranes were characterized by ATR-FTIR, SEM and contact angle measurements. The SEM images of membranes surfaces were clearly indicated that the PS membrane exhibited discrete pores whereas no pores were seen for the composite membranes. The composite membrane contact angle (110°) was increased compared to the PS membrane (75°). The performance of the composite membranes was evaluated for desalination and water purification. It was observed that the membranes did not show any water permeation for brackish water desalination under reverse osmosis (RO) conditions up to 250 psi applied pressure. However, the membranes exhibited water flux of 1-5 LMH and >98% NaCl rejection when tested them under the FO conditions in which water containing about 30000 ppm NaCl as the draw solution and tap water of about 160 ppm total dissolved solids as the feed. Interestingly, the water flux under the FO conditions was increased when the pressure on the feed water side was slightly increased to about 20 psi. Further, the composite membranes showed the rejections of >98% for benzoic acid, salicylic acid and aspirin when the water containing 100-250 ppm of these solutes were used as the feed solutions under the FO conditions. Considering that the water transport in the RO and FO processes occur through solution-diffusion mechanism, the difference in the water permeability of the composite membranes under the RO and FO conditions clearly indicates that there is a large difference in the extent of diffusion of water molecules in the tri-block copolymers blend ultrathin active layer under the FO and RO conditions.

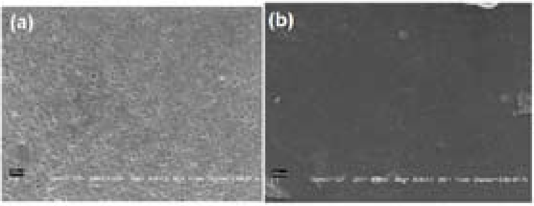


Figure 1. SEM images of membranes surfaces (a) PS and (b) composite.

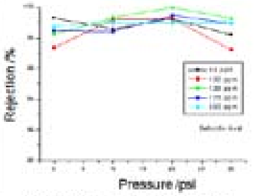


Figure 2. Rejection of salicylic acid under FO conditions.

References:

[1]. Xie, M.; Nghiem, L. D.; Price, W. E.; Elimelech, M. *Water Research*, 46 (**2012**) 2683-2692.
[2]. Cocchini, U.; Nicolella, C.; Livingston, A. G. *Chem. Eng. Sci.* 57 (**2002**) 4461-4473.
[3]. Wang, K. Y.; Chung, T. S.; Amy, G. *AIChE Journal*, 58 (**2012**) 770-781.
[4]. Ge, Q.; Wang, P.; Wan, C.; Chung, T. S. *Environ. Sci. Technol.* 46 (**2012**) 6236-6243.

BC10

Fabrication of Hybrid Nanofibres *via* Block Copolymer Template

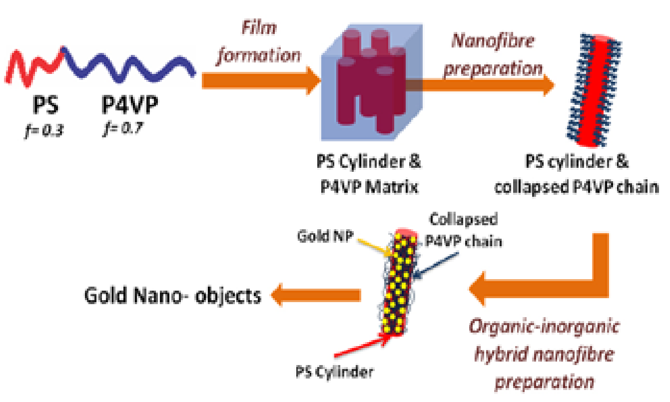
Jit Pal*[a], Sunita Sanwaria[a], Rajiv Srivastava[a], Bhanu Nandan[a], Andriy Horechyy[b], Manfred Stamm[b]

[a]*Department of Textile Technology, Indian Institute of Technology, Delhi*
Hauz Khas, New delhi-110016, India
[b]*Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, Dresden 01069, Germany*

***Presenting Author**: *jitpal2564@gmail.com*

We report a novel method for preparing polymer nanofibres with diameter < 100 nm *via* self-assembly of block copolymers. The polymer nanofibres were prepared from a cylinder forming polystyrene-*block*-poly (4-vinylpyridine) (PS-*b*-P4VP) by selectively swelling the matrix phase formed by the P4VP block in a selective solvent. The nanofibres so prepared were composed of PS block and had a hairy shell constituted from P4VP blocks. The presence of P4VP hairy shell in such nanofibres allows for loading a number of functionalities on these nanofibers. In the present work, we successfully deposited gold nanoparticle on the surface of the polymer nanfibres via both *in-situ* and *ex-situ* approaches resulting in the formation of gold/polymer hybrid nanofibres. The diameter of the nanofibers could easily be tuned as well as the type of functionality loaded. Hence, the approach allows for the preparation of a range of organic-inorganic hybrid nanofibres of tunable diameter. Moreover, the polymer could then be further removed by oxidative heating of the hybrid nanofibres to prepare pure inorganic nanostructures of diameter < 30 nm. The organic-inorganic hybrid nanofibers so prepared could have potential applications in optoelectronic devices, sensors and as catalysts.

Keywords: Nanofibres, block copolymer, hybrid nanofibres



Schematic illustration for the preparation of preparation of organic–inorganic hybrid nanofibres

References:

[1] Pal, J.; Sanwaria, S.; Srivastava, R.; Nandan, B; Horechyy, A; Stamm, M.; Chen, H. *J. Mater. Chem.*, **2012**, 22, 25102

BC11

Synthesis of Well - Defined Amphiphilic Four – Arm - Star Poly(D,L-lactide)-*b*-Poly(*N*-vinylpyrrolidone) Block Copolymers

K. Ramesh,[1,2] Avnish Kumar Mishra,[1] Nira Misra,[2] Biswajit Ray[1*]
[1]*Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi – 221005, India*
[2]*School of Biomedical Engineering, Indian Institute of Technology-*
Banaras Hindu University, Varanasi – 221005, India
*Corresponding author: Email: biswajitray2003@yahoo.co.in

Well-defined four-arm star-poly(D,L-lactide)-*b*-poly(*N*-vinylpyrrolidone) [S-(PDLLA-*b*-PNVP)$_4$] block copolymers have successfully been synthesized via ring opening polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization and monitored by ^{1}H NMR, and size exclusion chromatography. TEM, ^{1}H NMR spectroscopy, fluorescence spectroscopy and dynamic light scattering studies support the formation of micelles from these block copolymers in water. Thermal properties studies of these block copolymers by TGA, DTA and DSC also support the formation of block copolymers.

References:

[1] Patel VK, Mishra AK, Vishwakarma NK, Biswas CS, Ray B. Polymer Bulletin 2010; 65: 97-110.
[2] Mishra AK, Patel VK, Vishwakarma NK, Biswas CS, Raula M, Mishra A, Mandal TK, Ray B.Macromolecules, 2011; 44: 2465-73.
[3] Ramesh K, Mishra AK, Patel VK, Vishwakarma NK, Biswas CS, Paira TK, Mandal TK, Misra N, Ray B. Polymer, 2012; 52: 5743-53.
[4] Patel, V. K.; Vishwakarma, N. K.; Mishra, A. K.; Biswas, C. S.; Maiti, P.; Ray, B. Journal Of Applied Polymer Science, 2012, (DOI: 10.1002/app.38037).

BC12

Controlled Synthesis of Amino Acid Based pH-responsive Chiral Polymers *via* RAFT Polymerization

Kamal Bauri, Shashank Pant and Priyadasi De*
Polymer Research Centre, Department of Chemical Sciences
Indian Institute of Science Education Research - Kolkata
Mohanpur-741242,Nadia,West Bengal, India

** E-mail: p_de@iiserkol.ac.in;*

the past few decades a tremendous research efforts are being devoted to incorporate amino acid moieties into the synthetic polymers either in the main chain or in the pendant chain [1-3], because their inclusion into synthetic polymers will lead to better biocmpotability, improved aqueous solubility and possibility of highly ordered hierarchical structures through intra- and inter-chain associations via non-covalent forces such as hydrogen-bonding, hydrophobic-stacking, and electrostatic interactions. Reversible addition-fragmentation chain transfer (RAFT) polymerization was employed for controlled synthesis of chiral acrylate and methaclyate polymers having leucine and isoleucine as pendant group. Leucine/isoleucine side chain polymers are of interest due to their high hydrophobicity and role in the formation of *α*-helices structures. Those homopolymers have been used as macro-CTAs to prepare corresponding diblock copolymers with methyl (meth)acrylate. All homopolymers and block-copolymers showed chiroptical properties. Deprotection chemistry strategies have been used to make them smart pH-responsive materials. As-synthesized amphiphilic block copolymers formed spherical core-shell micelle in water as proved by atomic force microscope (AFM) (Figure 1) and dynamic light scattering (DLS).

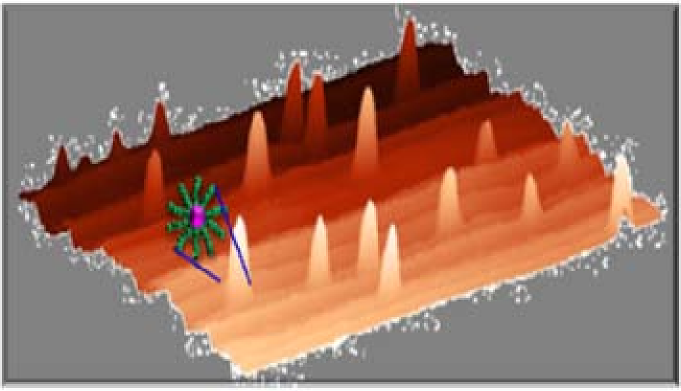


Figure 1. Tapping mode AFM 3D height image of amphiphilic block copolymer micelles

References:
[1] Deming, T. J. *Nature (London)* 390 (**1997**) 386
[2] Sun, H.; Gao, C. *Biomacromolecules* 11 (**2010**) 3609
[3] Bauri, K.; Roy. S. G; Pant, S.; De, P. *Langmuir* 29 (**2013**) 2764

BC13

Selective Incorporation of Radical/Ion into Micro-domains for Organic Memory Applications

Kohei Aoki[a], Takeo Suga[b] and Hiroyuki Nishide[a]*

[a]*Dept of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan*
[b]*Waseda Institute for Advanced Study (WIAS), Waseda University, Tokyo 169-8555, Japan*
E-mail: a-kohei@ruri.waseda.jp; nishide@waseda.jp

Block copolymers (BCPs) have attracted considerable interest owing to their self-assembled nano-scaled structures that have been widely utilized as well-defind templates or scaffolds for soft nanolithography [1]. Selective functionalization of block copolymer-based microdomains could be utilized to construct the functional interface for charge-transport and -separation in the organic thin film devices. Precise interface functionalization with redox-active radicals and ions was considered as an important factor for organic memory application (Fig. 1). We have already reported that successful incorporation of functional groups into several BCP-based nanostructures with lamellar, cylinder and sphere, which exhibited different memory performance depending on the morphology [2].

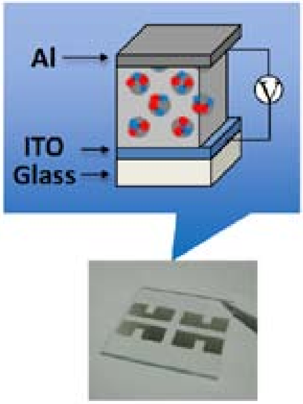


Fig. 1 BCP memory device.

We focused on the combination of well-defined, conventional block copolymer templates such as poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) and ionic liquid (**IL**), which can serve as the carrier of functional groups for selective incorporation into micro-domains [3]. Self-assembled nanostructures of PS-*b*-PEO were varied with the phase-selectively incorporated TEMPO and ionic liquid, which were characterized by DSC, AFM, TEM and solid-state NMR (Fig. 2). The correlation between the phase morphology and organic memory characteristics will be also reported.

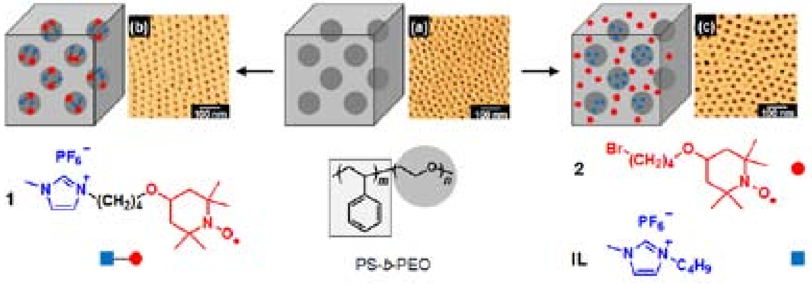


Fig. 2 Radical/ion-containing PS-*b*-PEO films: (a)in the same domains. (b)in the separate domains.

References:

[1] Hawker, C. J., et al., *Adv. Mater.*, 21 **(2009)** 4769.
[2] Suga, T.; Takeuchi, S.; Nishide, H. *Adv. Mater.*, 23 **(2011)** 5545.
[3] Lodge, T. P., *Science*, 321 **(2008)** 50.

BC14

Novel Pendant Carboxylic Acid Containing Tri-block Copolymers Syntheses and Their Self-assembled Morphologies in Tetrahydrofuran and Water Mixtures

T. Rajasekhar, M. Trinadh, V. Santhosh, A. V. Sesha Sainath*

Polymers and Functional Materials Division, CSIR-Indian Institute of Chemical Technology,
Hyderabad 500 007, Andhra Pradesh, India. E-mail: avssainath@yahoo.com; avss@iict.res.in

Pendant carboxylic acid based (meth)acrylate polymers and their copolymers have potential applications in drug delivery, multi-responsive reversible gels and making micron- and nano-size particles formation by their self-segregation nature [1, 2]. The polymerization of carboxylic acid containing monomers with controlled macromolecular architecture and explore their applications is still challenging research area in polymer science and technology.

Di-/tri-block copolymers were successfully prepared by controlled radical polymerization techniques. At first, Otsu et al reported that the tetraethylthiuram disulfide is able to polymerize styrene by thermally to produced telechelic polystyrene (TPS) and resulted TPS is further photo-initiated [3, 4] to produce ABA type copolymers. This method suffers lack of molecular weight control and it is not employed for wide verity of functional monomers. Desimone et al reported that the synthesis of ABA type copolymers by using TPS by photo-initiation to produce fluro tri-block copolymers [5]. Moreover several research groups worked on styrene based di- or tri-block copolymers with controlled macromolecular architectures. Recently, styrene and carboxylic acid containing block copolymers preparation and their nano-segregations were reported by Eisenberg et al [6]. We first time report the initiation of TPS by radical initiator, azobisisobutyronitrile with 4-(acryloyloxy) benzoic acid (reversible addition-fragmentation chain transfer process) to produce pendant carboxylic acid functionalized ABA type block copolymers. The resulted tri-block copolymer assemblies were compared with the non carboxylic acid functionalized tri-block copolymer in THF and H_2O mixtures.

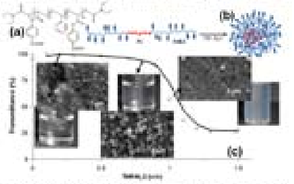


Figure 1. (a) PABA-b-PS-b-PABA structure, (b) formation of particles in THF and H_2O mixture and (c) variation of transmittance at 550 nm with respect to THF/H_2O (v/v) at RT (the insets are SEM images and dispersions at arrow marked point).

The synthesized tri-block copolymers were characterized by ^{1}H and ^{13}C NMR and thermal behaviour by TGA and DSC studies [7]. The polymers molecular weights were calculated from ^{1}H NMR spectra and GPC curves. The pendant carboxylic acid containing tri-block copolymers exhibited sphere type particle aggregations in THF and water mixtures. The average particle size and agglomerations of the particles were increased with increasing the volume ratio of water in THF and water mixture. The average particle sizes were calculated from DLS for various THF/H_2O volume ratios (0-1.5). The average particle sizes start from 200 to 900 nm (THF/H_2O: 0.1-1.0 v/v). The polymers having pendant carboxylic acid groups show potential applications in membrane and drug delivery systems.

References:

[1]. Stadler, B.; Price, A. D.; Zelikin, A. N. *Adv. Funct. Mater.* 21 (**2011**) 14.
[2]. He, W.-D.; Sun, X.-L.; Wan, W.-M.; Pan, C.-Y. *Macromolecules* 44 (**2011**) 3358.
[3]. Otsu, T. *J Polym Sci Part A: Polym Chem.* 38 (**2000**) 2121.
[4]. Sainath, A. V. S.; Yonetake, K.; Aita, T.; Inoue, T.; Koyama, K. *Liquid Crystals* 30 (**2003)** 565.
[5]. Guan, Z.; Desimone, J. M. *Macromolecules* 27 (**1994**) 5527.
[6]. Zhang. L.; Eisenberg. A. *Science* 268 (**1995**) 1728.
[7]. Rajasekhar, T.; Trinadh, M.; Gopinath, J.; Santhosh, V.; Sainath, A. V. S. *Proceedings of Poly Tech – 2012, International Conference on Advances in Polymeric Materials & Nanotechnology, Pune, India* 1 (**2012)** 118.

BC15

NR/PEO Block Copolymers for Complexation of Potassium and Sodium Ions

Mrudula M S* and M R Gopinathan Nair
School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala -686560, INDIA

Metal ions are essential species for numerous areas of industrial applications and in environmental and biological systems. A wide range of physical and chemical processes are available for uptake of metal ions from aqueous medium. But most of them are sludge producing or not cost effective. (1). In recent years, insoluble polymeric sorbents having different functional groups that can be complexed with metal ions have become well – known for the removal of metal cations from aqueous solutions (2). The polymeric hydrogels incorporated with different chelating groups are promising materials in the field of hydrometallurgical applications, water purification, agriculture, bioengineering, food industry and other fields(3). Hydrogels are polymeric materials containing a large number of hydrophilic groups capable of absorbing and retaining water in their three dimensional networks. They swell by absorbing water and shrink on drying (4). In recent years, the synthesis of hydrogels with chelating groups has received considerable attention for rapid and inexpensive metal ion separation and concentration. It was found that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, and sulphonic acid groups could be used as complexing agents for metal ions in aqueous solutions (5).

In the present work polyethylene oxide (PEO) which is immobilized with crosslinked short chains of natural rubber (NR) has been used for complexation with alkali metal ions. For this purpose polyethylene oxide and short chains of natural rubber are block copolymerized. Since natural rubber is hydrophobic and polyethylene oxide is hydrophilic they form excellent hydrogels which can swell in aqueous medium and shrink on drying.. Swelling characteristics may be varied by varying the PEO molecular weight. One such product formed from PEO of 6000 molecular weight is used in this study.

The prepared copolymeric hydrogel can act as chelating exchangers due to the presence of electron donor oxygen atoms of PEO. So they can form metal complexes and can remove metals from aqueous medium. The effect of initial metal ion concentration on the metal ion adsorption capacity was investigated for KCl and NaCl aqueous solutions of four different concentrations. The adsorption capacity increases from 93.34 mg/g to 355.79 mg/g for potassium ion and for sodium ion it increases from 43.03 mg/g to 157.29 mg/g when initial concentration of each metal ion increases from 5 mg/l to 20 mg/l. The NR/PEO block copolymers showed 94.14% removal efficiency for potassium (20 mg/l) and 90.02% for sodium (20 mg/l). The distribution coefficient for potassium ion is 4.07 and that of sodium ion is 1.30 at the initial concentration 20 mg/l. The experimental data showed that the adsorption capacity, removal efficiency and distribution coefficient are high for potassium ions compared to that of sodium ions. The adsorption isotherm models were applied on experimental data and it is found that the Langmuir isotherm model was the best for potassium ions while the Freundlich isotherm model was the best one for sodium ion. From the Freundlich isotherm, the slope value, $n<1$, indicates that the sorption of ions onto the polymer is a concentration – dependent process. This may be attributed to the fact that with progressive surface coverage of the adsorbent, the attractive forces between the metal ion species such as van der Waals forces increase more rapidly than the repulsive forces and consequently, the metal ions manifest a stronger tendency to bind to the polymer surface.

References:

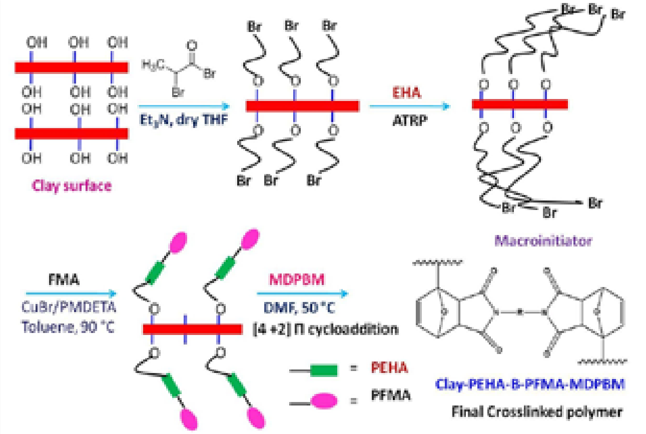
[1] Ekebafe, L. O.; Ogbeifun, D. E.; Okieimen, F. E. *African Journal of Environmental Science and Technology*, 6(7) **(2012)** 275
[2] Kasgoz, H.; Kasgoz, A.; Sahin, U;Temelli,T. Y.; Bayat, C. *Polymer-Plastics Technology and Engineering*, 45 **(2006)** 117
[3] Ei-Hag Ali, A.; Shawky, H. A.; Abd El Rehim, H.A.; Hegazy, E.A. *European Polymer Journal,* 39 **(2003)** 2337
[4] Uzum, O. B.; Karadag, E. *Advances in Polymer Technology*, 00 **(2011)** 1
[5] Kradag, E.; Saradin, D.; Guven, O. *Sep. Sci.Technol.*, 30 **(1995)** 3747
[6] Fromm, K, M. *Coordination Chemistry Reviews*, 252 **(2008)** 856

BC16

Thermally amendable Block Copolymer/Clay Nanocomposite via surface initiated ATRP and 'Click Reaction'

Nabendu B Pramanik, Dhruba J Haloi, Dibyendu S Bag, Nikhil K Singha*
Rubber Technology Centre, Indian Institute of Technology Kharagpur,
Kharagpur- 721302
*nks8888@yahoo.com

Surface initiated polymerization (SIP) is an important synthetic tool to tailor the surface properties of nanoparticles. Surface initiated atom transfer radical polymerization (SI-ATRP) is an important method of SIP to graft different (co)polymers into different surfaces. This investigation reports the preparation and characterization of poly(2-ethylhexyl acrylate)-*block*-poly(furfuryl methacrylate) (PEHA-b-PFMA)/clay nanocomposite from clay surface via ATRP and its post polymerization modification via Diels Alder reaction. In this case nano-clay surface was first modified to incorporate the ATRP initiator followed by ATRP of 2-ethylhexyl acrylate (EHA). Then FMA was polymerized onto the clay-PEHA-Br segment (Scheme-1). Here the 'click reaction' of Diels-Alder (DA) and retro-DA (rDA) reaction was used as to prepare thermally amendable functional copolymer. The DA reaction was carried out between the reactive furfuryl group of PFMA unit of PEHA-b-PFMA/clay nanocomposite as a diene and bismaleimide (BM) as the dienophile. Retro-DA reaction takes place at higher temperature leading to cleavage of DA crosslinking to get back the starting materials. ^{1}H-NMR, GPC, TEM, TGA and DSC analyses were carried out to characterize the block copolymers. The block copolymer showed two glass transition temperatures (T_g), one is for soft segment of PEHA and another one is hard segment of PFMA in DSC analysis.
The thermoreversible properties of block copolymer/clay nanocomposite were characterized by FT-IR and DSC analysis.



Scheme 1. Preparation of block copolymer via SI-ATRP and click reaction

References:

[1] Haloi, D. J.; Ata, S.; Singha, N. K. *Ind. Eng. Chem. Res.* 51**(2012)** *9760*.
[2] Wudl, F. et al. *Science* 295 (**2002**) *1698*.
[3] Veldman, B.; Kaully, T.; Feller, R. K.; Falcao, E.; Wudl, F. *Macromolecules* 42 **(2009)** *6848*
[4] Kavitha, A. A.; Singha, N. K. *Macromolecules* 43 **(2010)** *3193*.
[5] Abid, S.; Gharbi, R. E.; Gandini, A. *Polymer* 45 **(2004)** *6469*.
[6] Goiti, E.; Huglin, M. B.; Rego, J. M. *Polymer* 42 (**2001**) *10187*.

BC17

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

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

Block copolymer-supramolecular assembly (BCSMA) with small additive molecules has generated widespread research attention in the areas of nanoscience and nanotechnology due to their formation of fascinating set of periodic structures in the nanoscopic length scale[1]. In this approach, a low molar mass additive is associated with one of the blocks by noncovalent interactions such as metal coordination, hydrogen bonding, Van der Waals forces, π-π interactions and electrostatic effects[2]. These supramolecular assemblies offer advantages over the covalently linked analogues, since different functionalities can be incorporated into the assemblies simply by substituting the small molecules. A number of tunable morphologies are readily accessible using a single block copolymer either by varying the stoichiometry between the small molecules and block copolymer or by redistributing the small molecules between the two microdomains using external stimulus, such as heat. After forming ordered structure from these supramolecular assemblies, the small molecules can be easily removed to obtain highly order nanoporous template which can be further used for nanofabrication to create periodic arrays of nanomaterials on solid substrate [1b]. Instead of removing the small molecules, organometallic compounds can be used as small molecule additive and the periodic structure created by one of the block copolymer and the organometalic compounds can be easily transformed into metal nanostructures [3]. The shape, size and periodicity of the nanomaterials can be tailored by playing with block copolymer composition, stoichiometry of the small molecules, thickness of the film etc. One of the example of such block copolymer supramolecular system with organometallic compound is polystyrene- *block* -poly(4-vinyl pyridine) (PS-b-P4VP) and ferroceneacetic acid (FAA). Figure 1 shows schematically the fabrication of ordered and aligned arrays of iron oxide nanomaterials using supramolecular assembly of PS- *b* -P4VP and FAA. After fabricating the thin film from the supramolecules, the periodic cylindrical microdomains created by P4VP and FAA are transformed into iron oxide nanostructures by either pyrolysis or plasma etching techniques (Fig. 2).

Here we will mainly describe some of the block copolymer supramolecular system with organometallic compounds developed in our group recently for creating such large scale controllable periodic arrays of nanomaterials.

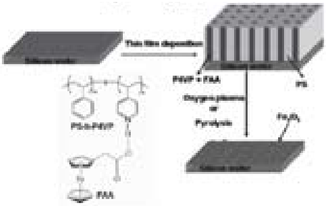


Figure.1 Schematic presentation of fabrication of iron oxide pattern using supramolecular approach.

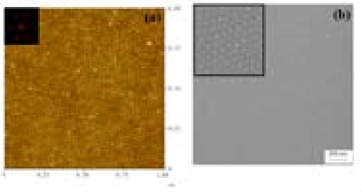


Figure.2 (a) AFM height images of PS- *b* -P4VP (FAA) (0.5 mol of FAA to 1 mol of 4-vinyl pyridine monomer unit) supramolecular thin films annealed in 1,4-dioxane. (inset FT pattern) (b) SEM image of iron oxide arrays by plasma etching of that thin film.

References

[1] (a) Hamely, I. W. *The Physics of Block Copolymers; Oxford University Press: New York, (***1998**).(b) Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. *J. Am. Chem. Soc.* 125 (**2003**) 12211.
[2] (a) Ikkala, O.; ten Brinke, G. *Science*, 295 (**2002)** 2407. (b) Kuila, B. K.; Gowd, E. B.; Stamm, M.; *Macromolecules,* 43 (**2010**) 7713.
[3] Kuila, B. K.; Rama, M. S.; Stamm, M. *Adv. Mater.,* 23 **(2011)** 1797.

BC18

Transport Studies of Block Copolymeric Hydrogels Based on Natural Rubber and Polyethylene oxide in Cationic Dye Solutions

Prema Sukumar, M.R. Gopinathan Nair*
School of Chemical Sciences, Mahatma Gandhi University,
Priyadarshini Hills P.o., 686560, Kottayam, Kerala, India
** Corresponding email i.d., mrg.nair@rediffmail.com*

Investigation of the mechanism of solute diffusion in hydrogels has received considerable attention in recent years because of the important applications of hydrogels in various fields such as membranes in water purification and separation, catheters, contact lenses, agriculture, food industry, medicine and biotechnology[1-2]. They are used as adsorbents for removal of some agents in environmental applications in immobilized enzyme kinetics, in bioengineering and also as carriers of water, pesticides and fertilizers in agriculture[3-9].

Development of new polymeric materials, from renewable natural resources in our laboratory has led to the synthesis of natural rubber and polyethylene oxide (PEO) based block copolymers. They were found to be highly phase separated systems which can imbibe large quantities of water owing to the hydrophilic character of PEO giving rise to excellent hydrogels.

Block copolymers (BCs) of varying compositions were prepared from hydroxyl terminated liquid natural rubber (HTNR) and polyethylene oxide (PEO) of various molecular weight. Two phase morphology of these NR/PEO BCs was confirmed by transmission electron microscopy analysis. The hydrophilic PEO enables these BCs to swell in water and in aqueous cationic dyes, viz., malachite green (MG), crystal violet (CV), safranineT (ST), methylene blue (MB) and bromocresol green (BCG). The diffusion and permeation coefficients of BCs increases with the PEO content. The swelling studies also point to the fact that the order of interaction of the dyes with the BCs is MG > CV > ST > MB > BCG. The diffusional exponent value is Fickian in water and in dye solution for BC-1 and for the rest of the BCs it is anomalous type. Hence it is inferred that the rate of chain relaxation is greater than the rate of diffusion in BC -1 during swelling whereas in the others, rate of polymer chain relaxation and diffusion are similar. Sorption kinetic studies reveal that dye absorption follows first order kinetics. Temperature dependent swelling studies suggest that diffusion of the penetrants is controlled by thermodynamic parameters rather than the penetrant size or their molar mass which do not exhibit a correlation with the activation energy values.

References

[1] Sanghi, R.; Bhatttacharya, B.; Singh, V. Cassia angustifolia seed gum as an effective natural coagulant for decolourisation of dye solutions. *Green Chem.,* 4 **(2002)** 252.
[2] Namasivayam, C.; Arasi, D.J.S.E. Removal of congo red from wastewater by adsorption onto waste red mud. *Chemosphere*, 34 **(1997)** 401.
[3] Moozyckine, A.U.; Davies, D.M. Green S as a prototype for an environmentally-degradable dye: the concept of a green dye in future Green Chemistry. *Green Chem*., 4 **(2002)** 452.
[4] Akhtar, S.; Khan, A.A.; Husain, Q. Potential of immobilized bitter gourd (Momordica charantia) preoxidases in the decolourization and removal of textile dyes from polluted wastewater and dyeing effluent. *Chemosphere*, 60 **(2005) 2**91.
[5] Crini, G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci*., 30 **(2005)** 38.
[6] Senkal, B. F.; Yavuz, E. Preparation of poly (vinylpyrrolidone) grafted sulfonamide based polystyrene resin and its use for the removal of dye from water. *Polym. Adv. Tech*., 17 **(2006)** 928.
[7] Hashem, A.; Abdel-Halim, E.S.; Socker, H.H. Bi-functional starch composites prepared by gamma-irradiation for removal of anionic and cationic dyes from aqueous solutions. *Polym. Plast. Tech. Eng.*, 46 **(2007)** 71.
[8] Ohmine, I.; Tanaka, T. Salt effects on the phase transition of ionic gels. *J. Chem. Phys*., 77 **(1982)** 5725.
[9] Katayama, S.; Hirokawa, Y.; Tanaka, T. Reentrant phase transition in acrylamide-derivative copolymer gels. *Macromolecules,*17 **(1984)** 2641.

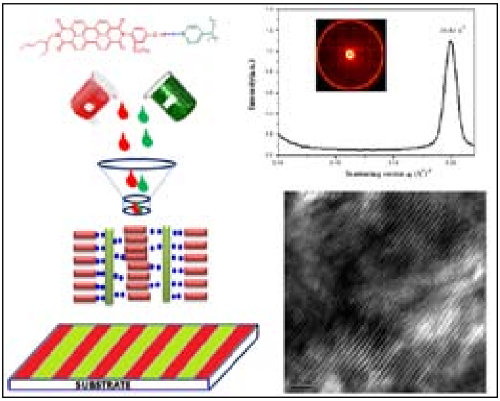
BC19

Nanostructured Crystalline Comb Polymer of Perylenebisimide by Directed Self-Assembly: Poly(4-vinylpyridine)-Pentadecylphenol Perylenebisimide

*Rekha Narayan and S. K. Asha**
Polymer Science & Engineering Division,
*CSIR, NCL,*Pune-411008, Maharashtra, India.
Corresponding author E-mail: (sk.asha@ncl.res.in)

Solution processable nanostructured functional organic semiconductor materials with tailored property profiles have emerged as an indispensable requirement as the constituent building blocks of organic and large area electronics (OLAE) [1, 2]. However the device development using n-type semiconductors (electron carriers) is till date far from the performance achieved with p-type (hole carriers) materials. As a result, there is currently a growing interest in developing new n-type materials with device performances of the same order as the ones already achieved with p-type semiconductors. Among the Rylene diimide dye based n-type (acceptor) semiconductors, the perylene bisimides (PBI) are promising materials for n-type semiconductivities, due to their outstanding combination of unique photochemical and electronic properties [3].However, their use in various applications requires considerable efforts to overcome their intrinsic low solubility. The alternative method of blending low molecular weight rylene imides with other polymers to prepare smooth films has the inherent problem of macrophase separation.

We address the prevailing situation, demonstrating that a perylene bisimide small molecule, suitably functionalized for hydrogen bonding interactions, could be organized into lamellar structure in the domain range 5 to 10 nm using the concept of supramolecular assembly with Poly(4-vinyl pyridine) (**P4VP)**, by simple solution mixing of the two components [4]. Detailed structure and properties of the supramolecular complex between **P4VP** and the perylenebisimide small molecule explored by means of using FTIR, ^{1}H NMR, SAXS, WAXS and thin film morphology using TEM would be the plot for discussion. The most important highlight of the work was the ability to retain the crystallinity of the perylene bisimide in the supramolecular polymer complex, thereby combining the advantage of the small molecule with the processability afforded by the polymer.



References

[1] Niu, Q.; Zhou, Y.; Wang, L.; Peng, J.; Wang, J.; Pei, J.; Cao,Y. *Adv. Mater.,*20 (**2008)** 964.
[2] Xin, H.; Kim, F.S.; Jenekhe, S.A. *J. Am. Chem. Soc.,* 130 (**2008)** 5424.
[3] Würthner, F.*Chem. Commun.*14 (**2004)**1564.
*[4] Narayan, R.; Kumar, P.; Narayan, K.S.; Asha, S. K. Adv. Func. Mater.***(2012)** *DOI: 10.1002/adfm.201202366*

BC20

Low Cost Stimuli-Responsive Flexible Thin Films

Roshan Jesus Mathew, Ravi Shankaran Dhesingh*
[b]*Nano-Bio Materials and Sensors Laboratory, PSG Institute of Advanced Studies,*
Peelamedu, Coimbatore-641 004, INDIA
**drs@ias.psgtech.ac.in; dravishankaran@hotmail.com*

The work focuses on fabrication ofstimuli-responsive flexible thin films, which can be used both as a temperature sensor and as a pH sensor, whose application can be extended to medical to defense purposes. The stimuli-responsive nature of the poly(methyl methacrylate) [PMMA] polymer is utilized and well established in the form of a low cost flexible thin film. Labeling of this transparent thermoplastic with congo red-diazo dye has revealed its simultaneous pH-responsive and temperature responsive ability. The flexibility and transparency of the film helps in using it in any surfaces. Its multi stimuli-responsive properties, viz, thermochromic and pH responsive ability were analyzed and confirmed by the degradation test studies of congo red dye labeled PMMA thin films. The degradation test studies proved the resistance capability of the film to acidic medium and the hydrophobic nature of the film approved its use for marine purposes. The results of the film subjected to UV irradiation and visible light supported the stability of the film which can be used as a sensor in any environmental conditions. The properties of the fabricated material promise its use as multi stimuli-responsive sensors in various applications such as food preservation, water treatment and environmental analysis. The UV spectrum analysis and the degradation studies have identified the role of the dye and the polymer in the flexible thin film for its stimuli- responsive behavior promising its future applications.

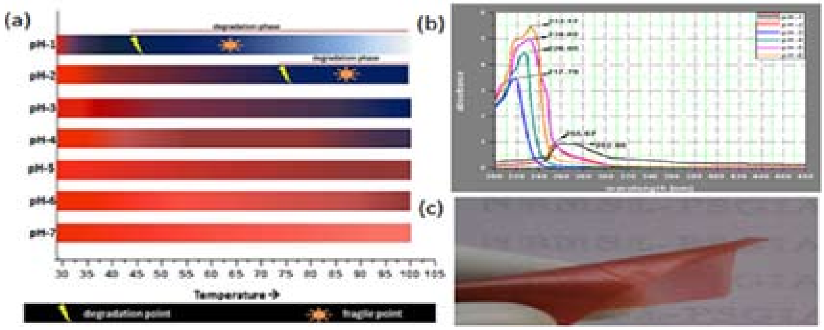


Figure (a) Temperature dependent color change of congo red dye loaded PMMA flexible thin films with pH variations
(b) Absorbance spectra of congo red labeled PMMA thin film with varying pH of the medium
(c) Images of as prepared congo red dyed PMMA flexible transparent thin film.

References:

[1] Steensma, D. P.,"Congo Red: Out of Africa?" . *Archives of Pathology and Laboratory Medicine* , **2001,**125 (2): 250–252.
[2] Wilkes, C. E.,*PVC Handbook*. Hanser Verlag, **2005**, ISBN 1-56990-379-4

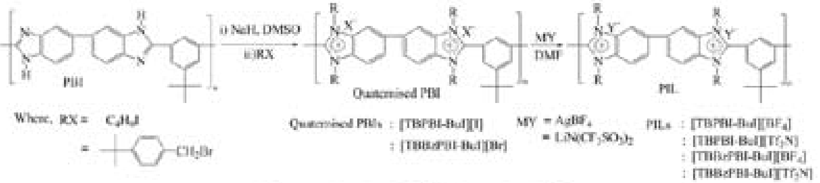
BC21

Film Forming Polymeric Ionic Liquids (PILs): Effect of Bulky Substitution on Physical and CO_2 Separation Properties

Rupesh S. Bhavsar and Ulhas K. Kharul*
Polymer Science & Engineering Division, National Chemical Laboratory, Pune – 411008, India
uk.kharul@ncl.res.in

The development of novel materials for CO_2 capture is of great importance in resource utilization and environmental preservation [1]. Though membrane based technique for CO_2 separation is highly advantageous over conventional techniques, applicability of polymeric membranes at elevated temperatures while maintaining their high CO_2 selectivity over other gases are major challenges [2]. These needs to be addressed by suitable membrane material design so that the membrane based process becomes techno-economically viable. Polymeric ionic liquids (PILs) are promising membrane materials for CO_2 separation due to their high CO_2 sorption-desorption characteristics [1,3]. Major challenge towards their use as a membrane is their film forming inability. Most of them are derived from vinyl monomers. To avoid brittleness, alternative strategies like crosslinking, grafting, etc. to convert them into a film form are demonstrated [4,5]. While adopting altogether different strategy, we demonstrated that PILs based on aromatic backbone (PBI) containing IL character on the main chain showed excellent film forming ability [6]. Though one of the major goal of film forming ability is achieved, gas permeability of these PILs need to be improved.

This work presents design of PILs containing bulky substitution on PBI for enhancement of gas separation properties. PILs were synthesized by *N*-quternization of polybenzimidazole using bulky alkyl group (*n*-butyl iodide, *tert*-butyl benzyl bromide, etc.); followed by anion exchange with $AgBF_4$ and $LiN(CF_3SO_3)_2$ (scheme.1). Investigations of physical and gas separation properties (sorption, permeation and respective selectivities) of resulting PILs will be presented.



Scheme 1. Synthesis of PILs based on PBI

References
[1] Xiong Y.B.; Wang h; Wang Y.J.; Wang R.M., *Polym. Adv. Technol.,* 22 **(2011)** 379-394.
[2] Aaron D.; Tsouris C., *Sep. Sci. Technol.,* 40 **(2005)** 321–348.
[3] Tang J.; Shen Y.; Radosz M.; Sun W., *Ind. Eng. Chem. Res.,* 48 **(2009)** 9113-9118.
[4] Hu X.; Tang J.; Blasig A.; Shen Y.; Radosz M., *J. Membr.Sci.,* 281 **(2006)** 130–138.
[5] Bara J.E; Hatakeyama E.S.; Gabriel C. J.; Gin D.L.; Noble R.D., *J. Membr.Sci.,* 316 **(2008)** 186–191.
[6] Kharul U.K.; Kumbharkar S.C.; Bhavsar R.S.; Shevate R.H., *WO 2012/035556* **(2012)**.

BC22

Dehydration of Acetic acid by Pervaporation using filled IPN membranes

S.B.Kuila[a*], S.K.Ray[b]
Asst. Professor[a], Department of Chemical Engineering
Haldia Institute of Technology, Haldia West Bengal
Mail ID : sunilbarankuila@gmail.com
Department of Polymer Science and Technology[b], University of Calcutta, 92, A.P.C. Road,
Kolkata-700009,

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

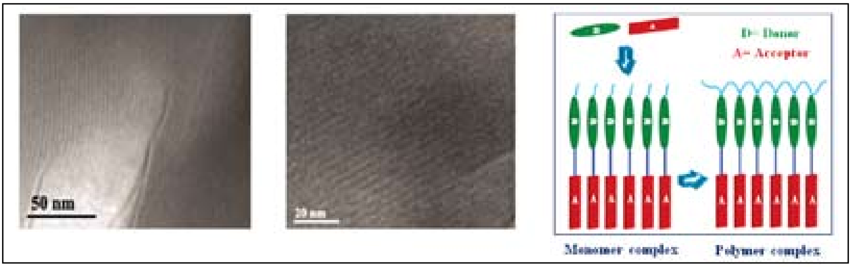
[1] R.Y.M. Huang, H. Moreira, R. Nufarforizo, Y.M. Huang,, Pervaporation separation of acetic acid-water mixtures using modified membranes, I. Blended polyacrylic acid (PAA)-Nylon membranes, J. Appl. Polym. Sci 35 (1988) 1191.
[2] K.R. Lee , J.Y. Lai, Dehydration of Acetic Acid/Water Mixtures by Pervaporation with a Modified Poly(4-methyl-l-pentene) Membrane**,** *J. Polymer Res*. 1(3), 1994, 247-254
[3] S.K.Ray, S.B.Sawant, J.B. Joshi, V.G. Pangarkar, 'Dehydration of acetic acid by pervaporation', J.Membr. Sci., 138, 1998, 1-17
[4] J.F.Lee , Y.C. Wang, Dehydration of Acetic Acid/Water Mixture by Pervaporation through a Chemically Modified Poly(4-methyl-1-pentene) Membrane, *Sep. Sc.& Tech.*, 33(2), 1998,187-200
[5] J.W. Rhim , S.W. Yoon , S.W.Kim , K.L. Lee, Pervaporation separation and swelling measurement of acetic acid-water mixtures using crosslinked PVA membranes**,** *J. Appl. Polym. Sc*, 1997

BC23

Nanostructure Formation of Donor-Acceptor Comb Polymer via Directed Self Assembly

Saibal Bhaumik and S.K. Asha*
Polymer Science and Engineering division, National Chemical Laboratory,
Pune-411008, INDIA

Well defined nano structures for organic semiconducting materials are very much desirable for optoelectronic application. Small molecule organic semiconducting materials have many advantages over their polymeric analogues, like well-defined structure, high purity etc. However, it is a challenge to solution process and to fabricate them into films due to their strong tendency to crystallize. Polymeric materials, on the other hand are easily solution processable. Nano technology is a fantastic tool to construct well defined shape, size and long range ordering. It is a challenge to assemble donor-acceptor materials in well defined long range nano organization for effective charge transport to the electrodes. Recently, well defined nano organization of an n type semiconductor based on perylene bisimide with the polymer poly(4-vinyl pyridine) (P4VP) in the domain range of 5-10 nm was achieved with the aid of hydrogen bonding and π-π interaction.[1(a-b)] Here we report the self-assembly of complementarily functionalized donor and acceptor materials based on phenylene vinylene and perylene bisimide respectively. Well defined nano structured supramolecular assembly was formed with the help of asymmetric perylenebisimide substituted with octyl-dodecyl chains at one end and functionalized with 4-amino pyridine at the other termini (ODAPy-UPBI), which was complexed with para phenylene vinylene with hydroxyl group at one end and polymerizable methacryl amide at the other termini (HO-MAm-OPV3) via non-covalent specific interaction like hydrogen bonding, π-π interaction etc.[2] Further organization of this donor-acceptor complex in the nano domain was achieved by the template polymerization of the donor using photoinduced polymerization. The resulting polymer complex was solution processable. Thin film morphologies of polymer complex showed uniform lamellar patterns in the range of 5-10 nm in transmission electron microscopy. In summary, we have designed and developed a simple approach to obtain well defined nano organization of donor acceptor materials in the domain range suitable for exciton dissociation via hydrogen bonding and π-π interaction.



References:

[1]. (a) Rekha Narayan , Prashant Kumar , K. S. Narayan , and S. K. Asha. *Adv. Funct. Mater* (**2012)** (b) Benjamin J. Rancatore, Clayton E. Mauldin, Shih-Huang Tung, Cheng Wang, Alexander Hexemer, Joseph Strzalka, Jean M. J. Fre´chet, and Ting Xu. *Acs. Nano* 4 *(***2010)** 2721

[2]. 0605/DEL/2012 Comb-Coil Supramolecular Crosslinked Polymer. Asha Syamakumari, Rekha Narayan, Shekhar Shinde, Saibal Bhaumik.

BC24

Synthesis and Characterization of Functionalized SIS Triblock Copolymer Elastomer and its Nanocomposites

S. Khanal [1], A. Shakya [1], G. H. Michler [2], J. M. Saiter [3], B. Youssef [3], R. Adhikari [1]
[1] Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal
[2] Institute of Physics, Martin Luther University Halle-Wittenberg, Halle/Saale, Germany
[3] AMME-LECAP International Lab EA 4528, Université de Rouen, France
E mail: santoshkhanal2003@yahoo.com, nepalpolymer@yahoo.com

Polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer was modified into an epoxidised version (ESIS) using performic acid. The ESIS was further acrylated to prepare the acrylated version (ASIS). The nanocomposites of each sample (SIS, ESIS and ASIS) were prepared using boehmite nanofiller via solution casting, which were characterised by Fourier transform infrared spectroscopy and transmission electron microscopy (TEM). The TEM investigations revealed that the epoxidation of the diene block enhanced the dispersion of the nanofiller in polymer matrix, which may be attributed to the improved compatibility between alkybenzene sulphonic acid coated inorganic filler and polar modified middle block of the copolymer. The segregation of the nanoparticles towards the interface of different microscopically segregated polymer domains was observed in the acrylated block copolymer based nanocomposite implying the incomplete acrylation of the block copolymer, which might segregate from the bulk unmodified or partially modified polymer.

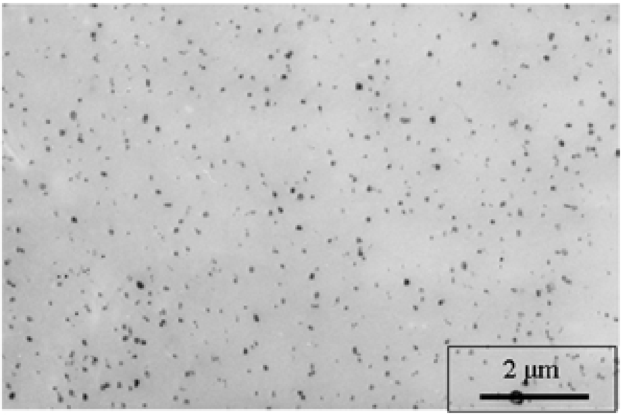


Figure 1. TEM images of SIS/5 wt.-% boehmite nanocomposite

BC25

Tuning of Surface Plasmonic Bands Using Nanopatterned Block Copolymer Templates

Seungmin Yoo, Soojin Park*
Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology,
Ulsan 789-798, Korea
e-mail: spark@unist.ac.kr

Metal nano-rings have recently attracted considerable attention from theoretical, experimental, and optoelectronic devices view points, since the quantum size effects and large surface to volume ratio of the nano-sized rings result in their unique properties, like magnetic, optical, electrical, or chemical sensing [1-5]. Self-organized block copolymer micelles that are capable of locating metal nanoparticles selectively in their cores and coronas can be used for nano-sized ring structures by a simple solvent swelling method [6-11]. Initially, we prepared nano-ring structures containing isolated gold nanoparticles. It can be converted to continuous gold nano-rings via electroless gold plating method. It is fairy efficient way to give a metal ring structure compared to conventional lithography which is highly expensive and complicate, such as electron beam lithography, lithographically patterned nanoscale electrodeposition and nanosphere lithography [12-14]. In addition to gold ring structure, we introduced silver nano-particles onto gold seed particles by well-known silver mirror reaction, which gives various surface plasmonic bands depending on silver contents. Using various metal nanopatterned arrays, we have examined optical properties for not only ring-type but also dotted metal nano-particles prepared by block copolymer nanopattern. This strategy opens up an effective way for preparing metal nanoparticle arrays with different optical properties on a rich variety of substrates.

References

[1] Aizpurua, J.; Hanarp, P.; Sutherland, D. S. Phys Rev Lett, 90(2003) 057401
[2] Kim, S.; Jung, J. M.; Choi, D. G. Langmuir, 22(2006) 7109
[3] Larsson, E. M.; Alegret, J.; Kall, M. Nano Lett, 7(2007) 1256
[4] Cai, Y. J.; Li, Y.; Nordlander, P. Nano Lett, 12(2012), 4881
[5] Huang, C. J.; Ye, J.; Wang, S.; Stakenborg, T. Appl. Phys. Lett.,100(2012) 173114
[6] Kruss, S.; Srot, V. Spatz J. P. Langmuir, 28 (2012) 1562
[7] Cho, H.; Choi, S.; Park, S. Nanoscale, 3(2011) 5007
[8] Pan, D.; Fu, Q.; Lu, J. Nanotechnology 23(2012) 305302
[9] Acharya, H.; Sung, J. W.; Sohn, B. H. Chem. Mater, 21(2009) 4248
[10] Park, S.; Wang, J. Y.; Russell, T. P. Nano Lett, 8(2008) 1667
[11] Wang, L. Montagne, F. Hoffmann, P. Chem. Commun, 25(2009) 3798
[12] Near, R.; Tabor, C.; Duan, J. S. Nano Lett, 12(2012) 2158
[13] Gwinner, M. C.; Koroknay, E.; Fu, L. W. Small 5(2009) 400
[14] Kosiorek, A.; Kandulski, W.; Glaczynska, H. Small 1(2005) 439

BC26

Functionalization of Electrospun Polyacrylonitrile (PAN) Nanofiber membrane for removal of Chromium (VI) from aqueous solution

Shabna Patel and Garudadhwaj Hota*
Department of Chemistry, National Institute of Technology,
Rourkela, Orissa-769008 INDIA

Recently, functionalized electrospun polymer nanofibers have attracted much attention because of their some special properties such as: high surface area-to-volume ratio, uniform pore size distribution, convenient recycling, and high equilibrium adsorption capacities. The surface functionalization of nanofibers can be applied widely to provide them improved properties, which will lead to a significant expansion of their applications in the field of adsorption of heavy metal ions from waste water.

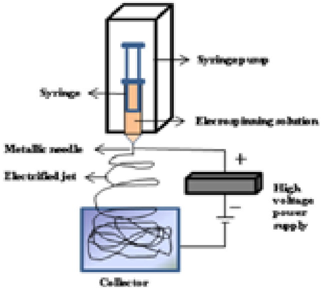


Figure 1. Schematic representation of Electrospinning set up

Polyacrylonitrile (PAN) nanofibers have been synthesized by Electrospinning method. The functionalization of PAN nanofibers membrane was done using Sodium hydroxide and Ethylenediamine (EDA) in order to modify the nitrile group (-CN). Then the functionalized PAN/NaOH/ EDA membrane has been used for the removal of Cr (VI) from the aqueous solution. Characterization of the functionalized PAN membrane was done by FTIR (Fourier Transform Infrared) spectroscopy, CHNS Analysis, Scanning Electron Microscopy (SEM), and UV-Visible spectroscopy analytical techniques. The effect of contact time on the adsorption of Cr (VI) by the functionalized PAN membrane was investigated and from the experimental result it was found that, the maximum removal of Cr (VI) was found to be 99% at 2 hour of contact time.

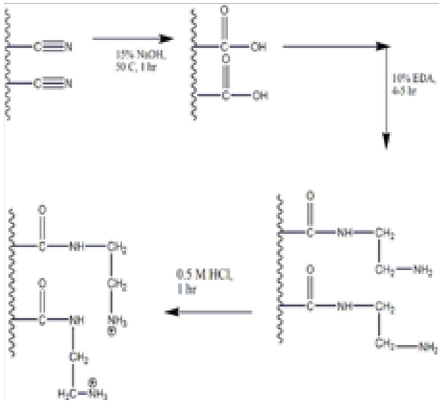


Figure 2. Schematic representation for functionalization of PAN Membrane

References:

[1]. Li, X.; Li, Y.; Zhang, S.; Ye, Z. *Chemical Engg. Journal* 183 (**2012)** 88
[2]. Thavasi, V.; Singh, G.; Ramakrishna, S. *Energy Environ. Sci* 1 (**2008)** 205
[3]. Zhang, H.; Nie, H.; Yu, D.; Wu, C.; Zhang, Y.; Zhu, L. *Desalination* 256 (**2010**) 141
[4]. Kampalanonwat, P.; Supaphol, P. *ACS Applied materials and interfaces* 2(**2010**) 3619
[5]. Schmuhl, R.; Krieg, H.M.; Keizer, K. *Water SA* 27 (**2001)** 1

BC27

Mapping of Ca^{2+} Rich Sites by Polymer conjugated Carbon Quantum Dots

A. Shanti Krishna, C. Radhakumary and K. Sreenivasan*
Laboratory for Polymer Analysis, Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences & Technology, Thiruvananthapuram -695012, India.
**Phone 091- 471 -2520248, Fax. 091- 471- 2341814. Email: sreeni@sctimst.ac.in*

Clinical fracture susceptibility, to a large extent, has been implicated to micro damage accumulated in bone in vivo due to mechanical loading and aging. Considering the gravity of this issue, extensive efforts have been expended to design methodologies to locate and visualize such types of damages. Many of these approaches are non-specific and fail to precisely locate the micro cracks. Carbon quantum dots (CDots), have attracted tremendous interest due to their unique properties such as water solubility and biocompatibility [1]. Strong fluorescence of CDots makes them ideal candidates for conjugating to various systems for drug delivery and imaging applications. CDots modified with calcium targeting ligands seems to have potential to locate bone cracks through fluorescence imaging. Hyaluronic acid (HA) is a biopolymer widely known for its nontoxicity and biocompatibility. HA is well known for its target specific drug delivery via HA-receptor mediated endocytosis [2].

In this study we modified HA with glutamic acid, a natural amino acid with strong binding affinity for calcium phosphates and this in turn is conjugated to CDots by the well known EDC chemistry. Different amounts of calcium-incorporated PVA gels were used as the *in vitro* analogue to bone tissue to study the calcium induced targeting and subsequent mapping. Additionally, this strategy can be used to deliver appropriate drug to facilitate rapid healing of the cracks. Our approach may possibly be employed in locating calcified regions also.

The imaging using fluorescence microscopy (Fig 1) undoubtedly indicates enhanced binding of functionalised CDots onto polymer gels containing increased quantity of calcium ions. The multicomponent system, we reported here, can be used both as a drug targeting and drug delivery vehicle, as well as for locating the injury site by measuring the strong fluorescence of the accumulated probes in the calcium rich sites. Synthesis and characterisation of the newly designed probes will be detailed in this presentation.

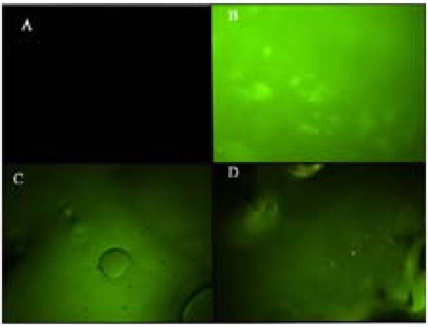


Figure 1. PVA gels A) Control, B-D) in-corporated with Ca^{2+}attracts functionalised drug loaded Cdots

References

[1] Zhu, A; Qu, Q; Shao, X., Kong, B; Tian, Y. *Angew. Chem. Int. Ed*, 51 (**2012**) 1.

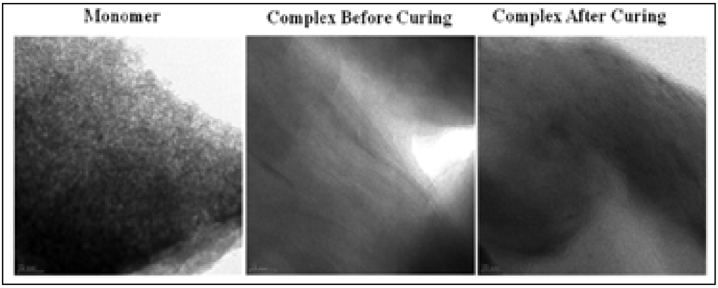
[2] Goh, E.J; Kim, K.S; Kim, Y.R; Jung, H.S; Beack, S; Kong, W.H; Scarcelli, G; Yun, S.H; Hahn, S.K. *Biomacromolecules,* 13 **(2012)** 2554.

BC28

Nanostructured Self Assembly of Unsymmetrical Perylene Bisimide Comb Polymer with Poly(4-vinyl pyridine)

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

Organic π-conjugated molecules like perylene and naphthalene bisimide are widely studied as n-type (acceptor) semiconducting materials. These n-type materials act as key component of various electronic and optoelectronic devices. In the device applications like photovoltaic cells, light emitting diodes and organic thin film transistors nanostructure plays an important role since the charge carrier mobility varies with various packing arrangements. Ikkala and Brinke et al have shown potential of supramolecular comb coil diblock copolymers to form nanostructured assembly. Their work was based on the formation of supramolecular comb coil di-block copolymers of PS-b-P4VP (Polystyrene-block- poly(4vinyl pyridine)) and surfactants like pentadecyl phenol (PDP).[1,2] Lamellar structures with long period was obtained indicating formation of well aligned nanostructures.



The objective of the present invention is to make use of non covalent interaction between a preformed polymer and suitably functionalized n-type semiconductor molecules. In our group asymmetrical PBI containing hydrogen bondable unit at one end and aliphatic branched tail at other end was explored for the formation of well defined nanostructured polymeric supramolecular assemblies.[3] Current effort is to obtain nanostructured, crosslinked n-type semiconductor material containing polymerisable units on other end rather than simple aliphatic chain. This approach is expected to provide better stability and improved packing of nanostructure. Unsymmetrical perylene bisimide (PDP-UPBI) monomer having hydrogen bondable hydroxyl group at one end and polymerizable group at other end was synthesized. PDP-UPBI formed 1:1 complex with the pyridine unit of Poly(4-vinyl pyridine) in nonpolar solvent via non covalent hydrogen bonding interaction. Complete complex formation was confirmed by different spectroscopic techniques. Polymerization of the anchored PDP-UPBI was carried out by photoinitiated polymerization in presence of photo initiator. It gave rise to formation of nanostructured supramolecular comb polymer as confirmed by TEM studies. Polymerisation process was traced by FT-IR and ^{1}H NMR techniques to ensure the maximum possible polymerisation.[4]

References

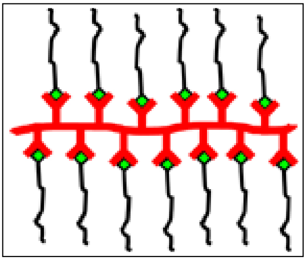
[1] Ruokolainen, J.; Makinen, R. ; Torkkeli, M.; Serimaa, R.; Makela, T.; ten Brinke, G.; Ikkala, O. *Science* 280 **(1998)** 557
[2] Ruokolainen, J.; ten Brinke, G.; Ikkala, O. *Macromolecules* 29 **(1996)** 3409
[3] Narayan, R.; Kumar, P; Narayan, K. S.; Asha, S. K. *Adv. Funct. Mater.* **(2012)** DOI: 10.1002/adfm.201202366
[4] 0605/DEL/2012 Comb-Coil Crosslinked Polymer. Asha Syamakumari; Rekha Narayan, Shekhar Shinde, Saibal Bhaumik

BC29

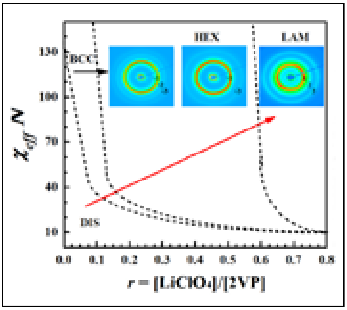
Transition and Conducting Behaviour of PS-*b*-P2VP Block Copolymer Supramolecules

Sudhakar Naidu[a] and Ryu Du Yeol[b]*
[a]*Department of Polymer Science & Engineering, National Chemical Laboratory, Pune -411008 INDIA*
[b]*Department of Chemical & Biomolecular Engineering, Yonsei University, Seoul -411008 South Korea*
**Corresponding address: dyryu@yonsei.ac.kr*

Block copolymers are proving fascinating class of materials with unique advantage of self-assembly into miscellaneous ordered nanostructures in 10-100 nm length scale. Order-to-order transitions (OOT) and Order-to-disorder transitions (ODT) can also observe with the adjustment of experimental parameters such as degree of polymerization (N), volume fraction of the blocks (Φ), the Flory-Huggins interaction parameter (χ) and temperature. It is well known that the block copolymer (BCP) attain specific properties with the addition of low molecular weight molecules as well as with macromolecules, which has applications in various fields. We have investigated the transition behavior for block copolymer (BCP) mixtures composed of a lamella-forming polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) and phenyl acetamide (PA) derivatives. Unlike a similar transition temperature for BCP mixtures with PA, measured by *in-situ* small angle x-ray scattering (SAXS) and depolarized light scattering (DPLS), an annealing temperature dependence for BCP mixtures with hydroxyl phenyl acetamide (HPA) indicates that only the complex by H-bonding mediation between the nitrogen units of P2VP block and hydroxyl group in the HPA enhances nonfavorable segmental interactions between two block components during heating process, leading to a significant increase in d-spacing for BCP mixtures with HPA. This result illustrates the importance of the availability for H-bonding mediation to control over transition behavior for BCP mixtures with the functional molecules.



The phase transitions of lithiumperchlorate ($LiClO_4$)-doped polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) were also studied as a function of temperature and ion salt concentration using *in-situ* SAXS and TEM. The effective interaction parameter (χ_{eff}) between two block components was evaluated for low molecular weight $LiClO_4$-doped PS-*b*-P2VP in a disordered state. With increasing quantities of $LiClO_4$, a remarkable increase in χ along with a volumetric change produced by the selective coordination of $LiClO_4$ to the ionophilic P2VP block led to morphological transitions from DIS-BCC-HEX-LAM structures. And also demonstrate that the ionic conductivity in the samples quenched from the different structures is morphology-independent, while it increases with increasing salt concentration.



References:

[1] Valkama, S.; Ruotsalainen, T.; Nykanen, A.; Laiho, A.; Kosonen, H.; ten Brinke, G.; Ikkala, O.; Ruokolainen, J. *Macromolecules* **2006,** 39, (26), 9327-9336

[2] Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Vahvaselka, S.; Saariaho, M.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1996,** 29, (20), 6621-6628.

[3] Cho, B. K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004,** 305, 1598-1601.

[4] Wanakule, N. S.; Panday, A.; Mullin, S. A.; Gann, E.; Hexemer, A.; Balsara, N. P. *Macromolecules* **2009,** 42, (15), 5642-5651.

BC30

Proton Exchange Membrane for Fuel Cell Fabricated from Pyridine Bridge Polybenzimidazole Copolymers

Sudhangshu Maity and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad - 500 046, INDIA.
E-mail: tjsc@uohyd.ernet.in

For stationary as well as transportation application; pollution free, eco-friendly and effective high temperature polymer electrolyte membrane (HT-PEM) fuel cell is the most attractive energy conversion device. Phosphoric acid (PA) loaded polybenzimidazole is the most promising and dedicated polymer for this application. In this present work, we have synthesized a meta and para linked series of random copolymers connected through the pyridine bridge tetramine and tetra aminobenzidine moiety. Introduction of flexible and bulky pyridine based group in the main polymer back bone which crucially monitor the physical properties, increase the d-spacing of the polymer, which helps the solubility and flexibility. As a result the solubility of polymers in the low boiling solvent formic acid (FA) are increases with the increasing of pyridine bridge random polymer. Pyridine bridge random polymer increases the mechanical stability, glass transition temperature (Tg) and capacity of phosphoric acid loading. The important parameter of fuel cell is the proton conductivity which also remarkable increases with increasing the pyridine bridge polymer part in the polymer backbone due to presence of extra hetero nitrogen atom. These acid doped membranes can be used further for application in high temperature membrane fuel cell for energy conversion.

Acknowedgement: We gratefully acknowledge for financial support and Senior Research Fellowship by DST and UGC during this work.

References:

[1] Sannigrahi, A.; Ghosh, S.; Maity, S.; Jana, T. Polymer 51 (2010) 5929.
[2] Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E.-W., Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. Fuel Cells 5 (2005) 287.
[3] Pu, H.; Wang, L.; Pan, H.; Wan, D. J Polym Sci. Part A Polym Chem. 48 (2010) 2115.
[4] Qing, S.; Huang, W.; Yan, D. Euro Poly J. 41 (2005) 1589.
[5] Sannigrahi, A.; Arunbabu, D.; Murali Sankar, R.; Jana. J. Phys. Chem. B 111 (2007) 12124.
[6] Maity, S.; Jana, T. (manuscript under preparation).

BC31

Micromolding Of Epoxy Vesicles By Self Assembling Polystyrene-Clay Nanocomposite Template

V. S. Prasad,* Asha Susan Chacko, Bindu P. Nair, T. T. Bijini, and C. Pavithran
Functional Materials, Material Science and Technology Division, CSIR-NIIST,
Thiruvananthapuram 695019, INDIA
vsprasad@niist.res.in

Polymer vesicles have received special academic and industrial attention due to their superior stability and toughness compared to phospholipid vesicles [1]. The physical, chemical and biological properties of polymer vesicles can be tailored by varying the structure and block lengths of the polymer making them potentially interesting systems for applications as advanced functional materials [2]. Epoxy vesicles of micrometer diameter were prepared from Bisphenol A diglycidyl ether resin crosslinked with diamine using POSS-modified clay-polystyrene template and characterised by OLM, TEM, SEM and EDS. The formation of the vesicle and the wall thickness was shown to be controlled by the amount of the hydrophobe concentrations (figures 1&2). The release of the mold was effectively done in presence of THF as well as in presence of methanol under ultrasonication and the reuse of the template was done under THF. This facile strategy can be effectively utilized for the synthesis of polymer micro vesicles by using self assembling inorganic-organic hybrid template micro-mold formed by self assembly which are reusable and may find use in storage applications.

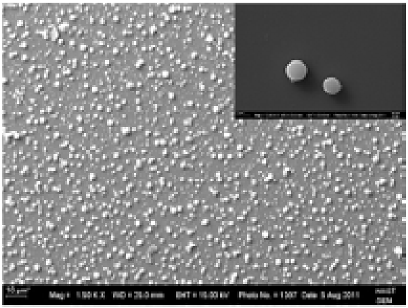


Figure 1. SEM of Epoxy Vesicles (10%)

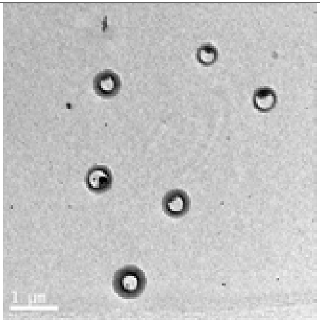


Figure 2. TEM of Epoxy Vesicles (10%)

References

[1] Nair, B.P.; Pavithran, C.; Sudha, J.D.; Prasad, V.S. *Langmuir,* 26 **(2010)**, 1431.

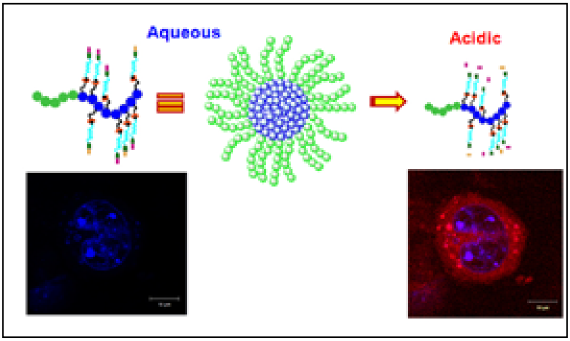
[2] Kuila, B.; Gowd, E. B.; Stamm, M. *Macromolecules*, 43 (**2010**), 7713.

BC32

Norbornene Based Polymers For Biomedical Applications

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

Three new monomers namely cis-5-norbornene- 6-(diethoxyphosphoryl)hexanote (mono **1**), norbornene grafted poly(ethyleneglycol)-folate (mono **2**), norbornene derived doxorubicin hydrazone linker (mono **3**) are synthesized. The synthesis and complete characterization of three monomers are clearly described. Their copolymerization by ring-opening metathesis polymerization (ROMP) to get the triblock copolymers **PHO-DOX-FOL**. Deprotection of phosphonic acid diethyl ester in **PHO-DOX-FOL** is carried by using trimethylsilyl bromide to get **PHOS-DOX-FOL.** Folic acid (FA) used as the receptor-targeted anti-cancer therapy, where the phosphoryl hexanote is used for iron particle (Fe_2O_3) attachment to evaluate for their tumor-targeting MRI contrast-agent. Doxorubicin hydrazone linker is used to release the drug exactly at the mild acidic conditions resembling the pH of the cancerous cells. FTIR, TGA are confirmed the iron particle (Fe_2O_3) anchoring to the **PHOS-DOX-FOL**. Drug release profile suggests the importance of having the hydrazone linker that helps to release the drug exactly at the mild acidic conditions resembling the pH of the cancerous cells. It is also observed that the drug release from micelles of **PHOS-DOX-FOL** is significantly accelerated at mildly acid pH of 5.5 to 6.0 compared to physiological pH of 7.4, suggesting the pH-responsive feature of the drug delivery systems with hydrazone linkages.



References

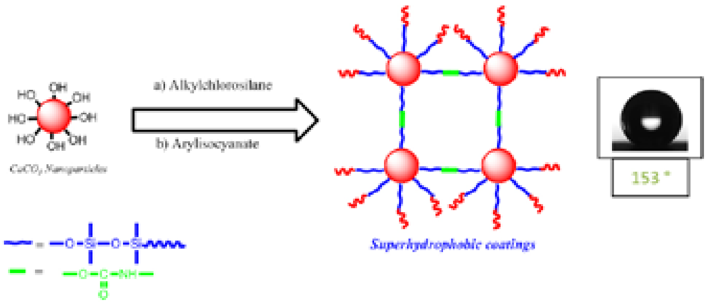
[1] Rao, V. N.; Mane, S. R.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *Biomacromolecules* **2012**, *13*, 221–230.
[2] Mane, S. R., Rao, V. N., Shunmugam, R. *ACS Macro Lett*. **2012**, *1*, 482-488.
[3] Mane, S. R.; Rao, V. N.; Chatterjee, K.; Dinda, H.; Nag, S.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *J. Mater.Chem.* **2012**, DOI:10.1039/C2JM33860B
[4] Rao, V. N.; Kishore, A.; Sarkar, S.; Das Sarma, J.; Shunmugam, R. *Biomacromolecules* **2012**, *13*, 2933.
[5] Mane, S. R.; Rao, V. N.; Chatterjee, K.; Dinda, H.; Nag, S.; Kishore, A.; Das Sarma, J.; Shunmugam, R. *Macromolecules* **2012**, *45*, 8037

BC33

Silane and Urethane Chemistry to Access Superhydrophobicity in $CaCO_3$ Nanoparticles

Vijendra Kumar[1] Santhosh Kumar KS[2]*, Sandhya KY[1], Reghunadhan Nair CP[2]
[1]*Department of Chemistry, Indian Institute of Space Science and Technology*
Thiruvananthapuram-695547, INDIA
[2]*Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre*
Thiruvananthapuram-695022, INDIA
*santhoshkshankar@yahoo.com

Superhydrophobic surfaces with water contact angle >150° enables antiwetting, anti-icing, anticorrosion, self-cleaning and antibacterial properties to materials [1-4]. This work reports for the first time, a facile and robust method for making superhydrophobic coatings from hydrophilic $CaCO_3$ nanoparticles. $CaCO_3$ nanoparticles on functionalization with alkylchlorosilane and further hydrolysis yield siloxane segments with –OH terminals on nanoparticle surface. Building urethane linkage in nanoparticles (isocyanate chemistry) resulted in superhydrophobic (SH) surfaces. The functionalization/urethane formation was evidenced in FTIR, Raman spectroscopy, SEM, and TEM analyses. The coatings exhibited static water contact angle as high as 153°. High repulsion of surface towards water droplet was observed during contact angle experiment. These $CaCO_3$-polymer coatings showed surface energy as low as 20.5 mJ/m^2 which is very close to the surface energy of 'benchmark' polytetrafluroethylene. The superhydrophobicity of coatings is attributed more to the micro/nano roughness as displayed in Atomic Force Microscopic images.



Scheme 1 Building superhydrophobic surfaces by silane and urethane chemistry on $CaCO_3$ nanoparticles

References:
[1] Gong, G. Wang; Li Q. Zhu; Hui C. Liu, and Wei P. Li. *Langmuir*, 27, (**2011**), 12275-12279
[2] Angelo, Accardo; Manfred, Burghammer; Emanuela, Di Cola; Michael, Reynolds; Enzo Di Fabrizio, and Christian Reikel. *Langmuir,* 27, (**2011**), 8216-8222
[3] Neelesh, A.; Patankar. *Langmuir,* 26, (**2010**), 7498-7503
[4] Zeshan, Hu; and Yulin, Deng; *Ind. Eng. Chem. Res.*, 49 (**2010**), 5625-5630

BC34

Block Copolymers and Nanostructured Films

Structural and optical properties of TiO_2 Nanofilms

M.Thaidun[1*],B.Venkata Rao[2],L.Raja Mohan Reddy[3]
Department of Physics,Loyola Degree College(YSRR),Pulivendla,YSR(Dt),A.P.,India
email : muttukuri.thaidun@gmil.com

Thin films of titanium dioxide (TiO_2) is a high dielectric material find applications as gate capacitor in MOSFET, antireflection coatings in silicon solar cells, photo catalysis, anti- pollution coatings, electro chromic devices for solid electrolyte and optical wave guides etc. Titanium dioxide films were formed on quartz and crystalline p-Si (100) substrates by DC reactive magnetron sputtering method. Pure titanium target was sputtered at a constant oxygen partial pressure of $5x10^{-2}$ Pa, and at different sputtering powers in the range 80 – 200 W. The films formed at sputter power of 80 W and annealed were of polycrystalline in nature with anatase phase of TiO_2. The films formed at sputter power of 120 W were of mixed phase of anatase and rutile TiO_2 [1, 2]. Further increase of sputter power to 200 W the content of anatase phase decreased as shown in fig.1. The crystallite size of the anatase TiO_2 films decreased from 40 to 20 nm with the increase of sputter power from 80 to 200 W. The crystallite size of the rutile phase TiO_2 films were increased from 10 to 30 nm with the increase of sputter power in the range 80 – 200 W. The optical transmittance spectra of the TiO_2 films formed at different sputtering powers are shown in figure 2.

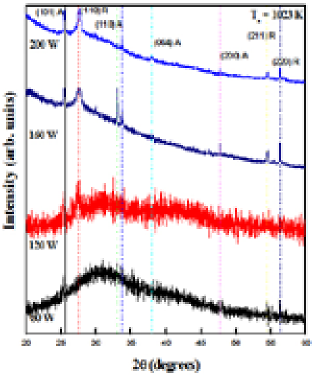


Fig-1

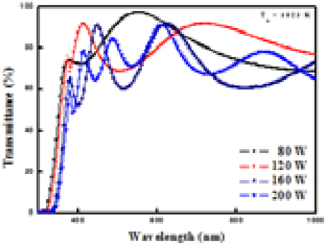


Fig-2

Reference
[1] JCPDS, International Center for Diffraction Data, card No. 084-285.
[2] G. He, Q. Fang, L. Zhu, M. Liu and L. Zhang, Chem. Phys. Lett., 395 **(2004)** 259.

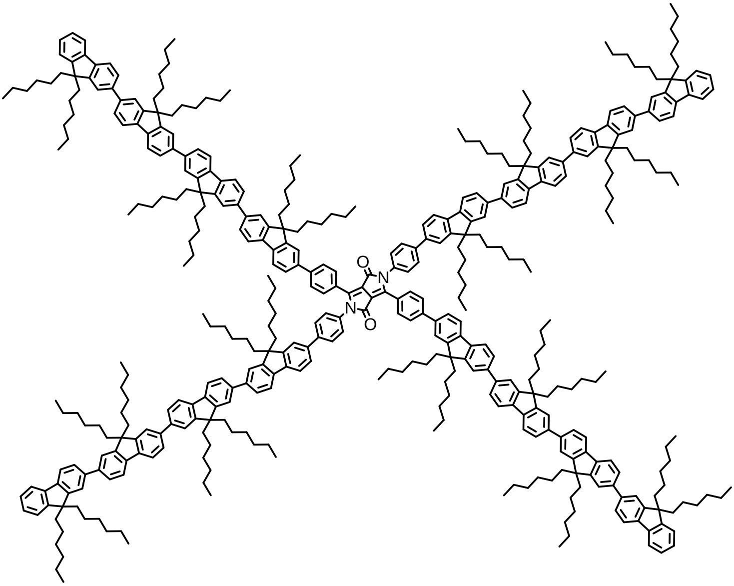
Conjugated polymers and device applications

Invited Talk

Complex conjugated architectures – from synthesis through to device applications

Peter J. Skabara
WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde,
Glasgow G1 1XL, Scotland
peter.skabara@strath.ac.uk

Well-defined and monodisperse oligomers can be considered to be intermediate of conjugated small molecules and polymers, and can feature the best of both sets of attributes. Precise HOMO/LUMO energy levels, high thermal stability, good solubility and excellent film-forming properties are common features that can be achieved in such materials. Moreover, the precise structure of the material is known (compared with polydisperse systems) and this makes our understanding of structure-property relationships much easier to establish. No single generic material is perfect and the main drawback of well-defined oligomers is in their synthesis. The synthetic procedures are normally more complex than for small molecules and polymers requiring, in some cases, several iterative steps. The synthesis and properties of some monodisperse conjugated star-shaped structures are presented.



Tuning Morphology and Charge Transport in Semiconductor Polymers and Block Copolymers

Martin Hufnagel, Ruth Lohwasser, Andreas Lang, Mukundan Thelakkat*
Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth
Bayreuth- 95440, Germany
** mukundan.thelakkat@uni-bayreuth.de*

One of the challenging aspects in designing novel functional materials is to incorporate the desired optical and /or electrical properties maintaining their film-forming and thermal characteristics to make them suitable for thin film device applications. An important criterion for photovoltaic applications is that these materials should have well-defined nanostructured morphology in thin films in order to be capable of fulfilling the complex functions of charge carrier transport in confined channels/geometries without adversely affecting the other complementary functions. This morphological control on a nanoscopic level controls the interface between the functional domains as well as the long term stability of such devices. We have demonstrated the chain of control on all length scales -from molecular to mesoscopic to macroscopic- using the self-assembly principle of fully functionalised block polymers for photovoltaic applications.

This contribution covers the design, synthesis and properties of several semiconductor homopolymers and block copolymers using modern methods of polymerization such as NMRP, RAFT, GRIM etc. Complex diblock polymers are also designed by combining one or more of these polymerization techniques with modular click chemistry. A variety of polymer architectures was achieved this way (fig.1). Here the electronic functionalities are incorporated either as pendant groups (PPerAcr) in acrylates or styrene oder as conjugated systems (P3HT) in main chain. In order to introduce main chain conjugated donor segment, poly(3-hexylthiophene), P3HT into block copolymers, the Kumada catalyst-transfer polymerization was optimized and combined with other methods. This allowed the synthesis of a series of P3HT-b-PPerAcr copolymers in which main chain conjugated hole conductor P3HT block was linked to side chain perylene bisimide acrylate (fig.2). We extended the synthetic strategy to fullerenes grafted polymers and blockcopolymers as well. These materials were characterized for their molecular crystalline structures using SAXS/WAXS. Moreover, the morphology in bulk and thin films were studied and the implication of morphology on charge transport is elucidated.

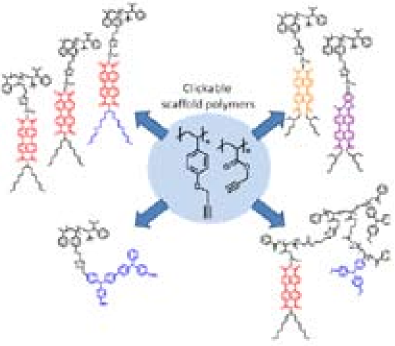


Figure 1. Synthetic strategy of diverse semiconductor polymers via click chemistry

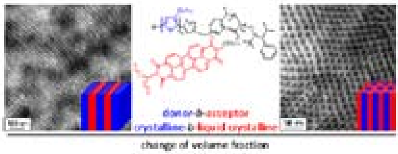


Figure 2. Tuning of morphology in P3HT-b-PPerAcr to get ordered nanostrcures of donor and acceptor.

References

[1] A. S. Lang,M. Thelakkat, *Polymer Chemistry,* 2 (**2011**) 2213-2221
[2] M. Sommer, S. Huettner, M. Thelakkat, *J. Mater. Chem.* 20 (**2010**) 10788-10797
[3] R. H. Lohwasser and M. Thelakkat, *Macromolecules*, 44 (**2011**) 3388–3397

Redox Polymer-mediated/ Dye-sensitized Solar Cell

Hiroyuki Nishide
Dept. of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
Dept. of Nanobio Materials and Electronics, Gwangju Institute of Science and Technology,
Gwangju 500-712, Korea
E-mail: nishide@waseda.jp

We have focused on aliphatic polymers bearing organic redox-active groups per repeating unit. The redox polymers are characterized by an ultimate population of the electron-releasing and -gaining site which allows efficient redox-driven electron transport throughout the polymer layer via self-exchange reactions. We are fabricating dye-sensitized photovoltaic cells to replace the iodine-containing electrolyte and/or the titanium oxide semiconductor in Graetzel-type one with the redox polymer layers for charge-separation and -transport in the cell. The cells displayed significantly high open-circuit voltage of almost 1 V. The cell performance parameters, the voltage, short circuit current density, and fill factor, were related with kinetic reactivity (k_0 and k_{ex}) and thermodynamic redox potential ($E_{1/2}$) of the redox molecules. Redox polymers are emerging as a new class of electroactive materials useful for various kinds of wet-type energy storage and conversion devices.

Acknowledgments This work was partially supported by Grants-in-Aid for Scientific Research (No. 24225003) from MEXT, Japan, and World-Class University program at GIST (No. R31-2008-000-10026-0) from MEST, Korea.

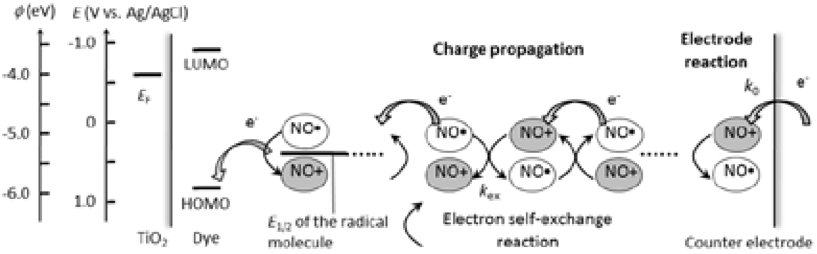


Figure Scheme for the mediation process with the nitroxide radical redox couple in a DSSC (ϕ= energy, E = redox potential, and E_F = Fermi energy).

References

[1] Nishide, H.; Oyaizu, K., *Science*, 319 (**2008**) 737.
[2] Oyaizu, K.; Nishide, H., *Adv. Mater*., 21 (**2009**) 2339.
[3] Choi, W.; Ohtani S.; Oyaizu, K.; Nishide, H.; Geckeler, K., *Adv. Mater*., 23 (**2011**) 4440.
[4] Choi, W.; Oyaizu K.; Nishide, H., *J. Am. Chem. Soc.*, 133 (**2011**) 19839.
[5] Sano, N.; Tomita, W.; Hara, S.; Min, C. M.; Lee, J. S.; Oyaizu, K.; Nishide, H., *ACS Appl. Mater. Interfaces*, 5 (**2013**) 1355.
[6] Kato, F.; Kikuchi, A.; Okuyama, T.; Oyaizu, K.; Nishide, H., *Angew. Chem. Int. ed.*, 51 (**2012**) 10177.

Ferroelectric Polymers for enhanced switching in all-polymer field effect transistors

Satyaprasad P Senanayaka and K. S. Narayan*
Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore -560064 (India)
*narayan@jncasr.ac.in

Low-cost printable field effect transistors (FETs) are typically associated with moderate performance and slow switching speed. The response of polymer field effect transistors (PFETs) to a gate voltage pulse is a manifestation of time scales involved in processes such as: dielectric polarization, structural relaxation and transport via interfacial-disordered-interfacial states. We examine the contribution to these processes by studying a range of dielectrics and polymer semiconductors. Based on theses selection of studies we arrive at a parameter which serves as a figure of merit and quantifies the different processes contributing to the switching response. We observe a cross-over from transport limiting factors to dielectric limiting factors for a specified set of device parameters.

Molecular Ordering, Charge Transport and Macroscale Mobility in Polymer Based Semiconductors

Mohan Srinivasarao [a,b], Karthik Nayani [a], Min Sang Park [a], Avishek Aiyar [c], Jung Ok Park [a], and Elsa Reichmanis [c]
[a] School of Materials Science and Engineering
[b] School of Chemistry and Biochemistry
[c] School of Chemical and Biomolecular Engineering
The Georgia Institute of Technology
Atlanta, GA 30332

Printed, flexible electronics are gaining traction as low cost alternatives to conventional semiconductor devices in industries ranging from health care to national security. The performance of such devices is critically dependent upon alignment of the semiconducting unit at the nano- through macro-scales. Significant structure-process-property relationships that allow for enhancement of long-range order will be described. Of note, we have observed a lyotropic liquid crystalline (LC) phase in poly-(3-hexylthiophene) (P3HT) via solvent-evaporation induced self-assembly [1]. *In-situ* polarized Raman spectroscopy was used to study the evolution of structure that eventually leads to a phase transition from an isotropic solution to an LC phase. Concurrent *in-situ* drain current measurements revealed variations in the current that correspond well with the time-lines for the phase transition, suggesting that P3HT undergoes a series of phase transitions ranging from isotropic, to liquid crystalline to finally, polycrystalline solid.

We have identified and characterized the structural features which appear in a thin film of regio-regular poly(3-hexylthiophene) (P3HT) drop-cast from dilute solution. Periodic structures observed at the edge of the film were interrogated by optical microscopy and atomic force microscopy. It is suggested that these structures originate from an instability at the leading edge of a liquid crystal-air interface. We also provide evidence that a solution of P3HT forms a liquid crystalline phase at higher concentration through the observation of distinct birefringence and characteristic textures under crossed polarizers using an optical microscope.

References:

[1] Min Sang Park, Avishek Aiyar, Jung Ok Park, Elsa Reichmanis and Mohan Srinivasarao, "Solvent Evaporation Induced Liquid Crystalline Phase in Poly(3-hexyl thiophene)", *JACS*, ***133*** (19), 7244-7247 (2011).

Modification of polymeric photorefractive device for improved grating formation

Nakjoong, Kim[a]*, Jin-Woo Oh[b], and Jongwan Choi[a]
[a]*Department of Chemistry, Hanyang University, Seoul, 133-791 Korea*
[b]*Department of Nanomaterials Engineering, Pusan National University, Busan 627-706, Korea*
kimnj@hanyang.ac.kr

During the last decade, various potential applications such as pattern recognition, phase conjugation mirror, and optically controlled spatial light modulator have been demonstrated using the photorefractive (PR) effect [1-3]. However, their PR performances are not good enough for practical applications because of their poor grating formation rate and high poling fields [4]. One way to enhance PR writing rate is to increase photo generation efficiency by using nanomaterials [5-7]. Gold nanoparticles (Au NPs) are well known material that have localized surface plasmon resonance (LSPR) property, which the excitation of LSPR in the Au NPs can lead to a strong enhancement in the electromagnetic field at the surface of the particles at visible and near-infrared wavelengths [8]. PR composites doped with Au NPs are expected to increase photo-charge generation efficiency by LSPR phenomenon.

Herein, we focused on modification of polymeric photorefractive device using nanoparticles for improved grating formation. In the photorefractive effect, photoconductivity is one of the most important parameters. The PR grating formation speed and space charge field formation are strongly dependent on the photoconductive properties. The PR composites doped with Au NPs was shown effective enhancement of photoconductivity and grating buildup speed due to improvement of photo-charge generation by plasmonic resonance coupling.

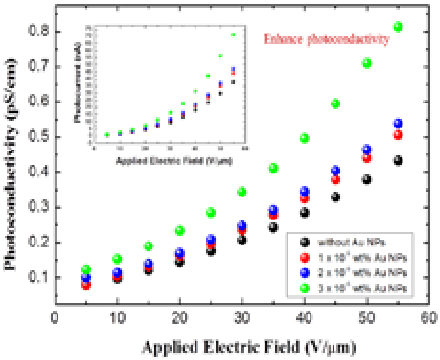


Figure 1. Photoconductivity of Au NPs doped polymeric PR device

References:

[1] Georges, M.P.; Scauflaire, V. S.; Lemaire, P. C. *Trends Opt. Photon.*, 62 (**2001**) 63
[2] Kamshilin, A. A.; Liu, S.; Tuovinen, H.; Prokofiev, V. V.; Jaaskelainen, T. *Opt. Lett.*, 19 (**1994**) 907
[3] Joo, W.-J.; Kim, N. *Polym. J. (Tokyo JT Japan)*, 36 (**2004**) 674
[4] Oh, J.-W.; Moon, I. K.; Kim, N. *J. Photochem. Photobiol. A: Chem.*, 201 (**2009**) 222
[5] Köysal, O.; Okutan, M.; San, S. E.; Dabrowski, R.; Ecevit, F. N. *Mater. Chem. Phys.*, 109 (**2008**) 253
[6] Choudhury, K. R.; Sahoo,; Jang, Y. S.; Prasad, P. N. *Adv. Funct. Mater.* , 15 (**2005**) 751
[7] Wang, F.; Chen, Z. Zhang, B.; Gong, Q.; Wu, K.; Wang, X.; Zhang, B.; Tang, F. Appl. Phys. Lett., 75 (1999) 3243
[8] Genov, D. A.; Sarychev, A. K.; Shalaev, V. M.; Wei, A. *Nano Lett.*, 4 (**2004**) 153

Graphene Domain Analysis using Liquid Crystal Texture

Dae Woo Kim[a], Yun Ho Kim[b], Seon Joon Kim[a], Hyung Wook Choi[a] and Hee-Tae Jung[a,*]
[a]*Dept. of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea*
[a]*Advanced Functional Materials Group, Korea Research Institute of Chemical Technology, Daejeon, Korea.*
** heetae@kaist.ac.kr*

The boundaries between domains in graphene materials strongly influence its electronic, mechanical, magnetic and thermal properties. However, existing approaches for domain visualization, which are based on electron microscopy and spectroscopy, are only effective for domains that are less than a few micrometres in size and need much time and efforts to analyze the domain structures. Here, we report a simple method for the visualization of arbitrarily large graphene domains by imaging the birefringence of a graphene surface covered with nematic liquid crystals. The method relies on a correspondence between the orientation of the liquid crystals and that of the underlying graphene, which we use to determine the boundaries of macroscopic domains. And we discovered the relationship between Cu domain and grown CVD domain structure by using this method. The sizes and shapes of domains of graphene grown on various Cu substrates well match those of the underlying Cu (111) domains. In contrast, other Cu domains, such as (100) and (101) do not strongly influence the domain structures of graphenes and furthermore, graphene islands with poly-domains (*ca.* 90%) are significantly nucleated, which play a role in the formation of poly crystalline graphene. This technique should therefore open a new direction for studies directed at the elucidation of factors that control the domains, structures and properties of graphene, which is critical to realizing their potential applications.

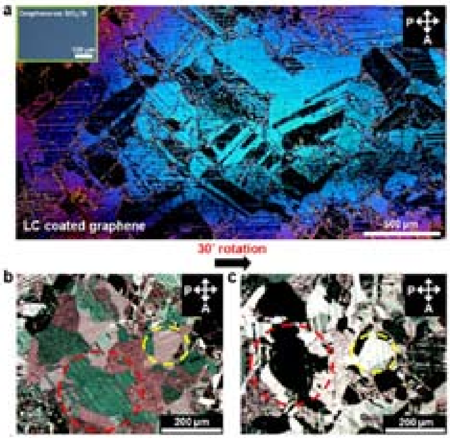


Figure 1. a, optically visualized graphene domains by observing the birefringence of a graphene surface covered with nematic liquid crystal. b, birefringent color transition as rotating the sample.

References

[1] Yazyev, O. V.; Louie, S. G.; *Nature materials,* 9 (**2010**) 806.
[2] Tsen, A. W.; Brown, L.; Levendorf, M. P.; Ghahari, F.; Huang, P. Y.; Havener, R. W.; Ruiz-Vargas, C. S.; Muller, D. A.; Kim, P.; Park, J. *Science*, 336 (**2012**) 1143.
[3] Kim, D. W.; Kim, Y. H.; Jeong, H. S.; Jung, H.-T. *Nature nanotechnology*, 7 (**2012**) 29.

Synthesis, Growth and Characterization of Functionalized Perylene based polymers and their Micro and Nanostructures for Organic Field Effect Transistor Devices

[1]Suresh Vasimalla, [2]Nimmakayala V. V. Subbarao, [3]Dipak K. Goswami, [1]Parameswar K. Iyer*
Department of Chemistry,[1] Center for Nanotechnology,[2] and Department of Physics,[3]
Indian Institute of Technology Guwahati, Guwahati-781039, Assam, INDIA.
* pki@iitg.ernet.in

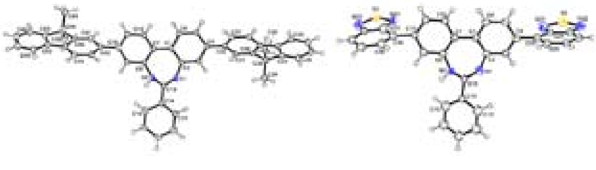
We report the synthesis, growth and morphology characterization of micron and nano sized semiconducting functionalized n-type polymers in various solvents. Comparative study was also performed with perylene tetracarboxylic diimide oligomers. The unique morphology, optical, electrochemical and electrical properties of these materials were characterized by SEM, FESEM, optical microscope, fluorescence microscope, polarized optical microscopes, UV-Visible, photoluminescence spectroscopy and cyclic voltametry (CV) which will be presented and discussed. The structural properties were also identified by the X-ray diffraction (XRD). All samples showed intense fluorescence color of orange red under visual observation and normal light. Rotating optical polarized microscopy imaging of a 1D microstructure under crossed polarization was performed to investigate polarized emission. The anisotropy birefringence was maximum when the 1D microstructure was aligned 45° to the direction of the polarizer and it was minimum when aligned parallel to the polarizer. The SEM and optical microscopy images reveals that the aligned crystallites have wire type structures of width and length in the range of 1-2 μm and 30–100 μm in THF, 100-200 nm and 2-5 μm in ethanol and methanol respectively. FET devices were fabricated on a silicon chip which showed enhanced carrier mobilities.

Synthesis of p- and n- type Conjugated Materials from a Common Intermediate

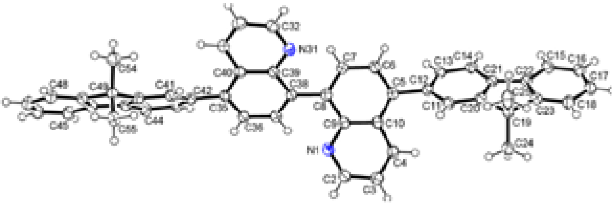
Dr. Josemon Jacob*, Manisha Tomar
Centre for Polymer Science and Engineering, Indian Institute of Technology,
Hauz Khas, New Delhi-110016, India
** Email: jjosemon@yahoo.com*

Conjugated materials constitute the active layer in many organic electronic devices including organic LEDs, field effect transistors, solar cells, sensors etc. Among the material classes widely investigated, polyphenylenes and polythiophenes have been most extensively studied due to their ease of synthesis as well as desirable optical and electronic properties. Most semiconducting polymers are of p-type and there is increasing need to identify new classes of p- and n-type materials for various applications. N-containing polymers can be of either p- or n-type depending upon the nature of incorporation of the nitrogen atom. Semiconducting materials based on oxadiazoles, pyridines, quinoxalines, anilines, carbazoles, quinolines, benzimidazoles, benzothiadiazoles, and bis(benzothiadiazole)s, have been developed and extensively investigated for use in organic solar cells and light emitting diodes.

In this talk, I will discuss our recent work in developing N-containing conjugated aromatics for applications in LEDs and solar cells. We have developed a precursor approach to synthesize several material classes starting from common intermediate, 2,5-dibromonitrobenzene. Synthesis of homopolymers and copolymers based on quinoline, isomeric biquinolines, cinnoline and diazepine can all be accomplished starting from the above intermediate. Our approach is unique in that the bromine atoms necessary for coupling are ideally substituted to generate extended conjugated structures by appropriate coupling, and are introduced prior to monomer synthesis avoiding unnecessary and non-selective bromination reactions. The optical and device properties of some of these material classes will be discussed.



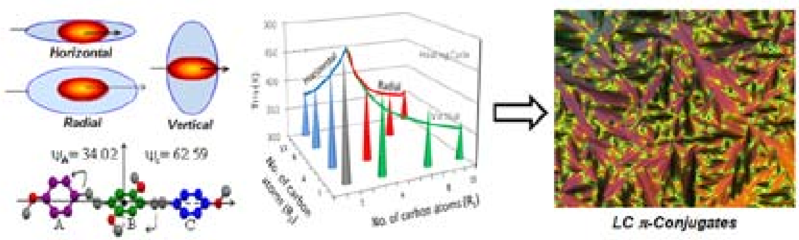
Single crystal X-ray structures of diazepine derivatives coupled with fluorene or benzothiadiazole (above) and a biquinoline unit coupled with flourene units (below).



Solid State Assemblies of π-Conjugated System: Unlock the Hidden Secrets

M. Jayakannan*
Department of Chemistry, Indian Institute of Science Education and Research (IISER)
Dr. Homo Bhabha Road, Pune, Maharashtra - 411008, INDIA.
E-mail: jayakannan@iiserpune.ac.in

π- Conjugated semiconducting oligomers and polymers are emerging as important classes of materials for applications in electronic devices. The performance of π-conjugated materials in electronic devices are mainly driven by the precise molecular arrangements in solid state. It has been a great challenge for synthetic chemists to establish direct correlation between molecular packing of chromophores with their self-assembled objects. This could be achieved by designing appropriate π- conjugated skeletons which could self-organize in solid state and also produce good quality single crystal structures. To address the above issue, our group has adopted the design principle in such a way that the molecules were constructed using simple hydrocarbon anchoring units in the π-backbone. A large number of oligophenylenevinylenes and their polymers were synthesized to optimize the correct molecular geometry for the π-conjugated self-assemblies in the solid state.[1-4] Single crystal X-ray structures were resolved for these π-system to study the roles of the liquid crystalline properties,[5] planarity versus non-planarity, inter-molecular non covalent forces such as weak CH/π interactions[7], photophysical characteristics[6] and so on. The role of fluorocarbon versus the hydrocarbon tails on the LC mesophase of the π-conjugated oligophenylenevinylenes were also resolved.[8] Recently, effects have also put to study the chemical structures and polymer chain topology on donor acceptor self-assemblies of segmented OPV polymers with electron deficient perylenebisimide chromophores. The presentation will focus on our research efforts and the present scenario on the above topic.



References:

[1] Amrutha, S. R.; Jayakannan, M**. J. Phys. Chem. B. 2006**, *110*, 4083-4091
[2] Amrutha, S. R.; Jayakannan, M. ***Macromolecules***, 2007, *40* , 2380-2391
[3] Amrutha, S. R.; Jayakannan, M. ***J. Phys. Chem. B*. 2008**. *112*, 1119-1129
[4] Amrutha, S. R.; Jayakannan, M. ***J. Phys. Chem. B* 2009**, *113*, 5083–5091
[5] Goel, M.; Jayakannan, M. ***J. Phys. Chem. B*, 2010**, *114*, 12508–12519.
[6] Murthy, A. V. R.; Goel, M.; Patil, S.; Jayakannan, ***J. Phys. Chem. B*. 2011,** *115, 10779-10788.*
[7] Goel, M.; Jayakannan, M. ***Chem. Eur. J.* 2012**, 18, 11987-11993.
[8] Goel, M.; Jayakannan, M. ***Chem. Eur. J*. 2012**, *18*, 2867-2874.

Amphiphilic Strategies towards Improved Electronic Performance of π- Conjugated Nanostructures

Bhawani Narayan, K. Venkata Rao and Subi J. George*
Supramolecular Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore 560064, India

Supramolecular ordering of π -conjugated molecules plays a vital role in the performance of organic opto-electronic devices.[1] Controlling the morphologies at the nanometer-scale in solution processable polymers during its fabrication via spin coating is challenging due to their structural defects. In this respect, the self-assembly of π -conjugated oligomers, with well defined chemical structure, in solution using supramolecular design principles, has attracted immense attention as it allows enhanced structural control over the organization and functional properties. However, these self-assembled nanostructures have often showed poor performance[2] compared to highly organized assemblies of their less processable counterparts, in the crystal and vacuum deposited thin film states.[3] In this talk, I will discuss our strategies to improve the electronic properties of these π-conjugated nanostructures.

In the first approach, we have employed an amphiphilic design for the self-assembly of p- and n- type organic semi-conductors. The strong hydrophobic interactions between the amphiphilic systems gave rise to less dynamic assemblies with high association constants. Furthermore, these highly ordered assemblies with stronger π – π interactions exhibited better mobilities.[4] We have further employed a non-covalent amphiphilic strategy to construct supramolecular charge-transfer nanostructures, with either alternate (mixed) or segregated (orthogonal) molecular organization of donor and acceptor molecules.[5] These novel CT nanostructures exhibited significant mobility without any external doping.[6] The details of these projects will be discussed during this talk.

[1] a) F. Würthner, *Angew. Chem. Int. Ed.* **2001**, *40*, 1037; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491.
[2] A. Saeki, Y. Koizumi, T. Aida, S. Seki, *Acc. Chem. Res.* **2012**, *45*, 1193-1202.
[3] C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater*. **2002**, *14*, 99–116.
[4] B. Narayan, S. P. Senanayak, A. Jain, K. S. Narayan, S. J. George, *Adv. Func. Mat*., **2013**, (DOI: 10.1002/adfm.201202298).
[5] a) K. V. Rao, K. Jayaramulu, T. K. Maji, S. J. George, *Angew. Chem. Int. Ed.,* **2010**, *49*, 4218; b) K. V. Rao, S. J. George, *Chem. Eur. J.* **2012**, *18*, 14286.
[6] A. A. Sagade, K. V. Rao, U. Mogera, S. J. George, A. Datta, G. U. Kulkarni, *Adv. Mater.,* **2013**, (DOI: 10.1002/adma.201203926).

Polyaniline nanotubes: Design, Synthesis and Applications

Utpal Rana, Sanjoy Mondal and Sudip Malik*
Polymer Science Unit,
Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India.
** E-mail: psusm2@iacs.res.in*

Polyaniline (PANI) is unique and the most promising conducting polymer because of its environmental stability, its profound reversible electronic structure conversion ability (due to charge-transfer doping/ dedoping) and associated optical and electrical properties that make PANI attractive as an electronic material for potential use in a variety of applications. Over the bulk counterpart, nanostructured PANI has recently received much attention because of several potential applications like electronic devices and gas sensor.

The present work reports the preparation, properties and application results of a comprehensive study on the optical, morphological and transport properties of polyaniline nanotube (nPANI) that are derived by *in-situ* polymerization method using organic dopant acid. Aromatic di, tri, tetracarboxylic acid, aromatic sulphonic acid and graphene oxide (GO) are used as a dopant acid. The formation of nPANI by soft template method using benzene tetracarboxylic acid (BTCA) dopant and characterization followed by extensive studies of their properties are investigated. The morphology of the nanotube formation mechanism has explained. Fluorescence PANI nanotubes using perylene tetracarboxylic acid (PTCA) with control optical, morphological and electrical properties of polymer are explored. The effect of the dopant functionality, position and number of functional group on the formation of nanostructure will be explored. The preparation of water soluble PANI using perylene disulphonic acid (PRSA) and its application to detect ascorbic acid by electrochemically up to mM concentration level will also be presented. The preparation of 1D GO/PANI nanotube from 2D GO nanosheets and *'in-situ'* reduction of GO to RGO by PANI and its application as supercapacitor devices will be discussed.

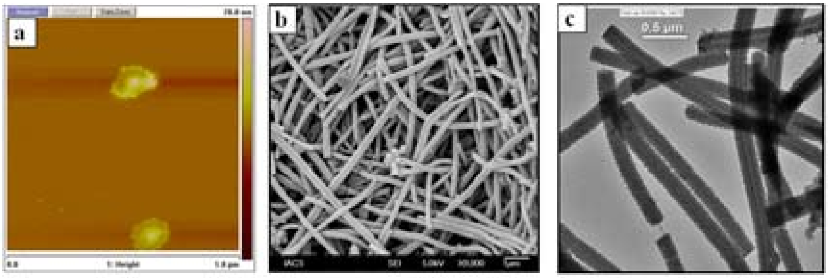


Fig-1:AFM topology of vesicle of aniline/organic dopant acid before polymerization. (b) FESEM and (c) HRTEM images of our synthesized one organic acid doped PANI.

References

[1] Rana, U.; Chakrabarty. K.; Malik, S. *J. Mater. Chem.*, 21 (**2011)** 11098-11100.
[2] Rana, U.; Chakrabarty. K.; Malik, S. *J. Mater. Chem.*, 22 (**2012)** 15665-15671.
[3] Rana, U.; Malik, S. *Chem. Commun.*, 48 (**2012)** 10862-10864.

Oral

Fabrication of a General Biosensing Platform from Polyaniline-Au Nanowires

Rupali Gangopadhyay*[a], Ankan Dutta Chowdhury[b] and Amitabha De[b]
[a]Centre for Advanced Materials, Indian Association for the Cultivation of Science, Kolkata 32, INDIA
[b]Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 64, INDIA
*Corresponding author : e-mail : camrg@iacs.res.in

Polyaniline nanowires (PAn-NW) have proved themselves to be promising materials for versatile fields of applications ranging from electronics to biotechnology. In this work we have introduced a novel method for functionalization of polyaniline nanowires for fabrication of a biosensing platform. The later is capable of immobilization of biomolecules of different origin and sensing their corresponding substrates in turn. We have followed interfacial polymerization method [1] to obtain PAn-NW dispersion with embedded gold nanoparticles (~8-10 nm) (Fig. 1). Electrodes coated with PAn-AuNP composite nanowires were then treated with β-Mercaptoethylamine (MEA) to add $–NH_2$ groups on PAn-AuNP surface. This way we can get electrodes coated with $–NH_2$ functionalized polyaniline NW. This makes a general platform for immobilization of biomolecules capable of interaction with $–NH_2$ groups without the hazards of functionalizing the biomolecules themselves.

We have exploited this biosensing platform for fabrication of three different biosensors. In one of our work we have immobilized single stranded DNA oligonucletide (ssdA) on this platform and have monitored its combination with the complementary strand (ssdT) following Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV) and Electrochemical Impedance Spectroscopy (EIS) techniques [2]. The system works well even at concentrations as low as 10^{-18} M (of target nucleotide) and produces substantially large peak current (mA) in DPV. On the other hand it produces a huge change in impedance at low frequencies (EIS), after hybridization with complementary strand. In a parallel work we have immobilized Glucose oxidase on this platform for fabrication of glucose biosensor. This system could be used for amperometric detection of glucose in aqueous solution over a wide concentration range of 1μM - 20mM [3]. The biosensor effectively performs a selective electrochemical analysis of glucose with a very low detection limit of 1μM glucose concentration and exhibits excellent sensitivity of 14.63 $\mu A m M^{-1} cm^{-2}$ in the presence of common interferrants avoiding generation of an overlapping signal from such interferers. In the third attempt we could successfully immobilize Lamin A antibody on the $–NH_2$ functionalized AuNP through the formation of amide bonding. Bioactivity of the antibody was appreciably retained after covalent attachment and its response towards the Lamin A protein could be nicely demonstrated via EIS technique upto a concentration as low as 10 μm. Therefore the efficiency of the general biosensing platform is established.

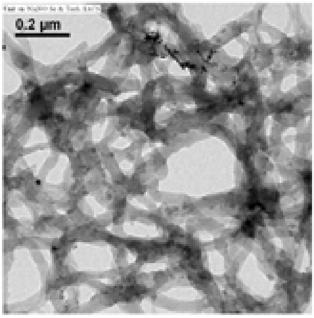


Fig. 1. PAn-NW decorated with AuNP

References :
[1] Huang J, Virji S, Weiller B H. and Kaner R B., *J Am Chem Soc*. 125 (**2003**), 314-315
[2] Gangopadhyay R, Chowdhury A D and De A, *Sens. Act. B (Chem)*, 171-172 (**2012**) , 777-785
[3] Chowdhury A D, Gangopadhyay R and De A (communicated)

Synthesis of Diblock Copolymers of Poly (3-hexylthiophene) and Poly (butyl acrylate) for Organic Field Effect Transistor

Shiny Nair[a], M. Kathiresan[a], Shivshankar R. Mane[b], Raja Shunmugam[b], V Natarajan[a], T Mukundan[a]*
[a]*Naval Physical and Oceanographic Laboratory, Kochi 21, India*
[b]*Indian Institute of Science Education and Research, Kolkata, India.*
** ms_npol@yahoo.in*

The use of organic semiconductors in thin-film transistors holds great promise, with applications ranging from drivers for flat-panel displays to sensors and large area flexible devices. For underwater applications, organic field effect transistors (OFETs) are ideal candidates to perform transimpedance amplification in large-area piezoelectric sensing devices. Because of its high hole mobility and ease of synthesis, regioregular poly (3-hexylthiophene) (rr-P3HT) is one of the most promising and most studied solution-processable materials. Due to its chemical structure, rr-P3HT possesses an array of desired electrical properties [1]. However, its chemical structure includes brittle and highly inflexible rod like microstructures.

Fig. 1Schematic of fabricated OFET

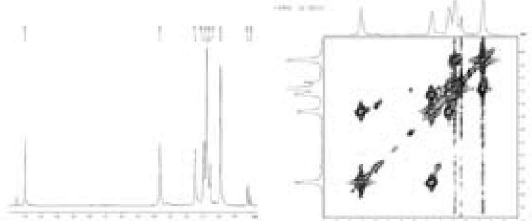


Fig. 2 (a) 1H spectrum and (b)Two-dimensional COSY) spectrum of rr-P3HT

To improve the properties of rr-P3HT, we have developed novel block copolymers of rr-P3HT employing atom transfer radical polymerization (ATRP). Such a block copolymer could self-assemble into a number of nanoscale morphologies, which would lead to the possibility that new electronic/structural copolymers could be designed and synthesized as components in new micro/nano electronic devices. The objective of the study is to produce a material that has the electrical properties of polythiophene and the flexibility of soft polymers such as poly (butyl acrylate). We describe a method for the synthesis of poly (3-alkylthiophene) block copolymers using vinyl terminated regioregular poly (3-hexylthiophene) as precursors via ATRP. The rr-P3HT was synthesized by the Grignard metathesis reaction and the formation of the product was confirmed through, ^{1}H NMR. The acrylate segment generated by ATRP technique and the formation of the block copolymer is confirmed by comparing the GPC results.

Si/SiO_2 based OFET was fabricated on a simplified TFT structure in which a heavily doped silicon wafer was used as the substrate, with a layer of thermally grown silicon dioxide (200 nm) serving as the gate dielectric [2]. A bottom contact configuration was employed with Pd metal acting as the source and drain electrodes. The synthesized block copolymer was spin coated on the wafer and patterned by UV photolithography and Reactive Ion Etching. The paper will discuss the field effect characteristics and charge mobility.

References

[1] Iovu, M. C.; Jeffries-EL, M.; Sheina, E.; Cooper, J. R.; McCullough, R. D.; *Polymer 46*, **(2005)**, 8582.

[2] Ji, T.; Kathiresan, M.; Shiny, N.; Soyoun, J.; Natarajan, V.; Vishnubhatla, R.M. R.; Varadan,. V. K.; in *Proc. SPIE—Nanosensors, Microsensors, and Biosensors and Systems* 6528, **(2007)**, 65281P-6.

The Influence of Side-chain Position on the Optoelectronic Properties of a Red-emitting Conjugated Polymer

Li-Ping Lu[1], Chris E. Finlayson[1,3], Dinesh Kabra[1,2], Sebastian Albert-Seifried[1], Myoung Hoon Song[1], Remco W. A. Havenith[4], Guoli Tu[5], Wilhelm T. S. Huck[6], and Richard H. Friend[1]*
[1]Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK.
[2]Department of Physics, Indian Institute of Technology Bombay, Powai Mumbai, India.
[3]Institute of Mathematical & Physical Sciences, Prifysgol Aberystwyth University, Wales SY23 3BZ, UK
[4]Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands.
[5]Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Luoyu Road, Wuhan, 430074, China.
[6]Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands.
E-mail: dkabra@iitb.ac.in

A study of the organic semiconductor poly ((9,9-dioctylfluorene)-2.7-diyl-alt-[4,7-bis(3-hexylthien-f-yl)-2,1,3-benzothiadiazole]-2´,2´´-diyl) (F8TBT) is presented, directly comparing a conventional form (F8TBT-out) with a form with varied alkyl side-chain position (F8TBT-in), in terms of optical properties and device performance in light-emitting-diodes (LEDs). [1] Computational simulations of the side-chain position with respect to the TBT unit reveal geometrical differences between F8TBT-out and F8TBT-in. π–π conjugation on the backbone of F8TBT-in is interrupted by a distortion of the benzothiadiazole ring, leading to a blue-shift of the absorption spectrum and increased photoluminescence quantum efficiency. Both conventional and hybrid LEDs demonstrate that devices with F8TBT-in show improved performance, as compared to F8TBT-out, illustrating how tuning the optoelectronic properties of conjugated polymers by varying the placement of side chains has an important role in device optimization.

References

[1] The Influence of Side-Chain Position on the Optoelectronic Properties of a Red-Emitting Conjugated Polymer, Li Ping Lu, Chris E. Finlayson, Dinesh Kabra, Sebastian Albert-Seifried, Myoung Hoon Song, Remco W. A. Havenith, Guoli Tu, Wilhelm T. S. Huck and Richard H. Friend *Macromolecular Chemistry and Physics* (DOI: 10.1002/macp.201200681).

Synthesis of highly conducting and crystalline polyaniline and it's application to supercapacitor

B. Rajender,[a] S. Palaniappan[a,b,*]
[a]Polymers & Functional Materials Division,CSIR- Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b]CSIR – Network Institutes for Solar Energy (NISE). India
email : palaniappan@iict.res.in

One of the most commonly active species in pseudocapacitor is electrically conducting polyaniline [1]. In this work, polyaniline salt (PANI-NTSA) is prepared by aqueous, emulsion and interfacial polymerization pathways using 1,3(6,7)-napthalene trisulfonicacid sodium salt as novel dopant. Polyaniline salt is characterized by FT-IR, FE-SEM, EDAX, X-ray diffraction, TGA, and conductivity measurements. PANI-NTSA is obtained in nano fiber (fig.1) highly crystalline form (fig.2)) with reasonably good conductivity (7 S/cm). This polyaniline salt is used as electrode in supercapacitor application in symmetric electrode configuration. This super-capacitor system is characterized by cyclic voltammogram, galvanostatic charging/ discharging, and electrochemical impedance spectroscopy. The result shows that the obtained polyaniline has excellent electrochemical characteristics with a capacitance of 265 F/g.

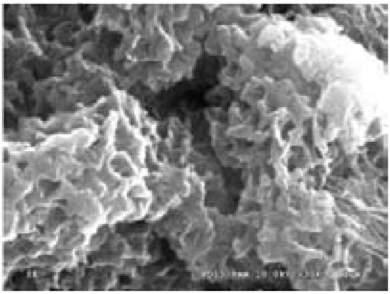


Figure 1. SEM image of PANI-NTSA

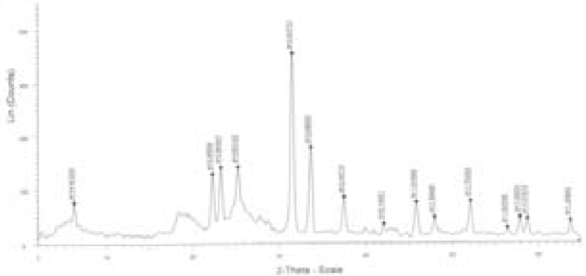


Figure 2. XRD pattern of PANI-NTSA

References:
[1]Bal Sydulu, S.; Palaniappan, S.; Srinivas, P. *Electrochim. Acta* 95 (**2013**) 251

Acknowledgments
The authors thank Dr. K.V.S.N. Raju, Head, PFM Division and Dr. Ahmed Kamal, Acting Director, IICT, Hyderabad for their support. The authors also thank DST, New Delhi for funding under the project entitled "demonstration of energy storage prototype supercapacitor device using nano hybrid material. One of the authors (Rajender) thanks UGC for SRF fellowship.

Reversible Assembly and Disassembly of Micelles by a Polymer that Switches between Superhydrophilic and Superhydrophobic Wettings

Rajashree Y. Mahale, Kingshuk Dutta, Arulraj Arulkashmir and Kothandam Krishnamoorthy*
Polymers and Advanced Materials Laboratory, CSIR-National Chemical Laboratory-Pune,
Pune, Maharashtra, India 411008 Fax number: +91-20-25902615
Email: k.krishnamoorthy@ncl.res.in

Amphiphilic molecules self assemble into nanoscopic assemblies in water, wherein the hydrophobic tail is buried in the assembly and the hydrophilic head group is exposed to water. Such amphiphilic assemblies (AAs) are in equilibrium with the amphiphiles, hence the AAs are known as fragile assemblies. Interaction of these AAs with complementary charge polyelectrolytes has been a method to impart more stability to the AAs. This indicates that the AAs retain its structure and the polyelectrolyte undergoes conformational change [1]. Considering this, we hypothesized that a charge bearing polymer, which resists conformational change should induce oppositely charged assemblies to disaggregate. Herein, we show that charge bearing rigid conjugated polymer can alter the structural features, and disassemble AAs, We also demonstrated reversible assembly and disassembly of AAs by controlling the number of charges on the rigid polymer. During the disassembly, the guest molecules sequestered in the AAs are released and the process can be repeated several times by regenerating the charges on the polymer. The rate of release of guest molecules has been modulated by changing the morphology of the charge bearing polymer. Upon disassembly, the amphiphiles which were constituents of AAs are bound to the charge bearing polymer that impart hydrophobicity to the polymer [2]. By controlling the charge on the polymer and subsequently dipping in AAs, the surface hydrophobicity was varied between superhydrophilic to superhydrophobic wettings [figure 1].

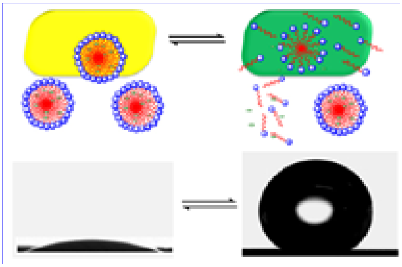


Figure 1: Cartoon showing polymer surface that assemble and disassemble AAs (top). The change in surface hydrophobicity as a function of applied potential and interaction with AAs (bottom) assemble and disassemble

References:
[1] Antonietti, M.; Göltner, C. *Angew. Chem., Int. Ed. Engl.* 36 (**1997**) 911
[2] Dutta, K.; Mahale, R.Y.; Arulkashmir, A.; Krishnamoorthy,K.; *Langmuir* 28 (**2012)** 10097

Electrochromic Switching and Nanoscale Electrical Properties of a Poly(5-cyano indole)-Poly(3,4-ethylenedioxypyrrole) Device with a Free Standing Ionic Liquid Electrolyte

B. Narsimha Reddy[a], Melepurath Deepa[a],*
[a]*Department of Chemistry, Indian Institute of Technology Hyderabad*
** mdeepa@iith.ac.in*

Poly(5-cyano indole) or PCIND and poly(3,4-ethylenedioxy pyrrole) or PEDOP films have been electro-synthesized for the first time in a hydrophobic ionic liquid: trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate. PCIND, being an anodically coloring electrochrome, exhibited a reversible switching between a transmissive yellow and a saturated green hue, with an absorption maximum at 650 nm in the fully oxidized state. Conducting atomic force microscopy studies revealed the PCIND film to be composed of an ensemble of segregated high current islands with a nanoscale electronic conductivity of 0.1 S cm^{-1} and a band gap of 1.41 eV. The cathodically coloring PEDOP film comprised of uniformly distributed and inter-connected high current carrying domains with a band gap of 1.82 eV and a conductivity of 5.4 S cm^{-1}. Kelvin probe force microscopy revealed the PCIND and PEDOP films to be composed of domains with high surface potentials and their localized Fermi levels were deduced to be 4.87 and 4.97 eV. Prototype electrochromic devices were fabricated using PEDOP and PCIND as cathode and anode with a transparent, electrochemically inert and thermally stable ionic liquid based, free standing polymeric gel film with a high ionic conductivity of 1.19×10^{-3} S cm^{-1} as the electrolyte. The device showed large coloration efficiencies of 480 and 796 cm^2 C^{-1} at visible and NIR wavelengths of 475 and 1100 nm respectively and a charge storage capacity of 6.8 mC cm^{-2}, which far exceeded the coloration efficiencies/capacities of the individual electrochromes, thereby demonstrating the synergy between the two colorants. The performance attributes of the device, which switched reversibly between red, green and blue hues, are an outcome of an interplay between the high nanolevel electron conduction capabilities (enable fast charge transport), low work functions (allow easier oxidation), and high ion storage capacities (increase optical contrast as more number of electrochemically addressable sites are accessed by the electrolyte ions) of the PEDOP and PCIND films. Our studies demonstrate the applicability of PCIND films as anodic electrochromes in energy efficient windows.

References

[1] Y. Hou, Y. Cheng, T. Hobson, J. Liu, *Nano Lett.* 10 (**2010**) 2727–2733.
[2] C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, *Nano Lett.* 10 (**2010)** 4025–4031.

Radar Absorbing Nanostructured Electroactive Polymers

Rusli Daik*, Norhidayah Abd Wahap, Dayang Dianasari Awang Jubli, Siti Syahirah Mohd Rusli, & Mohd Anuar Shamsuddin
School of Chemical Sciences and Food Technology, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
** rusli@ukm.my*

Electroactive polymers have been the subject of study actively since more than 40 years ago due to their potential as active materials in electric, electronic and optic applications [1]. Unique properties of electroactive polymers rely so much on electron delocalization within the polymers [2]. In this study, nanostructured polypyrroles were synthesized in acidic medium with the presence of appropriate surfactants as doping agents. Surfactant-doped polypyrrole nanoparticles with diameters of 30 nm – 130 nm were obtained when types of surfactants were varied. In some cases, polypyrrole nanowires were obtained. Study on electrical conductivity showed that all samples obtained were semi-conducting materials. Thermal conductivity of 0.6 W/mK was achieved when TMG was used as the doping agent. The samples of nanostructured surfactant-doped polypyrrole were also studied in terms of microwave absorption, which is an essential property in Electromagnetic Shielding (EMI) and Radar Cross-section (RC) applications [3]. It was found that the best sample produced was capable to absorb more than 70% of incoming microwave radiation.

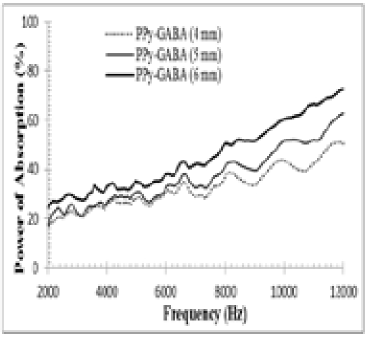


Figure 1. Microwave absorption power of PPy nanocomposite

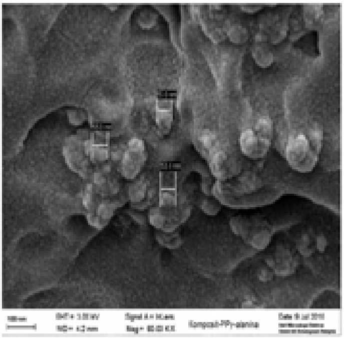


Figure 2. FESEM micrograph of the nanoparticles

References

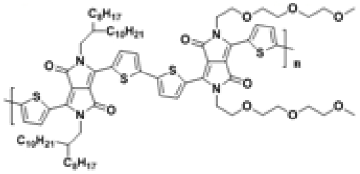
[1] Chandrasekhar, P., Naishadham, K. *Synthetic Metals* (**1999**) 105
[2] Phang, S., Daik, R., Amdullah, M. *Thin Solid Films* 477 (**2004**) 125
[3] Hakansson, E., Amiet, A, Nahavandi, S, Kaynak, A. *European Polymer Journal* 43 (**2007**) 205

DPP based Conjugated Polymers for High Efficient Organic Electronic Devices

Catherine Kanimozhi, Mallari A. Naik, S. Patil*
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India
** satish@sscu.iisc.ernet.in*

Since the inception of Donor-Acceptor-Donor (D-A-D) and Bulk Heterojunction (BHJ) concepts there has been a tremendous growth in OPVs and produced device with efficiencies up to 9.8% [1]. In recent time, the major focus of various research groups lies in using diketopyrrolopyrrole (DPP) as an acceptor in D-A-D architecture.[2-4] The electron-deficient nature of DPP, its planar backbone and intermolecular hydrogen bonding result in materials with strong π-π stacking interactions. DPP core when combined with electron rich units such as phenyl, thiophene and other aromatic heterocycles generated a library of compounds with D-A and D-A-D type arrangement.

Our research group has developed conjugated materials based on DPP core and contributed significantly to organic electronics research. Recently we have synthesized thienothiophene-DPP (TTDPP) and coupled with benzodithiophene to get polymer TTDPP-Benzodithiophene and obtained a device with 3.26% [5] efficiency, similarly when the polymer was used in inverted cell an efficiency of 4.3% was recorded. Organic thin film transistors (OTFTs) / OFETs using polymeric semiconductors are an emerging technology. Ambipolar organic field-effect transistors based on π-conjugated polymers are of interest for complementary-like electronic circuits. For this reason, a number of research groups in recent years have focused their efforts on the development of a range of high-performance conjugated polymers with p-type, n-type, and ambipolar properties. Recently in our research group we have demonstrated very high electron mobility of 3 $cm^2 V^{-1} s^{-1}$ [6] using DPP-DPP based conjugated polymer having solubilizing alkyl chain on every DPP (Figure 1, 2). The strong intermolecular donor-acceptor interactions between DPP units promote self-assembly of the polymer, which in turn leads to excellent charge transport properties.



N-CS2DPP-OD-TEG

Figure 1. Chemical Structure of the polymer.

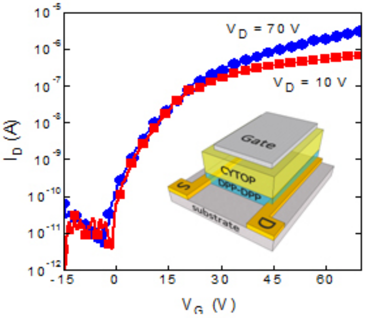


Figure 2. Transfer characteristics of the top-gate, bottom-contact transistor.

References

[1] M. Pfeiffer, K. Leo, J. Blochwitz-Nimoth, 2011, http://www.heliatek.com/?p=1346&lang=en
[2] A.P. Zoombelt, S.G.J. Mathijssen, M.G.R. Turbiez, M.M. Wienk, R.A.J. Janssen, *J. Mater. Chem.* 20 (**2010**) 2240.
[3] J.S. Ha, K.H. Kim, D.H. Choi, *J. Am. Chem. Soc.* 133 (**2011**) 10364.
[4] J.D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A.J. Heeger, F. Wudl, *J. Am. Chem. Soc.* 133 (**2011**) 20799.
[5] Kristen Tandy, Gitish K. Dutta, N.Venkatramaiah, Yuliang Zhang, Muhsen Aljada, Paul Meredith, Paul L. Burn, Satish Patil, E.B. Namdas, *Org. Electron.* 13 (**2012**) 1266.
[6] C. Kanimozhi, N. Yaacobi-Gross, K.W. Chou, A. Amassian, T.D. Anthopoulos, S. Patil, *J. Am. Chem. Soc.* 134 (**2012**) 16532.

Preparation and Properties of *N*-n-Butyl-*N*-methylpyrrolidinium Hexafluorophosphate-added Electrolyte Solutions and Membranes

Akiko Tsurumaki[a], Maria Assunta Navarra[b], Stefania Panero[b], Bruno Scrosati[b], Hiroyuki Ohno[a,*]
[a] *Department of Biotechnology, Tokyo University of Agriculture and Technology,*
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[b] *Department of Chemistry, The University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185 Rome, Italy*
** E-mail address: ohnoh@cc.tuat.ac.jp (H. Ohno).*

Polymer electrolytes are smart materials to make lithium batteries safe and thin. For practical uses, a commercialized electrolyte solution, 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate 1:1 wt/wt mixture (LP 30 Selectilyte^{TM}; LP 30 henceforth), has long been recognized and applied as a highly conductive electrolyte solution. However, the use of LP 30 presents safety hazards regarding the volatility, the limited temperature range for ion conduction, and fear of leakage of carbonate-solutions. In the present paper, *N*-n-butyl-*N*-methyl-pyrrolidinium hexafluorophosphate ($[bmpyr]PF_6$) was added to LP 30 in order to broaden the safety working range of LP 30 mixtures, and the hybrid electrolyte of LP 30-$[bmpyr]PF_6$ have been applied to the preparation of a polymer electrolyte.

Thermal and conductivity investigations were carried out with the mixture composed of dry LP 30, and dry $[bmpyr]PF_6$ ranging from 5 to 30 wt%. LP 30 starts to crystalize around -10 °C suppressing the ion conduction. Despite this behaviour, the crystallization point shifted to lower depending on the fraction of $[bmpyr]PF_6$, and the addition of 30 wt% $[bmpyr]PF_6$ allowed a significant ionic conductivity (> 10^{-3} S/cm) even at -27 °C. With a view of applying LP 30-$[bmpyr]PF_6$ hybrid electrolyte in lithium batteries, interfacial resistance change with Li metal was analyzed. In the case of LP 30 containing 30 wt% $[bmpyr]PF_6$, the interfacial resistance reached a constant value after 30 days and its number was slightly lower than that of pure LP 30. Based on these results, LP 30 with 30 wt% $[bmpyr]PF_6$ was proposed for galvanostatic charge-discharge tests. **Figure 1** shows charge-discharge profiles of lithium metal cells with $Li_4Ti_5O_{12}$ cathode or $LiFePO_4$ cathode. High efficiencies were observed in both cells and the cell with $LiFePO_4$ retained specific capacity over 164 mAh g^{-1} until 10 cycles, which is 96% of the theoretical value.

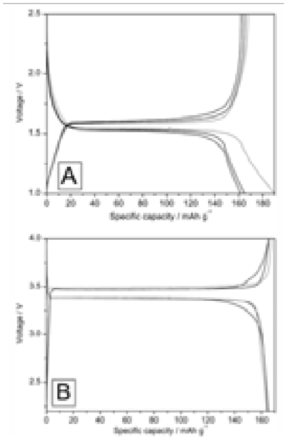


Figure 1. Charge-discharge profiles of (A) Li / electrolyte / $Li_4Ti_5O_{12}$ and (B) Li / electrolyte / $LiFePO_4$ at C/5 and C/3, respectively (1st cycle in gray, 5th and 10th cycles in black).

Additionally, the preparation of a polymer membrane was carried out by combining LP 30 with 30 wt% $[bmpyr]PF_6$ and poly(vinylidene fluoride-*co*-hexafluoropropylene), (Kynar Flex® 2801) matrix. Thermoglavimetric analysis showed that about 30 wt% of $[bmpyr]PF_6$ remained in the membrane, suggesting flame retardation. According to a previous study, the concentration of $[bmpyr]PF_6$ we used is high enough to control or strongly reduce the flammability of the resulting electrolyte. The membrane prepared here has conductivity of 4×10^{-4} S cm^{-1}, at room temperature, suggesting suitability for polymer electrolytes. Full electrochemical characterization of such membranes, and their transport properties, is under way.

References

[1] Tsurumaki, A.; Navarra, M. A.; Panero, S.; Scrosati, B.; and Ohno, H.; *J. Power Sources*, 233 **(2013)** 104.
[2] Lombardo, L.; Brutti, S.; Navarra, M. A.; Panero, S.; Reale, P.; *J. Power Sources*, 227 **(2013)** 8.

Poster

CP1

Supramolecular polymers of dipolar dyes: Perylene and Coronene monoimides

Ankit Jain, K.Venkata Rao, Chidambar Kulkarni, Subi J. George*.
New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR)
Jakkur P.O, Bangalore-560064, India
george@jncasr.ac.in

Self-assembly of π-conjugated systems has resulted in immense amount of research involving insights into the supramolecular organization behaviours of molecules.[1] Systematic and engineered self-assembly of molecules with optical and electronic functionality has led to the evolution of various assemblies, such as π-conjugated organogels with potential applications in organic electronics. Controlling the self-assembly of dipolar dyes to parallel head–head organization has been a topic of great research interest because of their potential application in non-linear optics.

Recently, we reported a novel approach to achieve frustrated dipolar assemblies through hydrogen bonding mediated supra-molecular polymerization of dipolar chromophores using the concept of repulsion between dipoles as they are forced into a head–head staggered organization.[2]

Furthermore, we have tried to extend this concept to dyes with higher dipole moment. Using the concept of co-assembly we have tried to stabilize an assembly of higher diploe moment in head to head fashion (Figure 1). We, expect this strategy to be useful in creating more dipolar assemblies for non linear optics.

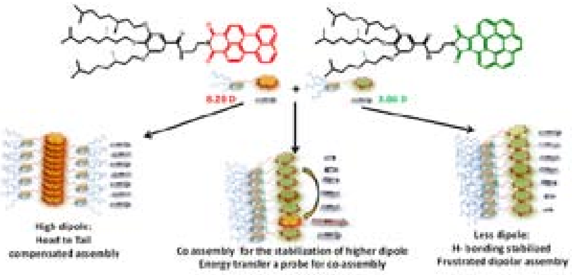


Figure 1. Schematic representing the assembly of dipolar monoimides

References
[1] Hoeben, F. J. M.; Jonkheijm. P.; Meijer, E. W.; Schenning. A. P. H. J. *Chem. Rev.*, 105 **(2005**) 1491.
[2] Jain, A.; Rao. K. V.; Kulkarni, C.; George. A.; George, S. J. *Chem. Commun.*, 48 **(2012**) 1467.

CP2

Continuous Flow Syntheses of Regioregular Poly(3-hexylthiophene)

Anshu Kumar[a], Sengottaiyan Thangapal[a], Ashok Kumar Majji[a], Anil Kumar[a,b,*],
[a]*Department of Chemistry, Indian Institute of Technology, Mumbai-400076 INDIA*
[b]*Centre of Excellence in Nanoelectronics, Indian Institute of Technology, Mumbai-400076 INDIA*
**Email: anilkumar@iitb.ac.in*

In recent times, 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, polythiophene based conjugated polymers have taken significant lead over other conjugated polymers in printable electronic applications. Commercially, two of the most successful polythiophenes are a) regioregular poly(3-hexylthiophene), **rr-P3HT** [1], used as an active semiconducting layer for various electronic devices such as photovoltaics and RF tags and b) Poly(3,4-ethylenedioxythiophene), **PEDOT** [2], used as a transparent hole transport layer in electronic displays as well as for flexible transparent conductor. Large scale syntheses with controlled molecular properties still remains a major challenge in this area. In this direction we have initiated a program to design new synthetic routes which are amenable for large scale syntheses with complete control over Critical Molecular Design Parameters **(CMDPs)** such as chemical purity, regioregularity, molecular weight and polydispersity as discussed below. Grignard Metathesis (GRIM) polymerization is one of the most commonly used method for the synthesis of high quality conjugated polymers based on aryl and heteroaryl monomers and was first reported in US patent for the synthesis of regioregular poly(3-hexylthiophene) [3]. GRIM polymerization proceeds by combining a soluble monomer having at least two leaving groups with an organomagnesium reagent to form a regiochemical isomer intermediate, and adding thereto an effective amount of Ni(II) catalyst to initiate the polymerization reaction. This results in the synthesis of various conjugated polymers based with controlled molecular weight (based on the ratio of monomer to catalyst) and low polydispersity. However there are certain bottlenecks in this process which hampers large scale syntheses of these materials with controlled CMDPs. Our approaches, including flow syntheses, in solving these issues will be discussed in this presentation.

References:

[1] McCullough, R. D. *Adv. Mater.*, 2 **(1998)** 10.
[2] Bert, L.; Groenendaal; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.*, 7 **(2000)** 12.
[3] a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.*, 3 **(1999)** 11. (b) Osaka, I.; Mccullough, R. D. *Acc. Chem. Res.*, 41 **(2008)** 1202.

CP3

Supramolecular Interaction Facilitated Small Molecule Films for Organic Field Effect Transistors

Arulraj Arulkashmir, Rajashree Y. Mahale, Satej S. Dharmapurikar, Manoj K. Jangid and Kothandam Krishnamoorthy*
Polymers and Advanced Materials Laboratory, CSIR-National Chemical Laboratory
Dr. Homi Bhabha Road, Pashan, Pune 411008 (India), Fax: + 91-20-25902615
E-mail: k.krishnamoorthy@ncl.res.in

Porphyrins are a class of small conjugated molecules (SCM) that have demonstrated an excellent performance in electronic devices because of its enhanced light absorption, good exciton diffusion and charge transport. Porphyrin molecules exhibit high charge carrier mobility but need to be sublimed on the substrate.Contrary to this, polymers can be easily processable by spin coating on substrates. By gaining the advantage from both polymer and small molecules one could achieve the better processable, high carrier mobility materials for Organic field effect transistors (OFET). In order to enhance the processability, metallo porphyrin (ZnTPP) and Poly4-vinyl pyridine (P4VP) has been utilized to make supramolecular complex by taking advantage of non covalent interaction between pyridine moieties of the polymer and metal porphyrins. This metal coordinated supramolecular complex (ZnTPP-P4VP) formation has been extensively studied in both solution and thin films. The porphyrin was found to be uniformly distributed throughout the polymer films without phase segregation at the interfaces, which is contrary to the existing approaches. Transistor devices have been fabricated and measured in atmospheric conditions show hole carrier mobility of 5 x 10^{-5} cm^2 V^{-1} s^{-1} and upon thermal annealing at 80°C, the charge carrier mobility was increased into 2 x 10^{-4} cm^2 V^{-1} S^{-1} [1]. High charge carrier mobility in low temperature annealing makes this ZnTPP-P4VP supramolecular complex as suitable material for flexible electronics.

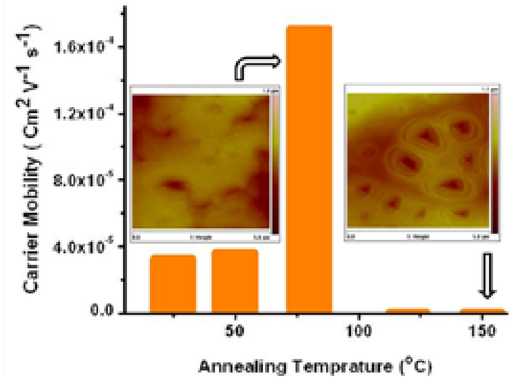


Figure 1. Plot showing Charge carrier mobility of ZnTPP-P4VP supramolecular complex as a function of annealing temperature.

References

[1]Arulkashmir, A.; Mahale, R. Y.; Dharmapurikar, S. S.; Jangid, M. K.; Krishnamoorthy, K. *Polym. Chem.*, 3 (**2012**) 1641.

CP4

Functional Amplified Fluorescent Polymers for Explosive Detection

Ashok Kumar Majji,[a] Anil Kumar,*[a] Phani Kumar Pullela,[b] Justin Kariyancheril Paul,[b] Shilpa Kammaradi Sanjeeva,[b] Swathi Korrapati,[b] Vijay Mohan Subramanian,[b] Raviprakash Jayaraman,[b] Sathyadeep Viswanathan[b] and Shankar Anand Kaipa[b]
[a]Department of Chemistry, Indian Institute of Technology, Mumbai-400076 INDIA
[b]Bigtec Pvt.Ltd, 2nd Floor,Golden Heights, 59th 'C' cross, 4th 'M' Block, Rajajinagar, Bangalore – 560010 INDIA
**Email: anilkumar@iitb.ac.in*

Conducting or Conjugated polymers also known as inherently conducting polymers (ICPs) provide an ideal platform for the design and fabrication of chemical and biological sensors because of their ability to respond reversibly to an external physical (temperature, light, electric, magnetic or mechanical) or chemical (pH, chemical agent) stimuli. ICPs exhibit changes in physical (conformation), optical and electrical properties on the applications of these stimuli. Therefore, these polymers have been developed for various applications such as Light Emitting Diodes (LEDs), memory devices, rechargeable batteries, super capacitors, electro optic materials photovoltaics, thin film transistors, RF tags, biological and chemical sensors, MEMS, actuators, electrochromic displays, electro active fabrics and host of other applications [1]. In the field of chemical and biomedical sensing, optical detection (fluorescence) is one of the most common and practical method for the design and fabrication of successful sensor because of the ease of availability of a fluorescent active guest- host system. However, majority of these sensors work in solution phase as fluorescence in thin films has always been a challenge. Therefore, it will be very attractive if one can design a system which exhibit fluorescence in solid state. The most ideal system should also have the ability to be functionalized with various chemical and biological host species with ease. In this direction, Amplified Fluorescence Polymers [2] AFPs, are the promising candidates for these applications.

In this presentation, we report on design, synthesis and application of AFP for explosive sensors. We will also highlight our recent results in the direction of processing these materials directly from solution resulting in possible printing of the sensors in future.

References:

[1] Handbook of Conducting Polymers (3rd edn), Skotheim, T. A., Reynolds J. R., CRC Press, Boca Raton/London/NewYork, (**2007**).
[2] a) Cox,J.R; Miller, P; Swager,T.M. *J. Am. Chem. Soc*, 133 (**2011)** 12910. b) Van Veller,B; Swager,T.M. *Chem. Commun*, 46 (**2010)** 5761. c)Lim, J; Swager, T. M. *Angew. Chem. Int. Ed*, 49 (**2010)** 7486. d) Andrew,T.L; Swager,T.M. *J. Org. Chem*, 76 (**2011)** 2976. e) Van Veller, B; Robinson, D; Swager,T.M. *Angew. Chem. Int. Ed,* 51 (**2012)** 1182. f) Sinha, J; Kumar,A. *Synthetic Metals*, 160 (**2010)** 2265. g) Enlow, M. A. *J.Mol. Graphics Modell,* 33 (**2012)** 12.

CP5

Synthesis of highly conducting and crystalline polyaniline and its application to supercapacitor

B. Rajender,[a] S. Palaniappan[a,b,*]
[a]*Polymers & Functional Materials Division,CSIR- Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b]*CSIR – Network Institutes for Solar Energy (NISE). India*
email : palaniappan@iict.res.in

One of the most commonly active species in pseudocapacitor is electrically conducting polyaniline [1]. In this work, polyaniline salt (PANI-NTSA) is prepared by aqueous, emulsion and interfacial polymerization pathways using 1,3(6,7)-napthalene trisulfonicacid sodium salt as novel dopant. Polyaniline salt is characterized by FT-IR, FE-SEM, EDAX, X-ray diffraction, TGA, and conductivity measurements. PANI-NTSA is obtained in nano fiber (fig.1) highly crystalline form (fig.2)) with reasonably good conductivity (7 S/cm). This polyaniline salt is used as electrode in supercapacitor application in symmetric electrode configuration. This super-capacitor system is characterized by cyclic voltammogram, galvanostatic charging/ discharging, and electrochemical impedance spectroscopy. The result shows that the obtained polyaniline has excellent electrochemical characteristics with a capacitance of 265 F/g.

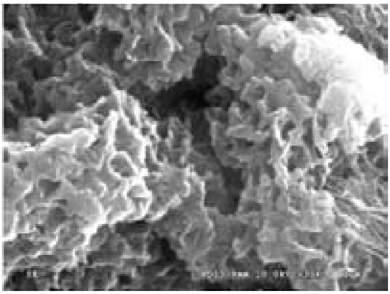


Figure 1. SEM image of PANI-NTSA

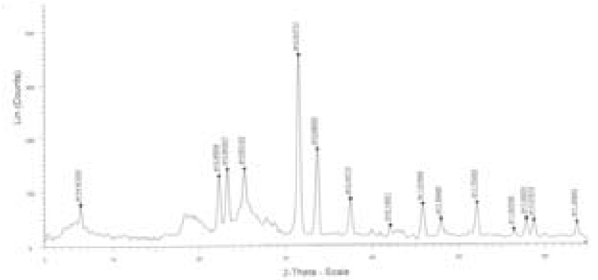


Figure 2. XRD pattern of PANI-NTSA

References:

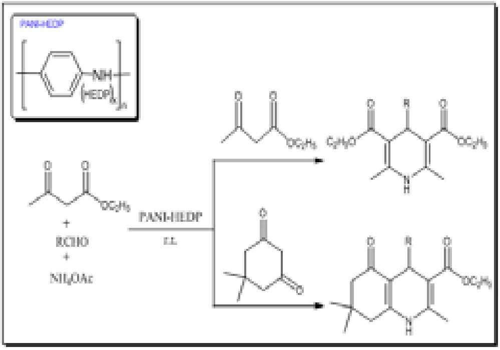
[1] Bal Sydulu, S.; Palaniappan, S.; Srinivas, P. *Electrochim. Acta* 95 (**2013**) 251

CP6

Nanosphere of Semi Crystalline Polyaniline Powder: An Effective, Versatile and Reusable Catalyst for Hantzsch Reaction

B. Ravi, B. Rajender, S. Palaniappan*
Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Hyderabad-500007 INDIA
E-mail : palaniappan@iict.res.in

Realizing the importance of polyhydroquinoline derivatives in the synthesis of various drug sources, numerous methods have been reported using various catalysts, for example, L-proline [1], silica perchloric acid ($HClO_4$–SiO_2) [2], FeF_3 [3], etc. However, these methods suffer from several disadvantages such as moisture sensitive or highly toxic in environment and unpleasant experimental procedure and reagents which are expensive, long reaction times, use of large quantities of volatile organic solvents, low yields, and harsh reaction conditions. Hence, there is still great demand for a new catalytic system with high efficiency and low catalytic loading. In continuation of our investigation on the use of new catalysts as conjugated conducting polymers as a reusable catalysts for carrying out chemical transformations [4], in this work, Polyaniline salt containing 1-hydroxyethane-1,1-diphosphonic acid with nanosphere morphology in semi crystalline powder form was successfully synthesized by interfacial polymerization pathway and demonstrated as polymer based acid catalyzed in the synthesis of 1,4-dihydropyridines and polyhydroquinoline derivatives. The advantages of this methodology are the easy synthesis of polymer containing acid group catalyst in powder form having easily handlable, efficient, versatile and reusable nature.



References:
[1]. Karade, N.N.; Budhewara, V.H.; Shindeb, S.V.; Jadhav, W.N. *Lett. in Org. Chem.* 4 (**2007**) 16
[2]. Maheswara, M.; Siddaiah, V.; Damu, G.L.; Venkata Rao, C. *Arkivoc* 2 (**2006**) 201
[3]. Surasani, R.; Kalita, D.; Dhanunjaya-Rao, A.V.; Yarbagi, K.; Chandrasekhar, K.B. *J. Fluor. Chem.* 135 (**2012**) 91
[4]. Palaniappan, S.; John, A. *Curr. Org. Chem.* 12 (**2008**) 98

CP7

Processable Powders Based on Insoluble Poly(3,4-ethylenedioxythiophene)

Bikash K. Sikder, Soumadwip Ghosh, Rekha Singh, Smita Mukherjee and Anil Kumar*
Department of Chemistry, Indian Institute of Technology Bombay,
Mumbai-400076, INDIA

We have been working in the area of design of new synthetic routes for the processable polymers based on thiophenes for semiconducting as well as transparent conducting applications. In this direction, we have chosen poly(3,4-ethylenedioxythiophene), **PEDOT,** as a potential candidate as hole transport and transparent conductor applications. In case of **PEDOT,** the final polymer is insoluble and hence is mainly processed from the aqueous dispersion of PEDOT with anionic polyeletrolyte poly(styrene sulfonate), **PSS,** and is commercially available under the trade name "**CLEVIOS-P"**[1-4]**.** Though this product is one of the most successful product based on any conducting polymer, the dispersion has certain issues such as limited shelf life and inability to fine tune the final surface properties of the resulting thin films. Therefore, it will be highly advantageous to develop a new synthetic route wherein the final polymer can be obtained in the powder form which can then be dispersed in water as and when needed. Furthermore, it will be highly productive to make this dispersion compatible with various additives; thereby the surface charge of the colloidal particles can be varied in the final dispersion. This will in turn help in fine tuning of the compatibility of the thin films with other thin films in the final device fabrication. In this direction we have now developed a new synthetic route which allows us to isolate the final **PEDOT** in powder which is easy to disperse in water in presence of various stabilizers. In fact we have now developed aqueous dispersions based on this PEDOT powder wherein we can vary the particle size from 200-1500 nm as well as we can control the surface potential. This opens up a whole new area of formulations of **PEDOT** for various electronic devices wherein these new materials can be explore either as the hole transport layer or as transparent conductor or both. Our Recent results in this direction will be discussed in this presentation.

References:

[1] "PEDOT: Principles and Applications of an Intrinisically Conducting Polymer", Elschner A., Kirchmeyer S., Lövenich W., Merker, U., Reuter, K., CRC Press, Taylor and Francis Group, Boca Raton/London/NewYork, 2011.
[2] Meng, H.; Perepichka, D. F.; Wudl F. *Angew. Chem. Int. Ed*. **2003**, *42*, 658-661.
[3] Meng, H.; Perepichka, D. F.; Bendikov, M.; Fred Wudl, Pan, G. Z.; Yu, W.; Dong, W.; Brown, S. *J. Am. Chem. Soc.* **2003**, *125*, 15151-15162.
[4] Koh, J. K.; Kim, J.; Kim, B.; Kim, J. H.; Kim, E.; *Adv. Mater*. **2011**, 23, 1641–1646.

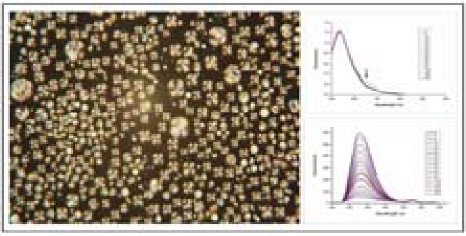
CP8

Chalcone and 1,2,3-Triazole containing Liquid Crystalline Luminescent Photo-curable Polyesters

C.Selvarasu And P.Kannan*

Department of Chemistry, Anna University, Chennai-600 025 INDIA

Synthesis of symmetrically 1,2,3-Triazole bearing mesogenic groups as main chains liquid crystalline polymers were synthesized by polycondensation reaction.The obtained polymers and their monomers were characterized with ^{1}H NMR, ^{13}C NMR, UV-vis, TGA, DSC, POM techniques. The length of the flexible spacers in the polymers and their monomers show significant influence on their properties such as the phase transition behaviors and the monomer reactivity. The polymerization reactivity of the monomers increases with an increase in the spacer length and only those monomers and polymers with a flexible spacer six show liquid crystallinity with their mesophases being Nematic Droplet, Nematic and Smectic phases.In addition, the polymers have proven to be easily cross-linkable with a difunctional primary amine under mild conditions both in solution and in film, demonstrating that they are very useful precursors for photoresponsive LCP networks. Furthermore, the photoresponsivity of the polymer solution in tetrahydrofuran and the crosslinked polymer film was also confirmed by their occurrence of the UV and visible light-induced photoisomerization.



References:

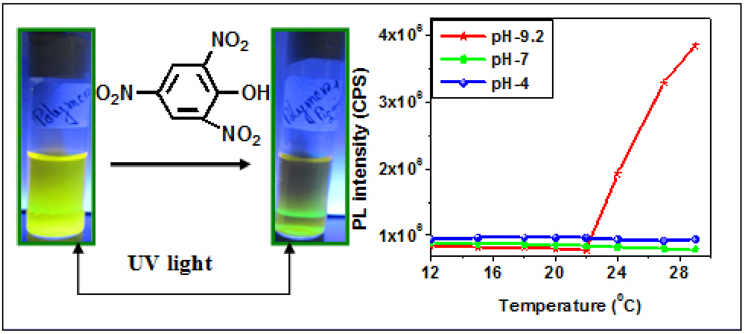
[1] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic L iquid Crystals* (Leonard Hill), Chap. 4.
[2] Gonzalez, Y., Ros, M. B., Serrano, J. L., and Perez- Jubindo, M. A., 1995, *L iq. Cryst.*, **18,** 751.
[3] Blackwood K M 1996 Science 273 909
[4] Craig A and Imrie C T 1995 Macromolecules 283617
[5] Craig A and Imrie C T 1994 J. Mater. Chem. 41705
[6] Coles H and Bankcraft 1993 Mol. Cryst. Liq. Cryst.237 97

CP9

Water soluble dual responsive polythiophene based graft copolymer with multiple applications

Dhruba P. Chatterjee[a,b], Sandip Das[b], Sanjoy Samanta[b] and Arun K. Nandi[b]*
[a]Krishnagar Government College, Krishnagar, Nadia-741101, West Benga
[b]*Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, INDIA*
E-mail: psuakn@iacs.res.in

Preparation of polythiophene based water soluble thermo and pH responsive graft copolymers have been done. Initiator moiety anchored polythiophene system 2,5 poly(3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene(TI) has been used as macroinitiator for polymerizing a mixture of methoxyethoxyethyl methacrylate(MeO_2MA) and 2-dimethylaminoethyl methacrylate(DMAEMA) in different feed ratios, in room temperature using copper based atom transfer radical polymerization (ATRP). Polythiophene-g-P(MeO_2MA-co-DMAEMA) (PTDM) thus prepared has shown considerable water solubility. $PMeO_2MA$ shows LCST at ~26 ^{0}C [1] in aqueous medium. Accordingly, aqueous solution of PTDM has shown increase of fluorescence intensity and particle sizes as observed by PL and DLS analysis respectively, when the temperature of the system is increased over 25 ^{0}C. This has been observed only for an aqueous solution having a pH of 9.2. However, in lower pH values (pH value of 4 or 7), change of temperature (input), in the region of LCST of $PMeO_2MA$, remains almost without effect on fluorescence intensity or particle sizes as outputs. Thus, the system functions as **AND** logic gate [2] using polythiophene as the fluorescence probe. In aqueous solution, PTDM exists as micelles with insoluble polythiophene core. Electron rich polythiophene segments involve in donor-acceptor interactions with electron deficient aromatic polynitro compounsds(PNC). Thus PTDM systems in aqueous solution has shown considerable quenching in fluorescence intensities in presence of PNCs like picric acid, dinitro phenol etc. Hence aqueous solution of PTDM may find application in explosive sensing also.



References
[1] Lutz, J.-F.; Akdemir, O.; Hoth, A. *J. Am. Chem. Soc.*, 128 **(2006)** 13046.
[2] Uchiyama, S.; Kawai, N.; Prasanna de Silva, A.; Iwai, K. *J. Am. Chem. Soc.*, 126 **(2004)** 3032.

CP10

Secondary Doped Polyaniline as Counter Electrode in Dye Sensitized Solar Cells

E. J. Jelmy, S. Mohanraj, A.R. Rajamani, Duraisamy Kumaresan* and Nikhil. K. Kothurkar*
Department of Chemical Engineering and Materials Sciences
Amrita Vishwa Vidyapeetham, Coimbatore-641112, Tamil Nadu, INDIA
rdkumares@gmail.com; nikhil.kothurkar@gmail.com

Dye Sensitized solar cells (DSSCs) have received considerable attention due to several advantages such as low cost and substrate-flexibility at moderately high current conversion efficiencies. In DSSC fabrication the nanocrystalline TiO_2 thin film and Pt coated fluorine doped tin oxide (FTO) substrate are commonly used as the photoanode and counter electrode respectively. In recent years, many attempts have been made by researchers to replace the Pt counter electrodes (CEs) by various cost-effective materials like carbon black, carbon nanotubes, graphene, conducting polymers like polypyrrole, and polyaniline. In the present study, secondary doped polyaniline (PANi ES) was prepared using chemical approaches for use as the CE of DSSCs. Polyaniline emeraldine base (PANi-EB) was prepared by de-doping of chemically synthesized PANi powder and subsequent re-doping with camphor sulphonic acid to obtain the PANi-ES form. Further, a 1 wt% solution of PANi-ES in m-cresol was transferred on to the FTO substrate by following a procedure from the literature [1]. The FTIR and UV-vis spectral techniques were used to confirm the secondary doping in PANi. In the FTIR spectra (Fig.1), the red-shift of quinoid and benzoid peaks in PANi-ES confirms the formation of polaron structures developed due to doping of PANi-EB. The UV-vis analysis indicated the expected extended delocalization of electrons in the PANi-ES form by the observed red-shift of the low energy band above 600 nm.

In the cyclic voltamogram, the current density of the second cathodic peak corresponds to the reaction , which takes place at the CE of a DSSC. This peak was found to be comparable with that of the Pt electrode and this indicates the potential suitability of PANi for the replacement of Pt in DSSC. The J-V characteristics for DSSCs made with Pt and PANi-ES electrodes recorded under 1.5G air mass irradiation (intensity of $100 mW.cm^{-2}$) show a light-to-current conversion efficiency of 3.19% for PANi-ES CE and 4.71% for Pt CE (Fig. 3) respectively. These results confirm the PANi-ES CE could be a good low cost substitute for the Pt photocathode in the large scale DSSCs production.

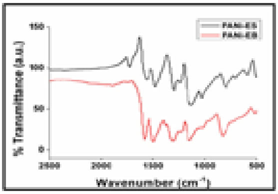


Figure 1: FTIR spectra of PANi-EB and PANi-ES

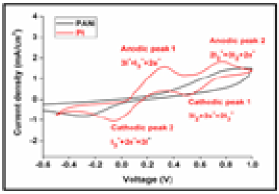


Figure 2: Cyclic voltamograms with PANi and Pt CE

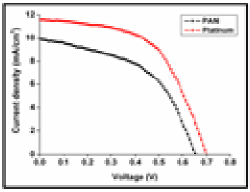


Figure 3: J-V curves of the DSSC using different CEs

Reference:

1. Jeon, S. S.; Kim, C.; Lee, T. H.; Lee, Y. W.; Do, K.; Ko, J.; Im, S. S. *Journal of Physical Chemistry C*,116 **(2012)** 22743.

CP11

Electro-catalytic Oxidation of Ammonia in Alkaline Media by Au-Polyindole Composite

Kashish,* Ashish Kumar and Rajiv Prakash
School of Materials Science and Technology, Indian Institute of Technology,
Banaras Hindu University, Varanasi-221005, India
** Presenting author; Email: kashish012@gmail.com; Tel: 9369236795*

The wider application of metal electrodes like Pt, Pd, Ru etc. in the area of fuel cell technology is impeded due to its high costs and by its poisoning during the oxidation of fuels. Present work proposes a composite having Au cluster embedded within polyindole (Au-Pin) as a promising electro-catalyst in the oxidation of ammonia in alkaline media. The chemical modification of this material in particulate form with conducting polymers is one of the methods which are capable of addressing above issues. Detail study of Au@Pin composite formation, characterization and its catalytic property for oxidation of ammonia is done with possible mechanism and also role of morphology on oxidation of ammonia is discussed. Voltammetric and chronoamperometric measurements show that Au@Pin composite has better tolerance capability than bare Glassy carbon and alone Pin modified GC electrodes. Electrochemical impedance spectroscopy reveals consistent results and charge transfer mainly through diffusion controlled process. The higher catalytic activity of Au@Pin composite towards ammonia oxidation in mixture of 1.0M NH_4OH+1.0M KOH electrolyte is observed in comparison to Pin probably due to synergic effect between Au cluster and Pin that prevents the formation of poisonable intermediates.

Figure 1: Schematic Representation of electro catalytic oxidation of ammonia in alkaline media

References
[1] Li, J.; Lin, X, Sensors & Actuators, 126 (2007), 527-535.
[2] Hung, C., Journal of Hazardous Materials, 163(2009), 180-186.
[3] Slijukic, B.; Banks C; Crossly A, Analytical Chimica Acta, 587(2007), 240-246.
[4] Hung, C.; Lin, C; Lou J, Journal of environmental engineering, 130(204), 193-200

CP12

Synthesis of Graphene Oxide Polyaniline Hybrid Composite by Interfacial Polymerization Method for Supercapacitor Application

M. Umashankar,[a] S. Palaniappan,[a,b,*] S. Bal Sydulu,[c] and S. Gopukumar[d,b]
[a]*Polymers & Functional Materials Division,CSIR- Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b] *CSIR – Network Institutes for Solar Energy (NISE). India*
[c] *Department of Chemistry, Osmania University, Hyderabad 500 007, India*
[d] *CSIR – Central Electrochemical Research Institute, Karaikudi – 630 006, Tamil Nadu, India*
email : palaniappan@iict.res.in

Electrochemical Capacitors also called Supercapacitors or Ultracapacitors are the energy storage devices intermediate between high energy density batteries and high power density capacitors. Carbon, metal oxides and conducting polymers are the active materials used in supercapacitors, but every material has its own advantages and disadvantages for e.g., Conducting polymers and metal oxides show larger capacitances compared to carbon materials due to faradaic reactions (Pseudocapacitors) occurring in the bulk of the material but with low power density than carbon which store energy only on the surface (EDLC). Among the conducting polymers and metal oxides generally metal oxides are expensive and toxic whereas the conducting polymers are easily synthesizable and cheap. So synthesis of conducting polymer - carbon composite can address for a possible solution for the fabrication of supercapacitor with better performance by synergistic effect of both the materials [1]. Recent researches were focussed on the application of graphite and its derivatives in supercapacitors and a few reports are available on PANI – Graphene Oxide composites [2,3].

In this study, polyaniline-graphene oxide (PANI-GO) hybrid composite is prepared by interfacial polymerization method. PANI–GO samples are characterized by FTIR, XRD, FE-SEM. Electrochemical characterization such as CV, CD and EIS analysis is carried out on the supercapacitor cells. In this study, the maximum specific capacitance obtained is found to be 365 F/g at 1 mV/s scan rate from cyclic voltammetry. The value of the specific capacitance, energy and power densities for the PANI–GO system calculated from CD studies at 2.5A/g discharge rate are found to be 325 F/g, 11 KW h/kg, and 1579 W/kg, respectively, with 98–100% columbic efficiency. In this work, graphene oxide is uniformly intercalated with pani nano fibres and the composite material showing a good candidate as electrode material in supercapacitors by incorporation of only 10wt% of graphene oxide with respect to aniline.

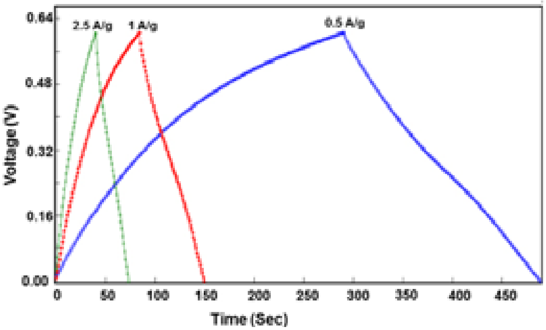


Figure 1: Schematic Representation of electro catalytic oxidation of ammonia in alkaline media

References

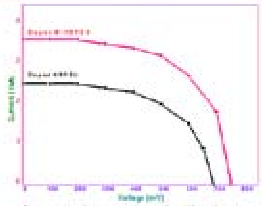
[1] Bal Sydulu S.; Palaniappan, S.; Srinivas, P. Electrochimica Acta 95 (2013) 251
[2] Qingqing, Z.; Yu, L.; Yiyu, F.; Wei, F. Electrochem. Acta, 90 (2013) 95
[3] Jiahua, Z.; Minjiao, C.; Honglin, Q.; Xi, Z.; Huige, W.; Zhiping, L.; Henry, A. C.; Suying, W.; Zhanhu, G. Polymer 53 (2012) 5953.

CP13

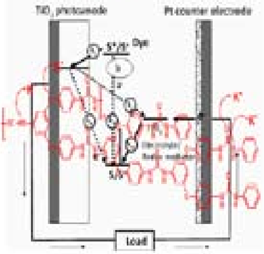
Performance of Novel Hyperbranched Poly(aryl-ether-urea)s Doped with N3-Dye in Nano-crystalline DSSC

Mahalingam Vanjinathan*
PG and Research Department of Chemistry, D. G. Vaishnav College, Chennai-106, India.
S. Sathiyaraj[a], A. Shanavas[a], A. Sultan Nasar[a], S. Amudha[b], S. Austin Suthanthiraraj[b].
[a] Department of Polymer Science, University of Madras, Guindy Campus, Chennai-25, India.
[b] Department of Energy, University of Madras, Guindy Campus, Chennai-25, India.
** mvanjinathan@gmail.com*

An amine-terminated hyperbranched poly(aryl-ether-urea) (HBPEU) was prepared from an AB_2-type blocked isocyanate monomer and then its end groups were modified into urea (M-HBPEU) by reaction with phenyl isocyanate. Both of the polymers were doped with N3-dye along with KI/I_2 to work as efficient polymer electrolytes in nano crystalline dye sensitized solar cell. The increment in the conductivity of doped HBPEU and doped M-HBPEU was very significant and reached its value at 8.2 x 10^{-3} and 4.1 x 10^{-2} S/cm^1 respectively. The current-voltage (I-V) characteristics of these two doped polymers measured under simulated sunlight with 1.5 AM at 60 mW/cm^2 generate photocurrent of 2.5 and 3.6 mA/cm^2, together with a photo voltage of 690 and 750 mV, and fill factor of 0.55 and 0.61 yielding a overall energy conversion efficiency of 2.4 and 4.1 % respectively. These results suggest that M-HBPEU show better cell performance and conductance properties than the HBPEU.



Current-voltage curve under illumination at 40 mV/cm² light intensity.

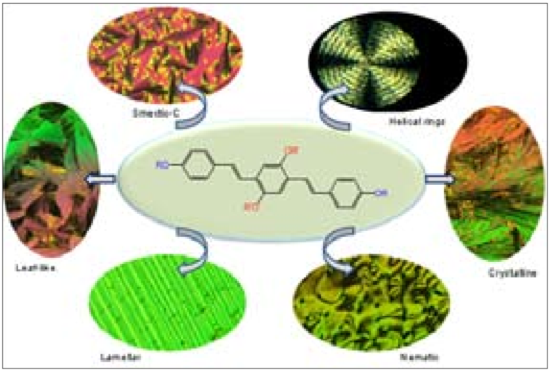


CP14

Molecular Self-assemblies in π-Conjugated Phenylenevinylenes

Mahima Goel and M. Jayakannan*
Department of Chemistry
Indian Institute of Science Education & Research (IISER-Pune)
Dr.Homi Bhabha Road, Pune 411008, Maharashtra, INDIA

π- Conjugated phenylenevinylenes are emerging as important semiconducting materials for optoelectronic applications such as light emitting diodes, photovoltaics, field effect transistors and so on. It has now been realized that the performance of these π-conjugated materials in electronic devices is highly dependent on the organization of individual molecules in solid state. Supramolecular assembly, which utilizes weak non-covalent forces for making organized molecular architechtures is one of the most promising approaches for molecular self-assembly of π-conjugates. Here in, we report, custom designed oligophenylenevinylenes and segmented PPV polymers for understanding π-conjugated self-assemblies in the solid state. A homologous series of Oligophenylenevinylenes (*OPV-n*) with tricyclodecanemethylene pendent units in the aromatic core and variable tail length in the longitudinal position produced sigmoidal transition in self-assembly from crystalline solids (*n* = 0-4) to ring banded liquid crystals (*n* = 10-15) via fan shaped cholesteric textures (*n* = 5-9). Single-crystal X-ray structures of OPV molecules revealed that the packing changed from herringbone (OPV- 4) to helical (OPV-12) and multiple CH/π interactions (in OPV-12) were identified as the main driving force for helical suprastructures. Diverse self-assemblies such as nematic, smectic, lamellar or leaf like patterns could be tuned by appropriate substituents in the middle aromatic core with a fluorocarbon or hydrocarbon side chain. The roles of OPV skeletons on the liquid crystalline properties, planarity versus non-planarity, inter-molecular non covalent forces such as weak CH/π interactions and π-π stacking, pitch and roll displacements in the crystal lattices and photophysical characteristics were investigated in detail by single crystal XRD analysis. Donor-acceptor assemblies of these OPV π- conjugates with perylenebisimide based chromophore was also studied using FRET mechanistic pathways.



References:

[1] Goel, M.; Jayakannan, M. Herringbone and Helical Self-assembly of π-conjugated Molecules in Solid State through CH/π Hydrogen Bond, *Chem. Eur. J.* **2012**, *18,* 11987-11994.

[2] Goel, M.; Jayakannan, CH/π Interaction Guided Molecular Self-assembly in π-conjugated Oligomers, *Chem. Eur. J.* **2012,** *18*, 2867-2874.

[3] Goel, M.; Jayakannan, M. Supramolecular Liquid Crystalline π-Conjugates: The Role of Aromatic π-Stacking and vander Waals Forces on the Molecular Self-Assembly of Oligophenylenevinylenes. *J. Phys. Chem. B.* **2010,** *114,* 12508.

CP15

Selective Detection of Cyanide by a Polyfluorene Based Organoboron Fluorescent Probe

Manas Kumar Bera, Chanchal Chakraborty, 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 conjugated polymers (CPs) become very much useful as signal-transducing materials for sensory applications because of their signal amplification properties and the versatility in their molecular design.[1] Polyfluorene is a class of conjugated polymeric materials, which shows a bright blue fluorescence with high photoluminescence quantum yield.[2] Conjugated polyfluorene are attractive sensor materials for the reasons of their electrical, optical, electrochemical and optoelectronic properties which can be greatly modified by very minor perturbations of the environmental stimuli and there exists amplification actions by a collective system response in macromolecules.[3]

It is known that cyanide is a very toxic substance and can directly lead to the death in few minutes. It damages to mammals by binding to a heme unit when it is absorbed through the lungs, gastrointestinal track and skin.

In this consequence, we have designed and synthesized one organoboron compound based polyfluorene fluorescent probes **PFBP** (Fig. 1) for the detection of toxic cyanide sensitively and selectively by fluorescence "turn off" mechanism. Bis-(bromohexyl)-polyfluorenes have initially synthesized by Pd catalyzed Suzuki cross-coupling polymerization. Organoboron appended polyfluorenes have finally achieved from the treatment with $(Mes)_2BF$. The polymer solution shows a bright blue luminescence under UV-irradiation which can be substantially quenched in the presence of toxic cyanide ion (CN^-) from the detection limit of 5μM, possibly due to the formation of strong covalent bond between the cyanide ion and a trivalent boron centre.

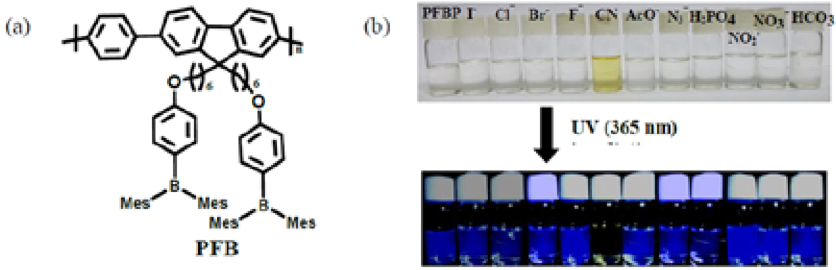


Fig. 1. (a) Chemical formula of PFBP and (b) chromogenic response of probe added with various monovalent anions under day light (above) and corresponding fluorogenic response (below) under UV light.

Reference
[1] Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.*107 (**2007**) 1339.
[2] Xia, R.; Heliotis, G.; Hou Y.; Bradley, D. D. C. *Org. Electron*, 4 (**2003**) 165.
[3] Heeger, P. S.; Heeger, A. J. *Proc Natl Acad Sci USA* 96 (**1999**) 12219.

CP16

Transport Properties of Core-Shell Structured TiO_2 / Polyaniline

*N. Narsimlu, B. Kavitha, Ch. Srinivas, D. Srinivasu, K. Siva Kumar
Department of Physics, Osmania University, Hyderabad. 500 007 INDIA
Email: narsimluou@gmail.com

Transport properties (V-I characteristics and Hall Effect studies) of Polyaniline, core-shell structured TiO_2/Polyaniline nanocomposites are studied at room temperature. The V-I characteristic of conducting polyaniline salt form follows non-ohmic relation. Here charge conduction is not only carried by free carriers (electron & hole) such as in intrinsic semiconductors but also is carried by the formation of polarons and bipolarons. Voltage-Ampere measurements were also performed on the TiO_2 /PANI core-shell structured nano-composite. The *V-I* characteristics results imply that additional current transport mechanism dominate in the composite. Current-voltage characteristics of PANI and PANI/TiO_2 can be expressed as $I = KV^m$ The exponent *m* is ~1 for Emeraldine base form, 1.66 for PANI ES form and 1.76 for PANI/TiO_2. The Hall Effect studies are providing valuable information regarding nature of the charge carriers, Hall Voltage, Hall Coefficient (R_H), carrier density (n) and carrier mobility (μ) of the material. In application part Polyaniline and TiO_2 hetero-junction have been fabricated for rectification. The V-I characteristics of PANI/TiO_2 rectifier indicate Schottky junction formation between PANI and TiO_2.

Keywords: TiO_2/Polyaniline core-shell structure, V-I characteristics, d-c conductivity, Hall Effect studies, Rectifier.

Acknowledgments:

The Authors are sincerely acknowledges the UGC-DAE CSR Mumbai center for providing the research (CRS) project No. UDCSR/MUM/AO/CRS-M-181/12/035.

Conjugated NDI-Donor Copolymers: Effect of varying Donor strength on the Photo physical, Electrochemical and n-type Semiconducting Properties

Nagesh B. Kolhe and S. K. Asha *
Polymer Science & Engineering Division, National Chemical Laboratory, Pune-411008
Email: sk.asha@ncl.res.in

Although excellent p-channel polymers are widely available, the achievement of high-performance n-channel polymers is more challenging. Semiconducting properties of core substituted naphthalene/perylenediimide polymers have been studied extensively in the last decade and they have been found to be potential materials due to their high n-type charge carrier mobility, low band gap and solution processability. Facchetti et al. reported naphthalene diimide based highly soluble and printable n-channel polymer P(NDI2OD-T2) exhibiting unprecedented OTFT characteristics (μ_e up to, 0.45–0.85 $cm^2V^{-1}S^{-1}$) under ambient conditions.[1] Here we report core substituted naphthalenedimide (NDI) donor-acceptor copolymers where the structure of the donor moiety was systematically varied. The effect of varying electron donating ability of donor on the photophysical, electrochemical and n-type semiconducting properties of donor-acceptor copolymer was studied. Subtle lowering of LUMO energy level up to 0.23eV was observed upon changing the donor from OPV (oligophenylene vinylene) to bisoxazole, which was further studied by theoretical calculation of HOMO, LUMO, and band gap using Density functional theory. Absorption spectrum recorded in solution as well as solid thin film showed charge transfer band formation which was further studied by emission spectroscopy. Quenching of emission was observed for NDI-PPV upon excitation of the CT band; whereas NDI-bisoxazole exhibited high intensity emission, thereby displaying the different extents of intramolecular charge transfer in the polymers. Considerable lowering of the LUMO and the electron deficient nature of these polymers make them promising candidates for use in field effect transistor and photovoltaics as n-type material.

Reference:

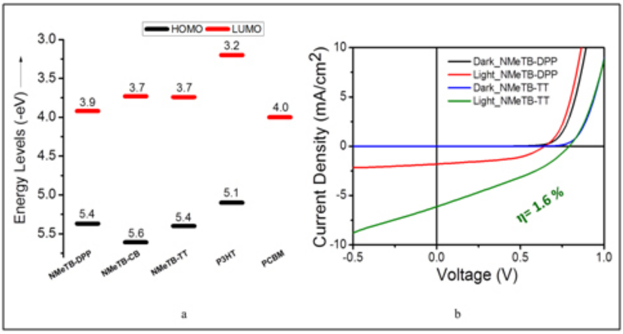
[1] Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F. Kastler, M.; Facchetti, A. Nature , 457 (2009) 679.

CP18

Molecular Engineering of Low Band Gap Copolymers For Organic Photovoltaic Applications

Raja Bhaskar Kanth Siram, Raveendra Kumar A and Satish Patil*
** Solid State and Structural Chemistry Unit, Indian Institute of Science,*
Bangalore 560012 INDIA

Solar cell technology is considered as being one of the most important ways to address growing global energy needs using a renewable resource such as harvesting energy directly from sunlight [1]. Polymeric solar cells (PSCs) are a promising alternative for producing clean and renewable energy due to the fact that there is the potential to fabricate them from lightweight flexible substrates onto large areas by solution processing at a low cost compared to silicon based solar cells [2]. In general the light absorbing component of the active layer consists of conjugated organic polymer [3]. The electronic properties of conjugated polymers can be tuned by introducing an appropriate electron rich (donor, **D**) and electron deficient (acceptor, **A**) alternating units in the main chain [4]. The latter enables accurate control over the optical properties of the polymer without affecting its electronic properties. Here, we report on a novel class of low band gap copolymers based on barbiturate core acting as the acceptor and various heteroaromatic derivatives such as carbazole, terthiophene as the donor moieties. The photophysical properties of these copolymers are characterized by UV-visible and fluorescence spectrometer and the electronic levels *i.e.,* HOMO and LUMO were determined by cyclic voltammetry. The band gap of these polymers was found to be in the range 1.5-1.9 eV as calculated from the optical absorption band edge. The energy level diagram of copolymers has shown in Figure 1 and compared with the standard polymer P3HT. From the fluorescence quenching studies these molecules perform the good photoinduced electron transfer to acceptor, PCBM. The general architecture of organic solar cells fabricated by using these copolymers as active layer is ITO/PEDOT-PSS/Copolymer:PCBM (1:3)/Ca/Al. The J-V characteristics of solar cells are shown in Figure 1b and obtained the high power conversion efficiency of 1.6%.



References

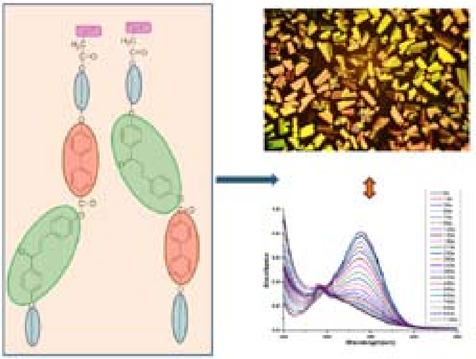
[1] Gregg, B. A.; Hanna, M. C. *J. Appl. Phys.* 93 (**2003**) 3605.
[2] Wong, W.-Y.; Wang, X.-Z.; He, Z.; Djurisic, A. B.; Yip, C.-T.; Cheung, K.-Y.; Wang, H.; Mak, C. S. K.; Chan, W.-K. *Nat. Mater.* 6 (**2007**) 521.
[3] Zhou, H.; Yang, L.; You, W. *Macromolecules* 45 (**2012**) 607.
[4] Huang, H.; Pickup, P. G. *Chem. Mater.* 10 (**1998**) 2212.

CP19

Chalcone-Biphenyl Based Liquid Crystalline and Photo Cross Linkable Polyesters

Ramkumar. V and Kannan. P*
Department of chemistry, Anna University, Chennai, Tamil Nadu - 600 025.

Two series of liquid crystalline and photo cross linkable Side chain polyesters containing chalcone and biphenyl were synthesized by free radical polymerization. Chemical structure of monomers and polymers were confirmed by FT-IR, 1H and 13C NMR spectroscopy. The molecular weight and molecule distribution of the polymers were studied by GPC Method. Thermal property was investigated by TGA and DSC.



Liquid crystalline nature was confirmed by hot stage optical polarized microscopy and DSC. The effect of substituents on the mesomorphic property was examined by polarized optical microscopy (POM) and Differential scanning calorimeter (DSC) measurements confirmed the different types of LC property. HOPM investigations displayed the different types of textures for polyesters and confirmed by DSC.

The photos cross linking nature of the polymers were investigated by UV-Visible spectroscopy. Thermo gravimetric analysis revealed that they were decomposed at high temperatures with good char yield.

References:
[1] Hiroyuki Mochizuki.; Takahiro Hasui.; Yasuhiko Kawamoto, *Macromolecules,* 36 (**2003**) 3457.
[2] Tomasz Ganicz * and Włodzimierz Stańczyk, C. *materials*, 2 (**2009)** 95.

CP20

Synthesis of Novel Tetraaniline-Terminated Polyurethane-Ureas for Functional Applications

A. Ravi[a], Chepuri R.K. Rao*[a], Ramanuj Narayana and K V S N Rajua
[a]*Polymers and Functional Materials Division, CSIR- Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, A. P. (state), India. Email:ramchepuri@iict.res.in*

Polyaniline (PAni) has been emerged as potential candidate for both fundamental research and technological applications because of its unique reversible proton dopability, excellent redox chemistry, and stability, and variable electrical conductivity, low cost and easy synthesis. The commercial applications of PAni, however, are limited owing to its poor processability and intractable nature [1-2]. In order to overcome these limitations, many approaches have been developed including use of oligomeric units such as tetraaniline or trianiline. Tetraaniline has attracted attention because of its solubility in many organic solvents, exhibit similar electro activity as PAni and exhibit reasonable electrical conductivity.

The work described here is about development of tetraaniline (TANi) [3] terminated polyurethane-urea conducting polymers (TANi-PU-TANi). Conducting Polyurethane-ureas were synthesized by the reaction between a diisocyanate (IPDI/ TDI/HMDI) with poly propylene glycol (PPG-2000/ 1000/ 425) as soft segments and trimethylol propane (TMP) as a cross linker to form pre-polymers. These pre-polymers were terminated finally by TANi to obtain conducting PU-Urea. The final polymers, abbreviated as TANi-PU-TANi, were doped with p-toluene sulphonic acid (p-TSA) for obtaining conductivity, the obtained free standing films were characterized by FT-IR, UV-Vis, SEM and XPS and thermal analyses. These films show good conducting properties of the order 1×10^{-3} S/cm. These conducting polyurethane ureas are expected as useful materials in several applications like conductivity based gas sensors, anti-static coatings, EMI shielding materials and anti-corrosion coatings.

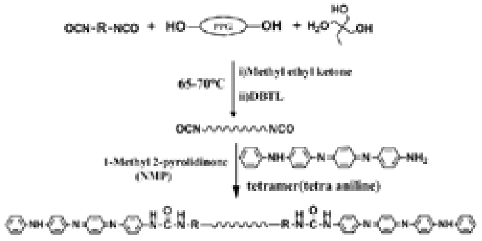


Figure-1:Tetraaniline terminated poly urethane urea

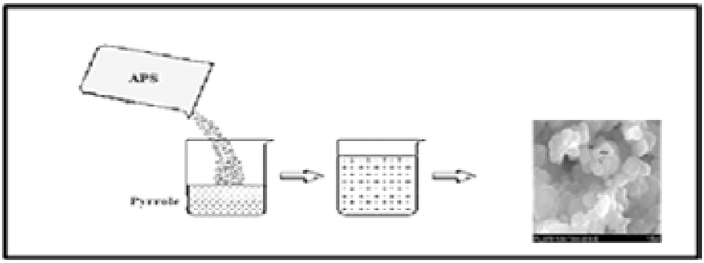
References:
[1] Oyama, N.; Ohsaka, T. *Synth Met* 18 (**1987**) 191.
[2] Mac Diarmid, A G; Mu S L, Somasiri, M. L. D.; Wu, W. *Mol Cryst Liq Cryst* 121 (**1985**) 187.
[3] Zhang, W. J.; Feng, J.; MacDiarmid, A. G.; Epstein, A. *J Synth Met* 84 (**1997**) 119.

CP21

Studies on Polypyrrole Nanoparticles Synthesized by Ultrasonication

Reetu Prabhakar, D.Kumar*
Department of Applied Chemistry and Polymer Technology
Delhi Technological University (formerly Delhi College of Engineering)
Shahbad Daulatpur, Bawana Road, Delhi-110042
email: dkumar@dce.ac.in;drdkumar@yahoo.co.uk

Development of nanoparticles based on π-conjugated organic polymers and studies on their properties have been attracted much attention of the researchers worldwide. The present work deals with the synthesis of polypyrrole (PPy) nanoparticles by ultrasonication technique using p-toluene sulphonic acid (p-TSA) as a dopant with drop wise addition of ammonium persulphate solution (APS). The reaction was carried out at 25ºC by varying the concentration of APS (0.025-0.1M) solution. The effect of APS concentration on PPy nanoparticles was investigated using Fourier transform infrared spectroscopy (FTIR) technique. The morphological behaviour of the samples was studied by scanning electron microscopy (SEM) whereas the crystallographic structures were determined by X-ray diffraction (X-RD) technique. The electrical conductivity of nanoparticles of polypyrrole has been measured by using four probe method.



References

[1] Jang, J.; NamY.; Yoon H. Advanced Materials.17 (2005) 1382–1386
[2] Duk Ki, Kim.; Kyung Wha, Oh.; Hee Jun, Ahn.; Seong Hun, Kim. Journal of Applied Polymer Science.107 (2008) 3925–3932
[3] Anjali A. Athawale.; Prachi P. Katre.; S. V. Bhagwat.; A. H. Dhamane. Journal of Applied Polymer Science. 108 (2008) 2872–2875

CP22

Electrochromism in Poly(3,4-alkylenedioxythiophenes)s: Structure v/s Morphology

Rekha Singh*, Bikash K. Sikder, Anshu Kumar and Anil Kumar
Department of Chemistry, Indian Institute of Technology Bombay, Mumbai-400076, INDIA
**Email: rekha@chem.iitb.ac.in*

Electrochromism refers to the change in colour on application of applied potential. Design, syntheses and characterization of new materials for electrochromic device application has become increasingly important due to the widespread application of these devices in fields such as displays (both transmissive and reflective), e-paper, optical shutters, smart windows, and night vision. [1] Development of low cost flexible devices with high contrast ratio and fast switching time is the need of the hour. Electrochromic materials based on organic conjugated polymers, specifically based on 3,4-alkylenedioxythiophenes, have emerged as one of the potential alternative in this direction. [2] Figure 1 represents some of the electrochromic polymers based on 3,4-alkylenedioxythiophenes along with their electrochromic contrast (difference in %T between bleached and colored state) in bracket. [3-5] As can be seen form Figure 1, the electrochromic contrasts increases with increase in inter-chain spacing and reaching a maximum value of 90% in case of Dibenzyl substituted derivative (Structure VI). Though the Dibenzyl substituted derivative does give maximum contrast, its insolubility restricts its application in large area display devices. Various efforts were undertaken to introduce solubility without compromising contrast but the cost of these soluble materials restricts their real potential. [6]

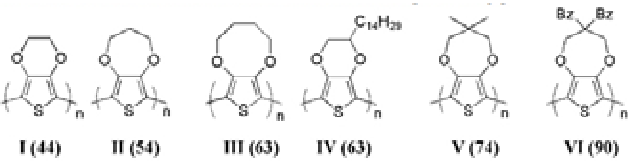


Figure 1. Structure of various electrochromic poly(3,4-alkylenedioxythiophenes) along with their electrochromic contrast.c

It is interesting to note that all these structures have the same dioxythsiophene backbone but exhibit large difference in electrochromic contrast. This is attributed to the change in the morphology of the resulting thin film on changing the structure of the monomer. Therefore, it will be interesting to explore if such morphology could be attained in thin films based on PEDOT (Structure I) which is one of the most successful and least expensive processable conjugated polymer available, commercially, under the trade name "CLEVIOS-P". Recently, Poverenov et. al. have shown that it is possible to increase the elctrochromic contrast in electrochemically polymerized EDOT from 50% to 71% by changing the solvent and electrolyte. [7] Therefore, it seems possible to improve the electrochromic contrast of PEDOT itself without changing the monomer by judicious choice of formulations. Furthermore, if this can be attained in a processable PEDOT formulation, it should lead to newer applications of PEDOT in high contrast electrochromic devices.

In this direction, we started looking into varying the morphology of PEDOT by changing additives, substrates and annealing conditions. Our recent findings do suggest that it is possible to get high contrast in PEDOT films via electropolymerization on different substrates. This is attributed to changes in morphology. Now we are exploring various methodologies wherein we are interested in increasing the electrochromic contrast in case of thin films derived from Clevios-P. Our recent results in this direction will be discussed in the presentation.

References

[1] P. M. S. Monk; R. J. Mortimer; D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*; Cambridge University Press UK, 2007.
[2] Beaujuge, P.M.; Reynolds, J. R.; *Chem. Rev.*, 110 **(2010)** 268.
[3] Kumar, A.; Morvant, M. C.; Welsh, D. M.; Reynolds, J. R.; *Chem. Mater.***,** 10 **(1998)** 896.
[4] Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R.; *Adv. Mater.*, 11 **(1999)** 1379.
[5] Krishnamoorthy, K.; Ambade, A. V.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *J. Mater. Chem.*,11 **(2001)** 2909**.**
[6] Mishra, S. P.; Krishnamoorthy, K.; Sahoo, R. Kumar, A.; J. *Polym. Sci. A: Polym. Chem.*, 43 **(2005)** 419.
[7] Poverenov, E.; Li, M.; Bitler, A.; Bendikov, M.; *Chem. Mater.*, 22 (**2010)** 4019.

CP23

Characterization Of Polymer Based Moderator Materials For Thermalisation Of Fast Neutrons

S Remakanthan*, Cherian Thomas, R Gunasekharan, CR Thomas
Rocket Propellant Plant, Vikram Sarabhai Space Centre, Trivandrum
s_remakanthan@vssc.gov.in

Neutron radiography have become a valuable tool in the field of NDE and testing of polymer materials. Objects containing light elements such as rubber, plastics can be made visible by neutron radiography even when they are enveloped by heavy elements. In recent years it emerged as a useful and complementary testing method with x-ray radiography. The images have been used for many applications which include inspection of electronic components, material analysis and evaluation of nuclear reactor fuel elements and testing of various pyrodevices in aerospace applications. Neutron radiography has a significant role for the non-destructive testing of various polymer materials such as gaskets and o-rings encapsulated in a high density metal case. Images have been mainly developed using thermal neutrons fluxes obtained from a nuclear source. Neutron sources are based on neutron producing nuclear reactions. Accelerator based sources are working by the common principle of hitting a target element with particle accelerated to very high energies and neutrons emerging from D-T reaction have average energy of about 14 MeV with incident protons. Slowing down of fast neutrons is essential for making a good radiograph. When neutrons collide with light nucleus, it loses more kinetic energy. Elastic scattering is most important in the production of slow neutrons emitted from a neutron source for radiography. Water, paraffin, graphite, heavy water and polyethylene are common neutron moderator materials. Neutron thermalization characteristics of different moderating materials are analyzed to optimize the flux emitted by a 14MeV D-T portable neutron generator. Thermal neutron flux densities were investigated using Monte Carlo Neutron-Particle Transport (MCNP) simulations. After the assessment of each moderator material HDPE was chosen as the primary moderator material out of the four moderator materials analyzed. This paper deals with the studies carried out towards selection of a suitable polymer material for moderation of neutrons.

References

[1] Paul E. Mix, Introduction to nondestructive testing, 2nd edition, A John Wiley & Sons, Inc, New Jersey.

[2] J.K. Shultis and R.E. Faw, An MCNP Primer, Department of Mechanical and Nuclear Engineering, Kansas State University, Revised Edition, 2011

[3] B.JPatil,S.TChavan,S.NPethe,R.Krishnan,V.NBhoraskar,S.DDhole,Designof 6MeVlinear accelerator based pulsed thermal neutron source: FLUKA simulation and Experiment, Elsevier,2011 A X da Silva,V RCrispim, Moderator-collimator shielding design for neutron radiography systems using ^{252}Cf, Elsevier Science Ltd, 2001

CP24

Polyaniline Binder for Functionalized Acetylene Black: A Hybrid Material for Supercapacitor

Singh Ajit,[a] Srinivasan Palaniappan,*[a,b] and S. Gopukumar[c,b]
[a] *Polymers & Functional Materials Division,CSIR- Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b] *CSIR – Network Institutes for Solar Energy (NISE). India*
[c] *CSIR – Central Electrochemical Research Institute, Karaikudi – 630 006, Tamil Nadu, India*
email : palaniappan@iict.res.in

Electrochemical capacitors are considered promising high-power sources in the application where high power density, high cycle efficiency and long cycle life are needed such as in wireless digital communication devices and electric vehicles [1, 2]. One of the most commonly active species in pseudocapacitor is electrically conducting polyaniline [3]. Polyaniline-doped with functionalyzed acetylene black material has been successfully synthesized and used as an electrode material in supercapacitor, wherein, this material contributes both pseudocapacitative (PC) and electrical double layer capacitative (EDLC) behaviour. Functionalization of acetylene black (AB) has been carried out and used as dopant for THF soluble polyaniline base (PANI) to prepare PANI-functionalized acetylene black (PANI-FAB). Formation of FAB and PANI-FAB is confirmed with the help of FT-IR and XPS study.

Functionalization of AB results in agglomerated FAB and doping with PANI results in agglomerated fibrous PANI-FAB, as compared to fibrous AB. High thermal stability of AB decreases on functionalization and again slightly increases for PANI-FAB. Functionalization of AB also results good bonding effect with PANI, where PANI acts as both PC and binder, instead of the higher amounts of binder (PVdF > 30 wt%) that are normally needed to hold AB. Electrochemical studies of material is carried out by cyclic voltammetric and electrochemical impedance spectroscopic methods. PANI-FAB supercapacitor cell shows capacitance of 132 Fg^{-1} for 1.5 mA current with very low charge-transfer resistance and low time constant.

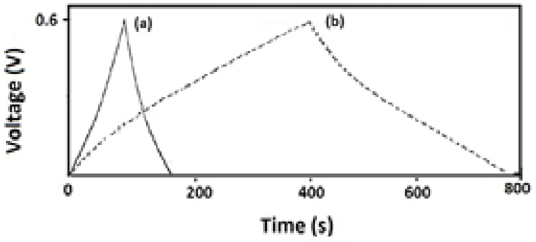


Fig. Cell CD of (a) FAB (b) PANI-FAB at 1 mA current.

References:

[1] Conway, B.E. *J. Electrochem.l Soc.* 138 (**1991**) 1539
[2] Kötz, R.; Karlen, M. *Electrochim. Acta* 45 (**2000**) 2483
[3] Bal Sydulu, S.; Palaniappan, S.; Srinivas, P. *Electrochim. Acta* 95 (**2013**) 251

CP25

Electrochemically Developed Photo Switchable Fulgimides Functionalized Polypyrrole On ITO Thin Films

S. Nithyanandan and P. Kannan*
Department of Chemistry, Anna University, Chennai-600025 INDIA

A new synthetic strategy has been developed for the fulgimides photochromic switch bearing electropolymerisable pyrrole units on conducting substrate, is reported [1-3]. The functionalised pyrrole monomers are ascertained by NMR and Mass spectral techniques. Analysis of the frontier orbitals, electronic structures of monomers are employed to understand the cyclization and cycloreversion of fulgimides, to predict and explain the switching properties of fulgimides necessary. To improve the yield of cyclisation in the synthesis of fulgide and fulgimide, trifluoro acetic anhydride (TFA) is employed as the dehydrating agent [4]. The electroactive polymer films prepared on indium tin oxide (ITO) electrodes are characterized by cyclic voltammetry and atomic force microscopy (AFM). The optical switching properties of the polymer films have been corroborated by UV/Vis spectroscopy. Although the films are photochemically stable, their mechanical stability with respect to adhesion to the electrode was found to be sensitive to both the solvent and the electrode material employed. The consistently electrochemically formed thin films can be switched between the open and closed state of the photochromic fulgimides moiety shown in Figure 1 [5].

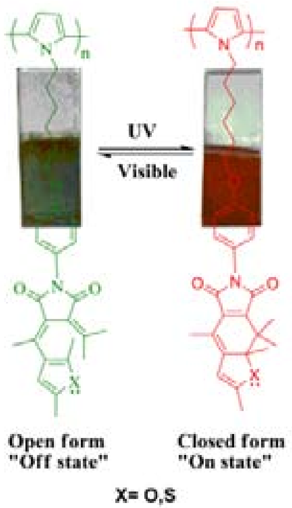


Figure 1. Photo switchable fulgimides functionalized polypyrrole backbone

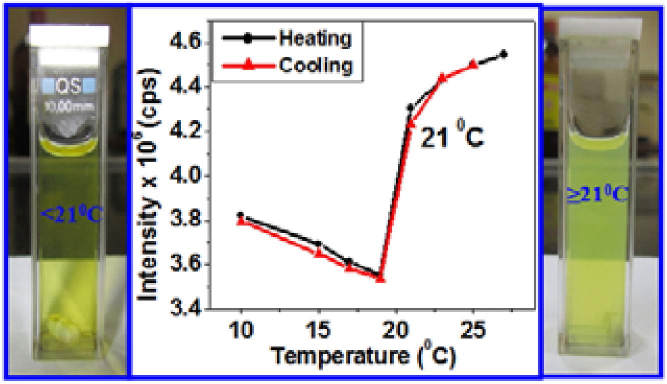
References
[1] M. Kondo, T. Tada, K.Yoshizawa, Chem. Phys. Lett. 412 (**2005**) 55-59.
[2] M. Irie, Chem. Rev. 100 (**2000**) 1685-1716.
[3] F. Dietz, N. Tyutyulkov, Chem. Phys. 265 (2001) 165-175.
[4] F. Dietz, N. Tyutyulkov, Phys. Chem. Chem. Phys. 3 (**2001**) 4600-4605.
[5] S. Kawata, Y. Kawata, Chem. Rev. 100 (**2000**) 1777-1788.

CP26

Thermosensitive water soluble poly (ethylene glycol) based polythiophene graft copolymers

Sandip Das, Sanjoy Samanta, Dhruba P. Chatterjee and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, INDIA
E-mail: psuakn@iacs.res.in

Diethyleneglycol methylether methacrylate (MeO$_2$MA) and oligoethylene glycol methylether-meth acrylate (OEGMA) are polymerized on polythiophene (PT) backbone to produce water-soluble PT-g-PMeO$_2$MA (PTD) and PT-g-P(MeO$_2$MA-co-OEGMA) (PTDO) using atom transfer radical polymerization.[1,2] They are characterized by ^{1}H NMR, ^{13}C 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 PMeO$_2$MA 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 20^{0}C. The LCST increases with OEGMA concentration in PTDO. The temperature dependent PL emission of PTD shows a minimum at 19^{0}C, followed by a sharp increase till 21^{0}C 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. The temperature dependent PL emission of PTD solution shows a sharp increase at the LCST due to collapse of the radiating PMeO$_2$MA fibrils forming a shell on the PT nanosphere preventing it from the quenching of excitons by the water molecules. This LCST gradually increases from 31 to 43^{0}C with increase in OEGMA concentration. The thermo-reversibility and LCST tunnability make it a novel system building it different and improved from similar others. The PL intensity increase is sharp near the LCST and this property might be useful to construct precession biosensors working under physiological condition and molecular thermometer.



References

[1] Balamurugan, S. S.; Bantchev, G. B.; Yang, Y.; McCarley, R. L. *Angew. Chem. Int. Ed.*, 44 **(2005)** 4872.

[2] Wang, M.; Zou, S.; Guerin, G.; Shen L.; Deng, K.; Jones, M.; Walker, G. C.; Scholes, G. D.; Winnik, M. A. *Macromolecules*, 41 **(2008)** 6993.

CP27

Sensor Applications of Norbornene Based Materials

Santu Sarkar and Raja Shunmugam*
Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata.
E-mail: sraja@iiserkol.ac.in

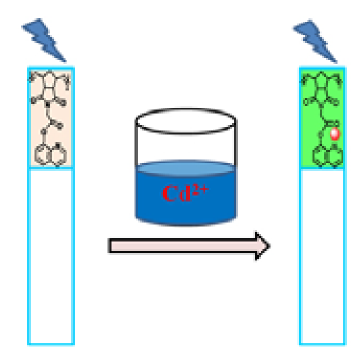


Figure 1. Demonstration of the Cd2+ sensing in water by polymer coated paper strip

We develop norbornene based sensors that have potential application in sensing area of heavy metals and nerve gas. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. To provide sensitive and selective sensor systems, fluorophores (e.g. Rhodamine, Hydroxyquinoline) with binding moieties are attached to norbornene backbone. It is found that hydroxyquinoline modified norbornene behaves as a fluorometric sensor molecule for Cd^{2+}, whereas terpyridine based norbornene acts as a nerve agent sensor.[1] Norbornene based monomers are polymerised by ROMP technique using Grubbs' Catalyst. Using UV & Fluorescence method, the sensing ability of the new molecules is confirmed. DFT calculation reveals the process of sensing mechanism.

References

[1] Sarkar, S.; Mondal, A.; Tiwari, A. K.; Shunmugam, R. *Chem. Comm.*, 48 (2012) 4223.

CP28

Morphology Control in BHJ Blend of Inverted Organic Solar Cell via Co-Solvent Addition

[a]Sarita S Nair, [a]D Kumar*, [b]Abhishek Sharma, [b]Nikhil Aggarwal
[a]*Department of Applied Chemistry & Polymer Technology, Delhi Technological University,*
(Formerly Delhi College of Engineering), Shahbad Daulatpur, Bawana Road,Delhi-110042, India
[b]*Moserbaer India Ltd. 66, Udyog Vihar, Greater Noida (U.P.)-201306, India*
**E-mail: dkumar@dce.ac.in; drdkumar@yahoo.co.uk Tel:+919811425817*

We verge on to extend the concept of solvent induced crystallization to inverted BHJ polymer solar cell. Well controlled nanoscale morphology was promoted via addition of secondary liquid additive, a marginal solvent cyclohexanone (CHN) in to well dissolved solution of P3HT-PCBM in 1, 2-DCB, followed by mild thermal annealing of the spin coated film [1, 2]. Aggregation of P3HT in co-solvent mixture was confirmed with UV-Visible spectra including a pronounced additional peak of crystallization at higher wavelength [3].

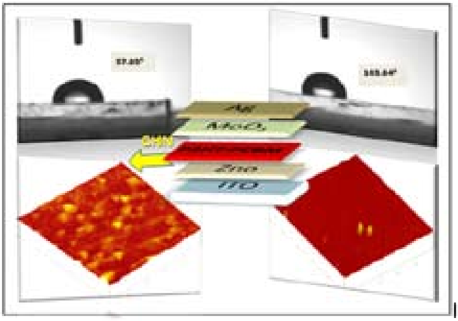


Figure1. Comparative Contact angle measurements (top) and AFM topography height images (bottom) of the cyclohexanone added blend casted film (left) and of the conventional unmodified film (right)

Such a modification also ingrained better wetting properties of film as evident of the decreased contact angle from 105.64^0 to 97.05^0 and better phase separation as seen from the AFM studies (fig.1). This modification made to the active layer blend though presented a drop in efficiency to 2.86% in contrast to 3.18% of unmodified device but this marginal drop may be an outcome of dilution of the blend solution with co-solvent. Confluence of stability of inverted architecture with apposite morphology via solvent mixture approach can clarify the demur glooming the polymer solar cells.

References

[1] Kim, J. H.; Park, J. H.; Lee, J. H.; Kim, J. S.; Sim, M.; Shim, C.; Cho, K.; *J. Mater. Chem*. 20 (**2010**) 7398.
[2] Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J.; J. Am. Chem. Soc. 130 (**2008**) 3619.
[3] Park, Y.D.; Lee, H. S.; Choi, Y. J.; Kwak, D.; Cho, J. H.; Lee, S.; Cho, K.; *Adv. Funct. Mater.* 19 (**2009**) 1200.

CP29

A Simple and Scalable Process for the Syntheses of Aqueous Dispersions based on Poly(3,4-ethylenedioxythiophene)

Soumadwip Ghosh, Bikash K. Sikder, Rekha Singh, Smita Mukherjee and Anil Kumar*
Department of Chemistry, Indian Institute of Technology Bombay,
Mumbai-400076 INDIA
Email:anilkumar@iitb.ac.in

Since the invention of electronic conductivity in otherwise insulating synthetic polymers, conducting or conjugated polymers also known as inherently conducting polymers (ICPs), have evolved from the academic curiosity to one of the important commercial material for wide ranging applications in many modern electronic devices. Conjugated polymers based on 3,4-ethylenedioxythiophene (PEDOT) have been explored extensively due to its thermal and chemical stability, high conductivity, high transparency in visible region and low oxidation potential [1]. Due to the insolubility of the PEDOT, it has been processed from the aqueous dispersion in presence of anionic polyelectrolyte poly(styrene sulfonic acid) (PSS). In this process, monomer EDOT is oxidatively polymerized in presence of anionic polyelectrolyte PSS resulting in the formation of stable dispersion. Various grades of aqueous dispersions of PEDOT:PSS are commercially available under the trade name of **"Clevios-P"**[2]. The general processes for the large scale synthesis of these dispersions are though the chemical oxidative polymerization of EDOT in water in presence of PSS. This results in the formation of a blue dispersion which is then purified by dialysis (to remove monomer, oligomers and other low molecular weight species) and ion exchange resins (to remove inorganic ions). Properties of the final dispersion depend strongly on the presence of these impurities and hence it becomes very important to do extensive purification. Since both of the above mentioned processes are slow and expensive for the large scale syntheses, it will be highly advantageous if these processes can be circumvented [3]. In this direction, we have now developed a new synthetic route which allows the syntheses of PEDOT:PSS dispersion without the need of dialysis or ion exchange resins. Furthermore, this process is amenable for scale-up. This opens up a whole new area of formulations of **PEDOT** for various electronic devices wherein these new materials can be explore either as the hole transport layer or as transparent conductor or both. Our Recent results in this direction will be discussed in this presentation.

References:

[1] "PEDOT: Principles and Applications of an Intrinisically Conducting Polymer", Elschner A., Kirchmeyer S., Lövenich W., Merker, U., Reuter, K., CRC Press, Taylor and Francis Group, Boca Raton/London/NewYork,(**2011**).
[2] Xia.Y., Ouyang. ACS Appl. Mater. Interfaces, 4 (**2012**) 4131
[3] Cloutet. E., Mumtaz. M., Cramil. H,. Material Science and Engineering C, 29 (**2009**) 377

CP30

Impurity Profiling of Regioregular Poly(3-hexylthiophene)

Sreelekha P. Gopinathan[a], Anshu Kumar[b], Ashok Kumar Majji[b], and Anil Kumar*[a,b]
[a]*Centre for Research in Nano Technology and Science (CRNTS),*
[b] *Department of Chemistry,*
Indian Institute of Technology Bombay, Mumbai-400076, INDIA
Email.anilkumar@iitb.ac.in

Regioregular poly(3-hexylthiophene), **rr-P3HT**, has been used as an active semiconducting layer for various electronic devices such as organic photovoltaics(OPVs), organic field effect transistors(OFETs) and sensors.[1] Purity of the semiconducting material is one of the most critical parameter for thin film device applications.[2] Metal impurities act as charge trapping sites and can induce hysteresis in device. This is the reason that the mobilities for rr-P3HT has been reported to vary from as low as 1.9 x 10^{-5} cm^2 V^{-1} s^{-1} to 0.24 cm^2 V^{-1} s^{-1}.[3,4] These variations could be due to impurities, chain ends, structural defects(regioregularity),crystallinity, molecular weight variation, PDI(polydispersity index) etc. Since the material is chemically synthesised by multistep processes, impurities and other anomalies peep in at different levels and remains undetected as they doesn't interfere with common analytical techniques(elemental analysis and NMR etc) and therefore it is difficult to quantify.

Two main routes for the synthesis of P3HT are Grignard metathesis polymerization(GRIM) and Reike polymerization, both of which gives high molecular weight regioregular materials with varying polydispersity index. But the aforementioned methods of polymerization use reactants and catalysts which leaves metallic/nonmetallic impurities even after stringent purification methods. The impurities generally present in rr-P3HT are Ni, Mg, P, Zn, Br, all in trace amount. The most common purification procedures which includes reprecipitation, Soxhlet extraction with various solvents, functionalised silica treatment are not able to remove ppm levels of the impurities. Understanding the relationship between the purity of the polymer, the processing and the resulting OFET performance is critical for the improvement of the device. This presentation involves the purification and characterization of P3HT to find the metallic impurities and their levels which will further be used to study their effect in organic field effect transistors.

References

[1] Franky. S, Editor. Organic Electronics: Materials, Processing, Devices And Applications, CRC Press, **2010**.
[2] Meg.M.E, James. M, Andreas.V. K, Sandra .J. R, Thin Solid Films 409 **(2002)** 198.
[3] Zhenan. B, Ananth. D, Andrew.J. L, Applied Physics Letters 69 **(1996)** 4108.
[4] Yi-Da. J, Tzu-Hao. J, Show-An.C, Applied Physics Letters 100 **(2012)** 023304-1.

CP31

Electrically Conducting Polyaniline Nanorods Synthesized in Electrochemical and Solid State Method

Subhendu Bhandari[a], Nikhil K. Singha[a], Dipak Khastgir[a,*]
[a] *Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur - 721302, India*
** khasdi@rtc.iitkgp.ernet.in*

Polyaniline (PAni) is considered to be one of the most important members in the domain of intrinsically conducting polymers (ICP) due to its ability of conducting electrical current through its backbone. PAni exists in different oxidation states [1] out of which suitably doped partially oxidized and partially reduced emeraldine salt is electrically conducting in nature. Due to having wide range of electrical conductivity, it has potential use in different fields e.g., capacitor, sensor, actuator, corrosion inhibitor, EMI shielding etc. It can be synthesized via different synthesis methods e.g., chemical, electrochemical [2], solid state [3], interfacial etc. Depending on differences of synthesis processes, reagents and conditions it can have different morphological structures [4] as well as differences in electrical conductivity.

In the present study, we have synthesized different PAni nanorods both in electrochemical and solid state synthesis process. Different types of nanorod-like structure were obtained in different synthesis processes at different synthesis parameters and using different dopants. In some cases, nano grains of dia. 60-90 nm are formed which combine together directionally to form nanorods whereas straight rod like structures of dia. 20-40 nm without joining smaller particles are also observed. Characterizations are carried out using SEM, TEM, FTIR, XRD and AC conductivity was measured to check frequency dependence of electrical properties.

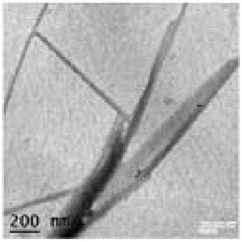


Figure 1. Polyaniline nanorod

Figure 2. Polyaniline nano-grains combines together to form nanorod

References:

[1] Kolla H. S.; Surwade S. P.; Zhang X.;MacDiarmid A. G.; Manohar S. K. *J. Am. Chem. Soc.* 127 (2005) 16771.
[2] Tang, Z.; Liu S.; Wang Z.; Dong S.; Wang, E. *Electrochem. Commun.* 2 **(2000)** 32.
[3] Bhadra S.; Kim N. H.; Rhee K. Y. *Polym. Int.* 58 **(2009)** 1173.
[4] Rezaei S. J. T.; Bide Y.; Nabid M. R. *Synth. Met.* 161 **(2011)** 1414.

CP32

Perylene Diimides as Electron Transporters in Polymeric Solar Cells

Sunil Kumar Kandapp[a] and Sridhar Rajaram*
[a]International Centre for Material Science, Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore, India
**E-mail: rajaram@jncasr.ac.in*

The use of donor acceptor polymers in high efficiency polymeric solar cells requires the use of highly absorbing electron transporters. To this end novel twisted perylene have been used as electron transporters in the devices. Lack of planarity disrupts stacking and leads to high short circuit current density along with good efficiency. The synthesis of twisted perylene along with their utility in devices will be presented.

References

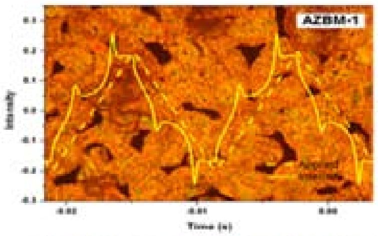
[1] S. Rajaram, R.Shivanna, S. K. Kandappa and K.S.Narayan, *The Journal of Physical Chemistry Letters* 3, **(2012)**.2405

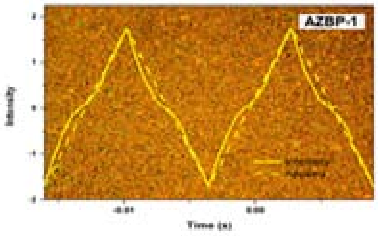
CP33

Photo and Electrically Switchable behavior of Azobenzene Containing Bent-Core Liquid Crystals and Their Polymers

M.Vijay Srinivasan[a], A. Roy [b] and P. Kannan*
[a] *Department of Chemistry, Anna University, Chennai 600 025, India.*
[b]*Soft Condensed Matter, Raman Research Institute, Bangalore 560 080, India.*
E-mail:pakannan@annauniv.edu

Three series (AZB-I, II & III) of novel azobenzene containing bent-core liquid crystals and their polymers exhibiting photo and electrical switching properties are reported. To explore the of structure property relation-ship in bent-core liquid crystals we synthesis three series of liquid crystalline polymers with 1, 3-phenylene unit as central core unit. Two series (AZB-I & II) of liquid crystals was constructed with five-ring and third series (AZB-III) six-ring systems using structurally non-symmetrical rod-like mesogens connected with 1, 3-phenylene unit. The significance of tail length (alkyl chain) on mesogen was explored; shorter alkyl chains all the series bent-core compounds exhibited non-switchable rectangular columnar B_1 phase. Whereas longer alkyl chains induces switchable lamellar mesophase for all the three series (AZB-I, II & III), among this, AZB-I & III shows B_2 phase exhibit antiferroelectric switching (AF) characteristics with synclinic organization (SmC_AP_A) of the molecules in the layers. The AZB-II series with higher homologues exhibit first B_7 mesophase bent-core liquid crystal materials with photo-active azo linkage, which exhibits ferroelectric (F) switching behavior (SmC_AP_F) of the molecules in the layers. The photo-switching properties of bent-core azo molecules were investigated using UV-Vis spectroscopy. The *trans* to *cis* photo isomerization is take place at 25 s for AZB-III and 30s for AZB- I & II and also thermally reversible.





References

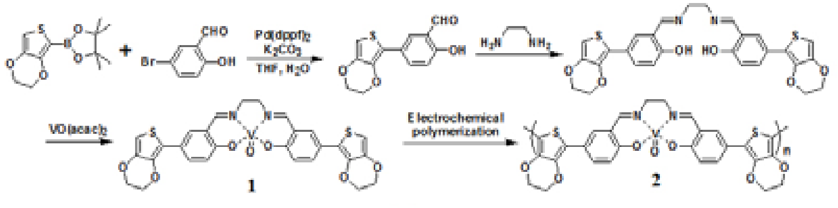
[1] Clark, N. A.; Lagerwall, S. T. *Appl Phys Lett* ,36 (1980) 899.
[2] Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J Mater Chem*, 6 (1996) 1231.
[3] Amaranatha Reddy, R.; Tschierske, C. *J Mater Chem* , 16 (2006) 907.
[4] Balamurugan, S.; Kannan, P.; Chuang, M. T.; Wu, S. L. *Ind Eng Chem Res*, 49 (2010) 7121
[5] Vijay Srinivasan, M., Kannan, P. and Roy, A. *J. Polym. Sci., Part A: Polym. Chem*, 51 (2013) 936.

CP34

Electropolymerized Macromolecular Metal Complexes and Their Application to a Solid-State Dye-Sensitized Solar Cell

Yoshito Sasada, Fumiaki Kato, Kenichi Oyaizu, and Hiroyuki Nishide*
Dept. of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
E-mail: center-break.gl@ruri.waseda.jp; nishide@waseda.jp

Dye-sensitized solar cells (DSSC) have attracted great attention as one of organic solar cells. A redox mediator plays important roles in DSSC, which are dye-regeneration and charge-propagation. A mediator having highly redox potential ($E_{1/2}$) should be contributed to improve open-circuit voltage (V_{OC}), which is determined by the energy gap between E_F of TiO_2 and $E_{1/2}$. A lot of mediators have been examined to replace the conventional I^- / I_3^- redox couple. In this report, VO(salen) derivatives exhibiting rapid and reversible redox property were applied to a DSSC as the mediator. The DSSC fabricated with the VO(salen) derivatives-based electrolyte was examined their photovoltaic property. We also tried to employ highly conductive macromolecular metal complexes, such as Co(salen) derivatives [1], as a hole-transporting layer (HTL) in a solid-state DSSC. Macromolecular VO complex films were prepared by electropolymerization and applied to solid-state DSSC.



Scheme

A VO(salen) derivative **1** was synthesized via 3 steps, and a polymer **2** film was formed onto ITO substrates by electropolymerization of **1**. The electropolymerization behavior depended on supporting electrolytes. The IR spectra of the resulting **2** film ($\omega_{V=O}$ = 840 cm^{-1}) suggested that the VO(salen) moieties were polymeric state in the **2** film. The **2** film showed a reversible redox wave at 0.7 V (*vs.* Ag/AgCl), which was appropriate to regenerate dye molecules. A solid-state DSSC composed of the **2** film as a HTL was fabricated to demonstrate a photoelectric response.

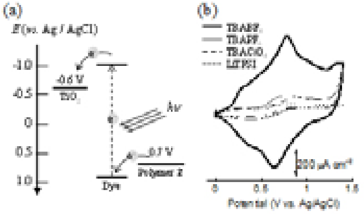


Figure (a) Energy diagram of solid-state DSSC utilizing 2. (b) Cyclic voltammograms of 2 with each electrolyte.

References
[1] Kingsborough, P, R.; Swager, M, T. *Adv. Mater.*, 10 **(1998)** 1100.

CP35

Oxygen Transport and Storage Properties of Cobalt Porphyrin Membranes

Natsuru Chikushi, Emiko Ohara, Ryutaro Kembo, Kenichi Oyaizu, and Hiroyuki Nishide*
Dept. of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
E-mail: nc-mail@akane.waseda.jp; nishide@waseda.jp

Cobalt porphyrin (CoP) complexed with an imidazole ligand selectively binds and releases oxygen reversibly (**Figure 1**). The CoP complex fixed in a polymer membrane acts as an oxygen carrier to facilitate oxygen transport and it also storages oxygen in a high concentration[1]. These membranes could be expected to enhance the performance of oxygen-using devices such as fuel cell and air battery. Here we report oxygen transport and storage properties of the CoP complexes in a network polymer and ligated with poly(imidazole).

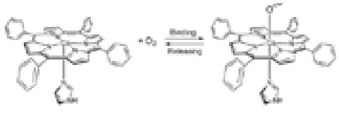
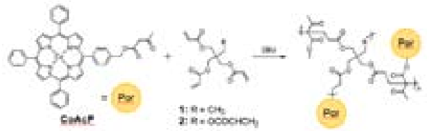
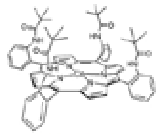


Figure 1. Oxygen-binding/releasing reaction of the CoP-imidazole complex.



Scheme Synthesis of the network polymer containing of cobalt porphyrin

Acetoacetate-substituted CoP (**CoAcP**) was synthesized from 4-methoxy carbonyl phenyl porphyrin with dicatene. A 70wt%-CoP containing membrane was prepared via Michael addition of **CoAcP** and tris- or tetra- acrylate(**Scheme**), to ve tough membranes based on high cross-linking density. The membrane was formed through upon porous support membranes with submicron thickness (*ca*. 500 nm). Oxygen permeability (P_{O2}) was higher than that of the nitrogen permeability (P_{N2}) and increased with a decreased in the upstream pressure. The oxygen/nitrogen permselectivity (P_{O2}/P_{N2}) at an upstream pressure of 1 cmHg was beyond 10.



CoTpivPP

The membrane of CoP ligated with poly(imidazole) was prepared from picket fence cobalt porphyrin, *meso*-tetrakis(*a,a,a,a*-*o*-pivalamidophenyl)porphinatocobalt(II) (**CoTpivPP**) [2], with poly(imidazole) ligand. CoTpivPP-imidazole complex demonstrate oxygen-binding/releasing reaction reversibly, which depended on the oxygen partial pressure even in the electrolytes for Li-air battery, such as *γ*-butyrolactone (GBL) with 1.0 M $Li(CF_3SO_2)_2N$. The electrolyte containing the CoTpivPP-imidazole complex dissolved oxygen several times larger than the oxygen-saturated GBL solution.

References

[1] Nishide, H., *Polymer for Gas Separation:*VCH Publishers, (**1992**) 183.
[2] Collman, J. P.; Gagne, R. R.; Halbert, T. R.; Marchon, J. C.; Reed, C. A. *J. Am. Chem. Soc.*, 95 (**1973)** 7868.

Polymer physics-structure and dynamics

Invited Talk

Molecular Aspects of Flow-Induced Crystallization of Polyolefins

Julie Kornfield, California Institute of Technology

The dramatic effects of flow on crystallization kinetics and morphology of semicrystalline polymers are well documented: flow can accelerate crystallization by orders of magnitude compared to the quiescent case, and induce highly oriented crystal morphologies. We seek molecular insight into the formation and growth of the oriented crystalline structures using *in situ* rheo-optical and rheo-WAXD techniques in combination with *ex situ* optical microscopy. To expose the role of very long chains in the formation of oriented precursors in isotactic polypropylene (iPP), we examined model binary blends of well-defined, long chains at very low concentrations in a matrix of much shorter---but still highly enthangled---short chains. Specifically, long chain concentration (*c)* is 2% or less, and long chains lengths of 1.0×10^6 and 3.5×10^6 g/mol (denoted 1M or 3.5M) are, respectively, 5- and 18-times longer than the matrix chains (1.86×10^5 g/mol). At these low concentrations of long chains, experiments can be compared at nearly identical conditions (shear stress, shearing time, total strain and total work done one the system) to isolate the effects of long chain concentration *c* and length. As *c* increases (at fixed shearing conditions), oriented precursors form sooner, the degree of orientation increases, and the parent:daughter ratio increases. Long chains appear to act cooperatively (effects increase nonlinearly with *c* up to *c**) and their effect tends to saturate beyond *c**. The magnitude of the effect of long chains is much greater for 3.5M than 1M: e.g., at c* the threshold stress for highly oriented growth is reduced 10% for 1M and 50% for 3.5M. The results do not support models that relate oriented precursors to the specific work imposed on the melt. Instead, the results motivate models that account for the dynamics of the longest chains and their interactions with growing precursors and with neighboring chains.

Direct Evidence for Stress Induced Meting and Recrystallization Mechanism during Tensile Deformation of Semi-crystalline Polymers

Yongfeng Men*
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, 130022 Changchun, P.R. China
* *men@ciac.jl.cn*

Stretching a semi-crystalline polymer sample transforms the originally isotropic spherulitical structure into a highly oriented fibrillar one. The underlying mechanism of such transition has been extensively debated. On the one hand, inter- and intra-lamellae slips have been considered to be responsible [1]; whereas on the other hands a process of stress induced melting of the original crystallites and recrystallization of the freed polymeric chain segments along the stretching direction has been also proposed [2]. Based on true stress-strain determination and recovery property investigation on a set of polyethylene of different crystallinity, Strobl et al. concluded that intra-lamellar crystalline block slips are activated at small strains whereas stress induced crystalline lamellae disaggregation-recrystallization starts to occur at a strain larger than yield strain [3]. This critical strain marking the onset of fibrillation is related to the state of amorphous entangled network and the stability of crystalline blocks but has no dependency on the number of tie molecules [4].

In an effort to seek direct experimental evidence on either mechanism, we made use of two selected systems. In one case, the structural evolution of poly(ε-caprolactone) (PCL) and its miscible blends with poly(vinyl methyl ether) (PVME) in different proportions was investigated as a function of strain by in situ synchrotron small-angle X-ray scattering technique. The critical fibrillation strain shifted to larger value with the increasing content of PVME. The discrepancy between the critical strains in these blends could be traced back to a reduction of moduli of the entangled amorphous networks upon addition of PVME. Furthermore, phase separation was detected in the initially miscible mixtures after lamellar to fibrillar transition indicating a complete "melting" of the original lamellar stacks of PCL to release PVME molecules previously located in the amorphous layer between adjacent lamellae. [5] In the second case, stretching induced structural changes in polybutene-1 with stable crystalline modification of form I at elevated temperature was investigated by means of in-situ synchrotron wide-angle X-ray diffraction technique. It was found that oriented metastable form II crystallites with polymer chain aligned along stretching direction gradually appear during tensile deformation. Based on the fact that a solid state I to II phase transition cannot take place due to the restriction in chain conformations and lattice dimensions in both phases, the observed occurrence of transition from form I to form II must proceed via a two-step process. First, those form I crystallites with their polymer chain direction tilted with respect to the stretching direction undergo a stress induced melting process because they experience larger shear stress than the rest. Second, the freed polymer chain segments which have lost their conformational memory in stable form I recrystallize into metastable form II crystallites with their chain direction preferentially aligned along the stretching direction. This result is considered to provide a direct evidence for stress-induced melting-recrystallization mechanism during tensile deformation of semicrystalline polymers. [6]

Acknowledgement

This work is supported by the National Natural Science Foundation of China (21134006).

References

[1] Bowden, P.B.; Young, R.J. J. Mater. Sci., 9 (1974) 2034.
[2] Flory, P.J.; Yoon, D.Y. Nature, 272 (1978) 226.
[3] Hiss, R.; Hobeika, S.; Lynn, C.; Strobl, G. Macromolecules, 32 (1999) 4390.
[4] Men, Y.F.; Rieger, J; Strobl, G. Phys. Rev. Lett., 91 (2003) 095502.
[5] Jiang, Z.Y.; Fu, L.L.; Sun, Y.Y.; Li, X.H.; Men, Y.F. Macromolecules, 44 (2011) 7062.
[6] Wang, Y.T.; Jiang, Z.Y.; Wu, Z.H.; Men, Y.F. Macromolecules, 46 (2013) 518.

Phenomenological theory of the morphologies of polymer crystallites

Yashodhan Hatwalne (Raman Research Institute, Bangalore, India), Jaya Kumar A. (Raman Research Institute, Bangalore, India), and M. Muthukumar (University of Massachusettes, Amherst, USA)

Abstract: I present a unified theory for the morphologies of polymer crystallites (banded spherulites, tents, and scrolls). This theory is based upon the interplay between elasticity of thin crystalline plates, and topological defects. In particular, I focus on the spontaneous chiral symmetry breaking that is observed in banded spherulites of achiral polymers such as poly(ethylene).

Confinement Induced Enhanced Dispersion of Nanoparticles in Ultra-thin Polymer films

Sivasurender Chandran, Nafisa Begam and Jaydeep K Basu*

Department of Physics, Indian Institute of Science, Bangalore, India

** basu@physics.iisc.ernet.in*

We report x-ray reflectivity and microscopy studies on nanoparticle embedded thin polymer films. Detailed analysis of the reflectivity data leads to the extraction of the depth dependent electron density profile, EDP, of the samples. The EDP varies remarkably with the thickness, volume fraction of nanoparticles, φ*p* as well as with grafting (*Mg*) and matrix (*Mm*) molecular weights. Figure 1 below shows the variation of the dispersed fraction of nanoparticles at the surface, interior and interface of such films for various values of the miscibility parameter, *f* (= *Mg*/*Mm*). Clearly, enhanced dispersion of the nanoparticles within the interior of the polymer films is visible for films with the lowest thickness.

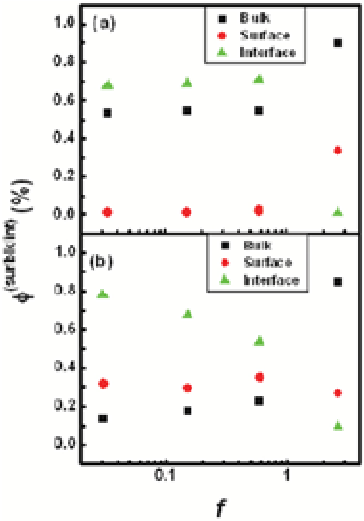


Figure 1. Volume fraction of gold nanoparticles for surface, bulk and interface layers in PS thin films of (a) 20 nm and (b) 60 nm clearly showing enhanced dispersion of the nanoparticles in the former.

Based on this analysis a phase diagram for distinguishing the dispersion and preferential segregation of the nanoparticles as a function of this miscibility parameter, for two different film thickness is constructed. We report the first observation of confinement induced enhancement of dispersion of nanoparticles in polymer thin films and elucidate the possible mechanism responsible for this observation. In addition, we discuss how the glass transition temperature depends both on confinement and nature of dispersion of the nanoparticles in the polymer films.

References

[1] Chandran, S, Basu, J. K. and Mukhopadhyay, M. K., J. Chem. Phys, 138 (2013) 014902.
[2] Chandran, S. and Basu, J. K., Eur. Phys. J E 34 (2011) 99

Long Time Response of Aging Amorphous Polymers

Yogesh M Joshi, Department of Chemical Engineering,
Indian Institute of Technology Kanpur, Kanpur 208016. INDIA.

Aging amorphous polymeric materials undergo free volume relaxation causing slowing down of the relaxation dynamics as a function of time elapsed since thermal quench. Resultant time dependency poses difficulties in predicting long time physical behavior of the same. In this talk we discuss application of effective time domain approach to the experimental data on aging amorphous polymers and demonstrate that it enables prediction of long time behavior over the exceptional time scales. We demonstrate that, unlike conventional methods, the proposed effective time domain approach can account for occurrence of physical aging over the duration of experiments. Furthermore, this procedure successfully describes time – temperature superposition and can allow incorporation of varying dependencies of relaxation time on aging time as well as complicated but known deformation history in the same experiments. This work strongly suggests that effective time domain approach can act as an important tool to analyze long time physical behavior of aging amorphous polymeric materials.

Rubber-like behaviour of Macroporous Colloidal Assemblies

Guruswamy Kumaraswamy[1], R. Raja[1,2], Sayam Sen Gupta[1], Dipak Kumar[3], Shankar Ghosh[3], Giyoong Tae[2]
[1]CSIR-National Chemical Laboratory, Pune, India.
[2]Gwangju Institute of Science and Technology, Gwangju, South Korea.
[3]Tata Institute of Fundamental Research, Mumbai, India.

I will describe macroporous materials obtained by freeze-casting of colloidal dispersions. In the freeze casting method, an aqueous colloidal dispersion is frozen, and a macroporous material that templates the ice crystals is formed. The freeze casting templating strategy is largely independent of the chemistry of the colloidal particles and we show results using colloidal dispersions of silica nano- and microparticles, polystyrene latex particles and hydroxyapatite particles. Large centimeter size scaffolds can be readily prepared using this method. Remarkably, these materials demonstrate reversible elasticity to large compressional strains. We demonstrate that even when we compress the samples to 15% of their original size, the applied strain is completely reversible. These materials can be cycled through several cycles of deformation without any change in their response. Interestingly, these materials show a shear modulus that increases linearly with temperature over a temperature range of over 100°C, suggesting a rubber-like entropic origin for the observed elasticity. This behaviour is in remarkable contrast to macroporous materials obtained by surfactant templating at room temperature, that we have reported previously. The surfactant templated materials are robust and can be readily handled, but are very brittle compared to the ice templated materials. We suggest possible reasons for the observed rubbery nature for the ice templated macroporous materials.

Shielding and de-shielding of hydrogen bonding motifs; from synthetic to bio-polymers

Sanjay Rastogi, Yogesh S. Deshmukh, Jules Harings, Maurizio Villani, Esther Vinken
Department of Materials, Loughborough University, Loughborough, England (UK)
Department of Bio-Materials, Maastricht University, The Netherlands
Department of Complex Fluids, National Chemical Lab., Pune, India
e-mail: s.rastogi@lboro.ac.uk

During the spinning process in spiders and silkworms ions are amongst several other parameters crucial for mediating the transition from the solubilized random coil and/ or helical conformation to crystalline β sheets. Prior to the assembly into β sheets, which give rise to a unique combination of properties, ions inhibit the interchain hydrogen bonding. In this presentation we will show that under specific conditions water can be a good solvent for a range of hydrogen bonded aliphatic polymers including polyamides. Depending on the presence of monovalent or divalent ions and their ionic strength, the dissolution temperature of polyamides can be suppressed to the extent that the amorphous polyamides can be obtained at room temperature. These amorphous polyamides can be oriented, and restoration of hydrogen bonding in the oriented structures can be perceived with the successful removal of the ionic motifs. With the help of dynamic NMR, FTIR spectroscopy and X-ray diffraction the dissolution process of polyamides, shielding and de-shielding process of hydrogen bonding is investigated. Different states of water molecules and their interaction with the polyamides will be also discussed.

References:

[1] Self-organization of Oligopeptides Obtained on Dissolution of Feather Keratins in Superheated Water; Jie Yin, Sanjay Rastogi, Ann E. Terry, and CrisanPopescu; *Biomacromolecules*2007, 8, pp 800-806

[2] Dissolution of Hydrogen-Bonded Polymers in Water: A Study of Nylon-4,6; S Rastogi, AE Terry, E Vinken; *Macromolecule*s 2004; 37(24) pp 8825 – 8828

[3] The Influence of Hydrogen Bonding on the conformaational Changes, the Brill Transition, and Lamellae Thickening in (Co) polyamides, Vinken, E., Terry, A.E., Koning, C.E. and Rastogi, S., *Macromolecules*, 39, 2006, pp 2546-2552.

[4] Vinken, E., Terry, A.E., van Asselen, O., Spoelstra, A.B., Graf, R. and Rastogi, S., "Role of Superheated Water in the Dissolution and Perturbation of Hydrogen Bonding in the Crystalline Lattice of Polyamide 4,6", *Langmuir*, 24, 2008, pp 6313-6326

[5] Jules A. W. Harings, Yefeng Yao, Robert Graf, Otto van Asselen, Rene Broos and Sanjay Rastogi; "Erasing Conformational Limitations in *N*,*N*′-1,4-Butanediyl-bis(6-hydroxy-hexanamide) Crystallization from the Superheated State of Water"; *Langmuir*, 25(13), 2009, pp 7652-7666

[6] PhD thesesTU Eindhoven ; Esther Vinken (2008); Jules Harings (2009); Maurizio Villani(2012) and Yogesh S. Deshmukh(2012)

A new Technique for measuring planar extensional viscosity of polymer solutions.

T.Sridhar and D.A.Nguyen
Department of Chemical Engineering, Monash University, Australia.

As is common for all complex fluids, a thorough understanding of the rheological response of semidilute polymer solutions requires the characterisation of its behaviour in a number of different flow fields. For instance, unlike for simple Newtonian fluids, material properties in extensional flows cannot be derived from a measurement of the material properties in simple shear flow alone. Essentially, the extensional viscosity is an independent material property that provides information about fluid behaviour that is not reflected in the shear viscosity alone.

The development of reliable experimental techniques to examine polymeric fluids under extensional flow conditions has proven to be extremely difficult. Until fairly recently, the steady-state elongational viscosity of a dilute polymer solution was only a theoretical quantity whose existence had not been established experimentally. However, a significant breakthrough in the reliable measurement of extensional properties of polymer solutions has occurred through the development of the filament stretching rheometer [1]. The filament stretching rheometer has so far provided benchmark experimental results on a number of systems, including both dilute and concentrated linear synthetic molecules, dilute solutions of DNA molecules, block copolymer solutions, and solutions of branched and star polymers [2,3]. In turn these results have assisted in a better understanding of the behavior of long chain molecules in strong flows.

As is well known, the current filament stretching rheometer can only produce a uniaxial extensional flow. Most studies of the extensional behaviour of dilute polymer solutions have focused on measuring the uniaxial elongational viscosity, and several Brownian dynamics simulation studies have been able to successfully predict the experimental observations [4]. Unfortunately, for semidilute polymer solutions, measurements of uniaxial elongational viscosity cannot be compared with simulations, since to this date it is only possible to simulate *planar* extensional flows, and not uniaxial extensional flows. For Newtonian liquids there is a well-known relationship between planar and extensional viscosity. However, there is no general relationship linking uniaxial and planar extensional viscosities for any fluid. What this implies is that if we want to validate the prediction of simulations, we need to be able to experimentally generate planar extensional flows, and to accurately measure the planar elongational viscosity. The capacity to produce planar extensional flows in the filament stretching rheometer will therefore be a significant modification of a proven experimental technique in order to produce benchmark data that accommodates an inherent limitation in simulation techniques.

In this talk we describe a modification of the filament stretching rheometer to enable the measurement of planar extensional viscosity. Comparison of results for the same fluid in uniaxial and planar extensional flows is also presented.

References:

[1] G. H. McKinley, and T. Sridhar, Annu. Rev. Fluid Mech., 34, 375, 2002.
[2] R.K. Gupta, D. A. Nguyen, and T. Sridhar, Phys. Fluids, 12, 1296, 2000; P. K. Bhattacharjee, J. P. Oberhauser, G. H. Mckinley, L. G. Leal and T. Sridhar, Macromolecules, 35, 10131, 2002; P. K. Bhattacharjee, D. A. Nguyen, G. H. Mckinley and T. Sridhar, J. Rheol., 47, 269, 2003; T. Sridhar, D. A. Nguyen, R. Prabhakar and J. R. Prakash, Phys. Rev. Lett., 98, 167801, 2007.
[3] P. Sunthar, D. A. Nguyen, R. Dubbelboer, J. R Prakash and T. Sridhar, Macromolecules, 38, 10200, 2005.
[4] Larson, R. G.; Hu, H.; Smith, D. E.; Chu, S. J. Rheol., 43, 267-304(1999); Jendrejack, R. M.; de Pablo, J. J.; Graham, M. D. J. Chem. Phys., 116, 7752 (2002); Hsieh, C.-C.; Li, L.; Larson, R. G. J. Non-Newtonian FluidMech., 113, 147 (2003); R. Prabhakar, J. R. Prakash and T. Sridhar, J. Rheol., 48, 1251, 2004; P. Sunthar and J. R. Prakash, Macromolecules, 38, 617, 2005.

Oral

Collapse Transition in Telechelic Star Polymer Solutions

Ashok Kumar Dasmahapatra* and G. Diwakar Reddy
Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati – 781 039, Assam, INDIA. (*Email: akdm@iitg.ernet.in)

Telechelic star polymers are functionalized star molecules, which have active (viz, functionalized) terminal units. Star polymers with functionalized end groups are amphiphilic copolymers that provide a unique opportunity to prepare nanoscale materials. The functionalized end groups form aggregate by mutual attraction (intra- and/or inter-molecular) to yield varieties of nanoscale structures. In a very dilute solution (much below overlap concentration), aggregation yields globular structure with aggregate of terminal units and the collapsed structure resembles to a "watermelon" [1]. For many chain systems (concentration above overlap concentration), a percolating network is formed due to intermolecular aggregate formation.

We present dynamic Monte Carlo simulation [2] results on the effect of branching on collapse behaviour of telechelic star polymers. We model a star molecule as a molecule containing f number of branches (or arms) originating from a common point (viz., the branch point). For a star polymer with f number of branches and each arm contains n number of repeat unit, the total number of unit becomes $N = f(n-1) + 1$. We take telechelic star polymers with varying f and n, keeping N almost constant. The terminal units are functional groups, which form aggregate due to mutual attraction, in the presence of suitable solvent condition. We observe that with increasing branching number and decreasing arm length (viz. keeping $N \sim$ constant), the collapse behaviour follows a non-monotonic trend with the degree of branching, in comparison with an equivalent series of star homopolymers. The non-monotonic behaviour of telechelic star polymer is attributed to the interplay between enthalpic gain due to end-monomer aggregation and entropic loss due to loop formation. Structural analysis reveals that, aggregation of end group yields a structure resembles to "watermelons" (WM). Simulation results for the systems with varying N (keeping f or n constant and varying n or f) shows the similar mechanism to the constant N system. We also present results on simulation of high functionality telechelic star polymer with shorter arm length, which produces some interesting results. We observe different scenarios depending on the mode of cooling: non-isothermal cooling results in the formation of single aggregate resemble to "watermelon" (WM) morphology (fig. 1) whereas isothermal cooling produces double aggregates [3]. Isothermal cooling may be a kinetically driven process, where crowding entropy (due to high monomer density near the branch point) dominates over enthalpic gain; whereas, in isothermal cooling, enthalpic gain dominates over entropic loss.

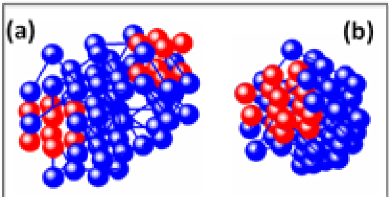


Figure 1. Collapsed structures for $f = 16$, $n = 5$: (a) isothermal and (b) non-isothermal experiments. Blue: m-units; red: c-units.

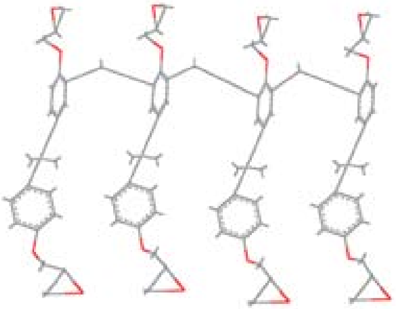
References

[1] Lo Verso, F.; Likos, C. N.; Mayer C.; Löwen, H. *Phys. Rev. Lett.* 96, (**2006**) 187802.
[2] Dasmahapatra, A. K.; Kumaraswamy, G.; Nanavati H. *Macromolecules* 39, (**2006**) 9621.
[3] Dasmahapatra, A. K.; Reddy, G. D. *Polymer*, (**2013**), doi: 10.1016/j.polymer.2013.02.048.

Nanoindentation of Dense, Crosslinked Glassy Epoxy, SU-8, and its Data Analyses

Sandipan Chattaraj[a], Prita Pant[b], Dnyanesh Pawaskar[c] and Hemant Nanavati[d, *]
a. Centre for Research in Nanotechnology and Science
b. Metallurgical Engineering and Materials Science Department
c. Mechanical Engineering Department
d. Chemical Engineering Department
Indian Institute of Technology Bombay
Mumbai-400076 INDIA, hnanavati@che.iitb.ac.in

SU-8, a negative photoresist, has been used widely in the microelectronics industry as a mask for device fabrication. It is also used as cantilevers for sensing applications and for high aspect-ratio and 3D lithographic patterning [1]. Most of the applications of SU-8 are as thin films on substrates. Hence, it is necessary to understand the material's localized and application-relevant mechanical behaviour. Nanoindentation is an important experiment to obtain such information. However, data analyses of nanoindentation using conventional methods [2] are not accurate in case of soft materials like polymers [3]. Refinements to these methods are necessary to accurately estimate elastic modulus and hardness. One of the sources of errors is the conventional power-law fitting of the unloading curve to calculate stiffness. Systemic errors in determining the stiffness will lead to inappropriate estimates of contact area, hardness and elastic modulus. Another source of error in determining elastic modulus and hardness, is the calibrating material. Calibrating with polycarbonate is more suitable than with quartz, when analyzing the raw load-displacement data of SU-8.



In the current work, the molecular structure of SU-8 has been simulated using Accelrys Materials Studio [4]. Figure 1 shows the SU-8 structure as constructed in 2D. Thin films of SU-8 have been prepared, nanoindentation experiments have been performed and the results have been analyzed with conventional methods by doing power-law fit and polynomial fit. Also, the effect of the calibrating material is investigated - a comparative study between the results with quartz and those with polycarbonate, has been perfomed. SU-8 has been characterized by DSC and FTIR spectroscopy. It has been established by FTIR spectroscopy that the degree of cross-linking increases substantially after the curing process. Finally, to interpret the nanoindentation data correctly, we propose a hybrid molecular-continuum constitutive model, containing direct load-displacement (instead of stress, strain and strain rate) mechanical elements - springs, dashpots and slider.

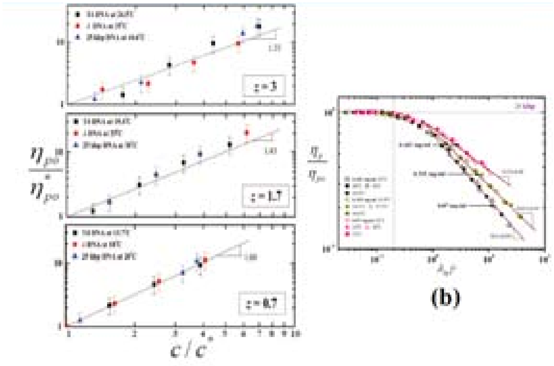
References:

[1] Campo, A.D. and Greiner, C. *Journal of Micromechanics and Microengineering* 17, 6 (**2007**) R81
[2] Oliver, W.C. and Pharr, G.M. *Journal of Materials Research* 7, 1 (**1992**) 1564
[3] Tranchida, D.; Piccarolo, S. ; Loos, J. and Alexeev, A. *Macromolecules* 40, 4 (**2007**) 1259
[4] "Materials Studio" Accelrys. 2001-2011 Accelrys Software Inc.

Shear rheology of semi-dilute DNA solutions: Close-to and Far from equilibrium

Sharadwata Pan[1,2,3], Duc At Nguyen[3], P. Sunthar[2,1], T. Sridhar[3,1], and J. Ravi Prakash[3,1,*]
[1] *IIT-B Monash Research Academy, IIT Bombay, Powai, Mumbai-400076, INDIA*
[2] *Department of Chemical Engineering, IIT Bombay, Powai, Mumbai – 400076, INDIA*
[3] *Department of Chemical Engineering, Monash University, Melbourne, VIC 3800, AUSTRALIA*
**For correspondence. E-mail: ravi.jagadeeshan@monash.edu*

Extensive theoretical and experimental studies have been carried out so far to investigate the rheological properties of dilute polymer solutions and polymer melts in shear flow [1 – 5]. However, a systematic experimental study to understand the rheological properties of polymer solutions in the semi-dilute regime is currently lacking in terms of understanding the influence of concentration, temperature and molecular weight. Knowledge of the rheological behavior of semi-dilute polymer solutions, which is characterized by significant hydrodynamic interactions and viscoelastic effects, is of crucial importance in a number of industrial and biological contexts. In this work, the shear rheology of linear DNA molecules in a wide range of molecular weights (25 – 165.6 kilobasepairs), temperatures and concentrations, has been investigated. DNA solutions have the advantage of being nearly perfectly monodisperse. Steady state shear viscosities, in both the dilute and semi-dilute regimes, have been determined.



(a)

(b)

The dependence of the zero shear rate viscosity on concentration is observed to display universal behaviour that can be understood in the framework of scaling theories for polymer solutions (see Fig. (a)). Further, the shear rate dependence of viscosity, at various temperatures and concentrations, can be collapsed onto master curves when interpreted in terms of a concentration dependent Weissenberg number (see Fig. (b)). The material functions obtained in this work will provide benchmark data that are useful for the characterization of these industrially important systems, and for the validation of theoretical studies.

References:

[1] Smith, D. E.; Babcock, H. P.; Chu, S. *Science* 283 (**1999**) 1724.
[2] Winkler, R. G.; Mussawisade, K.; Ripoll, M.; Gompper, G. *J. Phys.: Condens. Matter* 16 (**2004**) S3941
[3] Schroeder, C. M.; Teixeira, R. E.; Shaqfeh, E. S. G.; Chu, S. *Phys. Rev. Lett.* 95 (**2005**) 018301
[4] Jose, P. P.; Szamel, G. *J. Chem. Phys*. 127 (**2007**) 114095
[5] Kim, J. M.; Edwards, B. J.; Keffer, D. J.; Khomami, B. *Phys. Lett. A* 373 (**2009**) 769

Dynamics of Dense Microgel Suspensions

Samruddhi Kamble[a], Ashish Lele[a], Rajdip Bandopadhyaya[b], Suresh Bhat[a] and Sarika Bhattacharya[a]*
[a]*Polymer Science and Engineering Division, National Chemical Laboratory,Pune , India.*
[b]*Department of Chemical Engineering, Indian Institue of Technolgy(IITB), Mumbai India.*
** mb.sarika@ncl.res.in*

We investigate dense microgel suspensions of PolyN-isopropylacrylamide (PNIPAm) close to and above the glass transition volume fraction by using Diffusive Wave Spectroscopy. Being thermoresponsive, the particle size of a PNIPAm microgel decreases on increasing temperature. This allows for precise tuning of volume fraction of the suspension by changing temperature[1]. Concentrated suspensions showed a non-zero plateau in the decay of the temporal autocorrelation function indicating kinetically arrested state [2][3]. Increasing volume fraction by decreasing temperature caused a continuous evolution of the plateau to higher values (see Figure 1). At still lower temperatures of < 11°C (, the showed an extra plateau occurring at intermediate lag times. We attribute this complex dynamics to a Hertzian repulsive potential of the microgels caused by their dense-core/soft-shell microstructure. The long-time plateau results from a core-core repulsive interaction, while the extra plateau at intermediate times occurs due to brush-core interaction caused by the interpenetration of the brushes at high volume fractions (see Figure 2).

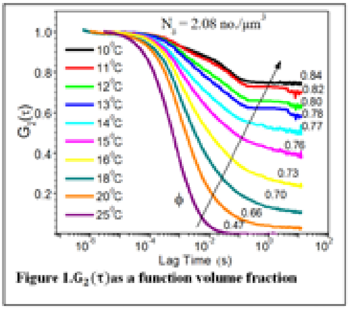


Figure 1.G_2 (τ)as a function volume fraction

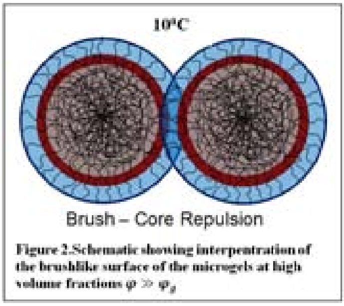


Figure 2.Schematic showing interpentration of the brushlike surface of the microgels at high volume fractions φ≫φ_g

References:

[1] Pelton and Chibante, "Preparation of Aqueous Latices with N- Isopropylacrylamide," *Colloids and Surfaces*, vol. 20, pp. 247–256, 1986.

[2] P.N.Pusey and W. Van Megen, "Phase behaviour of concentrated suspension sof nearly hard collloidal spheres," *Nature*, vol. 320, pp. 340–342, 1986.

[3] P. Chaudhuri, L. Berthier, P. I. Hurtado, and W. Kob, "When gel and glass meet: A mechanism for multistep relaxation," *Physical Review E*, vol. 81, no. 4, pp. 1–4, Apr. 2010.

Poster

PH1

Layered Double Hydroxide/Syndiotactic Polystyrene Nanocomposites: Structure, Morphology and Properties

Nagendra Baku, E. Bhoje Gowd*
Materials Science & Technology Division,
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Trivandrum, Kerala, India – 695019
bhojegowd@niist.res.in

Highly stereoregular syndiotactic polystyrene (sPS) has received considerable interest in recent years because of its high degree of polymorphism with five crystalline forms ($\alpha, \beta, \gamma, \delta,$ and ε). Each crystalline form was found to have different sets of properties and, therefore, this material can be used for different applications. In the present work, we have prepared nanocomposites based on sPS and layered double hydroxides by solution blending in xylene. Figure 1a shows the TEM image of unmodified Mg Al LDH. As can be seen, LDH sheets are uniform in size with a mean lateral size of 3 μm. Isothermal and non-isothermal crystallization studies were conducted on nanocomposites to understand how LDH sheets influence the kinetics of sPS crystallization. In isothermal crystallization studies, crystallization half-time ($T_{1/2}$) was found to decrease with the amount of LDH indicates the enhancement of crystallization rate. In non-isothermal studies, similar observation was made where melt crystallization temperature (T_c) of nanocomposites is higher in nanocomposites than the pristine sPS (Figure 1b). Enhance in the crystallization rate of sPS may be due to nucleating effect of LDH platelets.

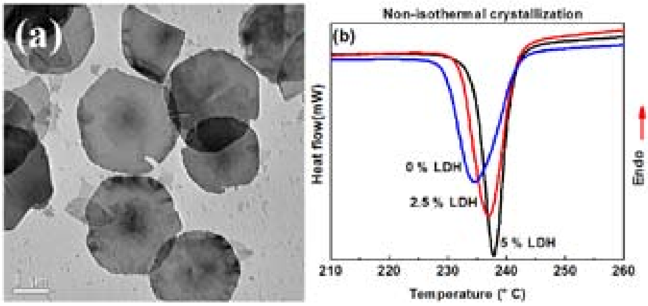


Figure 1: (a) Transmission electron microscopy (TEM) image of LDH (b) DSC cooling scans of sPS and sPS/unmodified LDH nanocomposites

Thermal stability of sPS has been significantly increased with the addition of LDH. Wide angle X- ray diffraction patterns of melt-quenched samples revealed that the sPS/LDH nanocomposites crystallized in to the thermodynamically stable *β*- form and amount of the *β*- form increases with increasing LDH content. A further study on the flammability of the nanocomposites is currently in progress.

References:

[1] Gowd, E. B.; Tashiro, K.; Ramesh, *C. Prog. Polym. Sci*. 34 **(2009)** 280.
[2] Adachipagano, P.; Forano, A.; Basse, J. *J. Mater. Chem.* 13 **(2003)** 1988.
[3] Leroux, F.; Besse, J. P. *Chem. Mater.* 13 **(2001)** 3507.

PH2

Structural and dynamical properties of polyethylenimine in explicit water at different protonation states: a molecular dynamics study

Chandan Kumar Choudhury, Sudip Roy*
[a]Polymer and Advanced Materials Laboratory, National Chemical Laboratory, Pune, India
* s.roy@ncl.res.in

Polyethylenimine (PEI) is a pH sensitive polymer [1] which acts a proton sponge in acidic conditions. Linear PEI is very efficient gene delivery agent [2]. Despite many experimental and theoretical efforts, fundamental understanding of the structure and dynamics of linear PEI chains in dilute solutions remains a topic of discussion. We will be presenting the structural properties of PEI at different protonation states (representative of different pH) using all atomistic molecular dynamic simulations. Our work reveals the structure of PEI at high and low pH is coiled and elongated, respectively (Fig. 1) [3, 4]. We will also present the dynamics and ordering of water molecules of the solvation shells of the PEI chain. From these calculations, we observe that the water molecules get ordered along the backbone and hop to the neighbouring solvation shell for a completely protonated PEI chain while for the unprotonated system, water molecules also hops to the spatially neighbouring shells. The residence time and the self-diffusion of water molecules in the solvation shells and their activation barriers will also be presented. We will conclude the study by correlating the solvation shell water dynamics and the structure of the PEI chain at different protonation states. In addition to the PEI in dilute solution, properties of bulk PEI will also be presented.

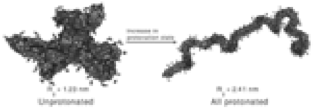


Figure 1. PEI conformation and its solvation shell at different protonation states.

References

[1] [1] J. P. Behr, Chimia 1997, 51, 34
[2] [2] L. Wightman et al. J. Gene Med. 2001, 3, 362
[3] [3] K. P. Sharma et al. J. Phys. Chem. B2011, 115 (29), 9059
[4] [4] C. K. Choudhury et al. Soft Matter 2013, 9, 2269

PH3

Heterophasic Polypropylene Copolymer EPR Understanding By Isothermal Crystallization and Transcrystallization

[a] Debabrata Mukhopadhyay*, Haldia Petrochemicals Limited,
[b] Dipak K Mana, Dept. of Polymer Science and Technology, University of Calcutta, India,
[b] Priyabrata Sarkar, Dept. of Polymer Science and Technology, University of Calcutta, India,
[a] Subhajit Dandapath, Haldia Petrochemicals Limited,
*Email: Debabrata.Mukhopadhyay@hpl.co.in,

Heterophasic Polypropylene Copolymer Understanding
The heterophasic copolymers are intimate mixtures of homopolymer and bipolymers and the product is termed as “heterophasic copolymer” as it is a mixture of two different products, homopolymer and bipolymer. The biopolymer so far is known to be comprising of amorphous ethylene – propylene copolymer phase (EPR), the present study will try to unfold the slice of the morphology by isothermal crystallization and melt shearing through transcrystallization in high melt flow index (~ 10) heterophasic polypropylene copolymer. The study will also try to unfold interfacial crystallization between polypropylene matrix and ethylene – propylene copolymer and model emerging thereof.

It has been seen that crystalline ethylene propylene copolymer phase at interface plays a role in controlling the overall morphology of heterophasic polypropylene copolymer as being depicted by modified model as also referred by other authors through other experimental route.

*contact

PH4

Rheological, Morphological and Fracture Toughness Behavior of MWNT Reinforced Stereo-Complex Polypropylene Nanocomposites

Dibyendu Das and Bhabani K. Satapathy*
Centre for Polymer Science and Engineering,
Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

The present paper deals with the fracture toughness assessment and their plausible correlations with rheological and morphological parameters of MWNT (0 to 3 wt %) reinforced stereo-complex polypropylene (i-PP/s-PP: 70/30). Nanocomposites based on i-PP/s-PP/MWNT were prepared by diluting i-PP/MWNT master-batch via melt-mixing in a co-rotating twin screw extruder. The crack resistance behaviors of the nanocomposites have been studied following the essential work of fracture (EWF) approach [1] and their interrelation to the morphological attributes have been discussed in the realms of dispersion and distribution characteristics. Improvement in the crack propagation resistance as indicated by the non-EWF (βw_p) values have been observed, as evident from the *Figure* below, till 1.0 wt. % of MWNT content in the nanocomposites followed by a linear decrease indicating tough to quasi-brittle transition.

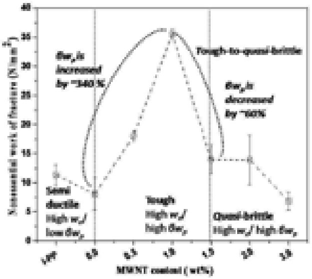


Fig.1: Variation of nonessential work of fracture with MWNT content

Rheological measurements, as an indirect assessment of fracture toughness, were carried out to study the influence of MWNT on the internal network structures of i-PP/s-PP blend matrix [2] and the interaction between them. The rheological results showed a fluid-solid transition in the composition range of 1.0-1.5 wt% of MWNT, beyond which a continuous MWNT network is formed throughout the matrix, which in-turns decrease the fracture toughness. To ascertain the nature of crack growth, time-synchronized deformation data prior to failure were acquired as images at various time scales using a structured specimen in a gray contrast and integral computation of all the deformation stages using GOM Aramis software. Furthermore, transmission electron microscope (TEM) and scanning electron microscope (SEM) analyses were done to study the dispersion/distribution and failure mechanism respectively.

References

[1] Bárány, T.; Czigány, T.; Karger-Kocsis, J. *Progress in Polymer Science* 35 **(2010)** 1257.
[2] Prashantha, K.; Soulestin, J.; Lacrampe, MF.; Krawczak, P.; Dupin, G.; Claes, M. *Composites Science and Technology* 69 **(2009)** 1756.

PH5

Modelling Sulfonated Poly(ether ether ketone), sPEEK for Rheological Studies

Madhusmita Tripathy[a]*, P. B. Sunil Kumar[a], Abhijit P. Deshpande[b]
[a] *Department of Physics, Indian Institute of Technology Madras,*
Chennai - 600036 INDIA
[b] *Department of Chemical Engineering, Indian Institute of Technology Madras,*
Chennai - 600036 INDIA
*madhusmita@physics.iitm.ac.in

Polymer electrolyte membrane or proton exchange membrane (PEM) fuel cell has attracted a lot of attention as one of the most promising non-polluting power source. One of the main components of this fuel cell is a polymer film separating the anode and cathode, which allows only protons to pass through while blocking the fuel from crossing over. Sulfonated poly (ether ether ketone), sPEEK(fig. 1 [1]) is such an emerging alternative to the widely used Nafion from DuPont [2]. We intend to investigate if externally imposed deformations (shear/extension) can alter the structure of water channels in the hydrated polymer, which are supposed to be the key to its performance.

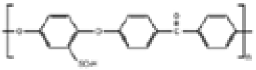


Figure 1 Schematic of a sPEEK monomer

To be close to the real polymer interactions, we intend to perform mesoscale molecular dynamics (MD) simulation for such studies, rather than taking up field theoretic approach used earlier for such complex polymeric systems[3,4]. The main task here is to come up with the correct mesoscale potentials. We have performed atomistic MD simulation on the system to collect various bonded (bond, angle, dihedral) and non-bonded (RDF) correlations between the suitably chosen 'mesoscale beads' or 'super-atoms' defined along the polymer backbone (fig. 2). We have used Boltzmann Inversion coarse-graining method [5], previously applied to relatively simpler polymers such as poly-isoprene [5] and poly-styrene [6], by which, starting with these atomistic correlation data, we can compute the realistic coarse-grained interaction potentials in an iterative manner. These mesoscale potentials will be used to perform MD simulation at a higher length and time scale which will eventually help in exploring the rheology of the polymer. I will be discussing the validity and applicability of this coarse-graining model.

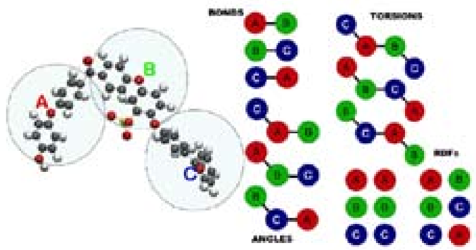


Figure 2 Atomistic to CG mapping for sPEEK

References

[1] Mahajan, C. V.; Ganesan, V. *Journal of Physical Chemistry B*, 114 (**2010**) 8357.
[2] Mauritz, K. A.; Moore, B. *Chemical Reviews,* 104 (**2004)** 4535.
[3] Komarov, P. V. ; Veselov, I.N.; Chu, P.P.; Khalatur, P.G. *Soft Matter*, 6 (**2010**) 3939.
[4] Komarov, P. V. ; Veselov, I.N.; Chu, P.P.; Khalatur, P.G.; Khokhlov, A.R. *Chemical Physics Letters*, 487 (**2010**) 291.
[5] Reith, D.; Putz, M.; Muller-Plathe, F. *Journal of Computational Chemistry*, 24(13) (**2003**) 1624.
[6] Sun, Q.; Faller, R. *Journal of Chemical Theory and Computation*, 2(3) (**2006**) 607.

PH6

Structural, Dielectric, Photoluminescence and Magnetic Properties of Ti3+, Cr3+and Fe3+: PVDF Polymer Films

M. Obula Reddy
Loyola Degree College(YSRR)
Mormphil@gmail.com

Transparent and more stable reference and 3d ions (Ti^{3+} ,Cr^{3+} & Fe^{3+}) each ion separately doped polymer films of good quality have been developed from poly (vinylidene fluoride) (PVDF) with a solvent of N,N-Dimethylacetamide (DMA) through a conventional solution casting method. The XRD profiles have confirmed semi-crystalline structures in α-, β- and γ- PVDF phases [1, 2]. Due to the presence of the transition metal ions in these films, significant improvement in the ionic conductivity measurement have been noticed and this encouraging situation could be explained upon employing free volume theory for validation. The dielectric behaviors of these films have been analyzed using dielectric permittivity (ε^1), dissipation factor (tan δ) and impedance spectra (Z^1 and Z^{11}) Fig.1(a-c) [3-6].

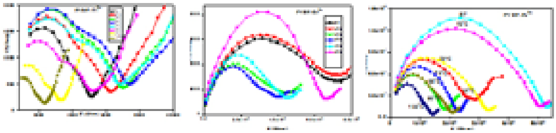


Fig.1 (a-c)

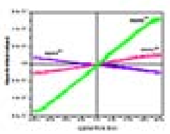


Fig. 2

VSM measurements have confirmed that the PVDF: Ti^{3+} exhibits anti-ferromagnetic nature, in regards to PVDF: Cr^{3+} film ferromagnetic nature and from the PVDF: Fe^{3+} film strong paramagnetic nature Fig.2(a-c) [7-8]. Thus the present study has successfully explored the fact that these optical materials are also potential enough in both conductivity and magnetic properties for their use in applications suitably.

References:

[1] Abdelaziz, J Magn Magn Mater,;279 **(2004)** 184-194.
[2] Park YJ, Kang YS, Park C, Eur. Polym. J., 41 **(2005)** 1002.
[3] Macdonald, J.R., J. Chem. Phys., 61(10) **(1974)** 3977-3996.
[4] Ravikumar RVSSN, Yamauchi J, Chandrasekhar AV, Reddy YP, Sambasivarao P J.Mol.Struct.; 740 **(2005)** 169-173.
[5] Ku CC, Liepins R,Electrical properties of polymers, Hanser Publishers,New York **(1987)**.
[6] Hedvig P, Dielectric Spectroscopy of polymers, AdamHilger,Bristol, **(1977)**.
[7] Chuanhui Xia, Chenguo Hu, Peng Chen, Buyongwan, Xiaoshan He ,Yongshu Tian, Mater. Res. Bull. 45 **(2010)** 794-798.
[8] Subramanian M, Tanemura M, Hihara T, GanesanV, SogaT, Jimbo T, Chem. Phys. Lett., 487 **(2010)** 97-100.

PH7

Structure of poly(methacrylic acid) chain in water – ethanol mixed solvent system investigated by molecular dynamics simulations.

Praveenkumar Sappidi and Upendra Natarajan
Molecular Modeling and Simulation Laboratory, Dept. of Chemical Engineering,
Indian Institute of Technology Madras, Chennai 600036.
Emails: praveenche@gmail.com; unatarajan@iitm.ac.in.
Ph. 91-44-22574184. Fax. 91-44-22574150, 22574152.

Conformational structure of an *atactic* poly(methacrylic acid) PMA chain in water – ethanol mixed solvent system was investigated by atomistic MD simulations using explicit solvent and ions. Ethanol concentration in the mixture is varied in the range 0% (vol/vol) - 90 %. The chain conformational properties such as R_g, torsion angle distribution, intermolecular and intra–chain hydrogen bonding characteristics and atom pair distribution functions were estimated. PMA chain in aqueous solution shows conformational transitions [1, 2]. PMA in water – alcohol mixture shows conformational transition that is driven by mixture composition (solvent quality) [3]. Our simulation results show increase in R_g with ethanol concentration in agreement with experimental results, the chain conformations are shown in figure 1. The number of hydrogen bonds between PMA – water molecules exhibits a decrease with increase in ethanol concentration. The hydrogen bonding between PMA and ethanol is enhanced by the overall concentration of ethanol, which shows the significance of the localization of ethanol molecules by displacement of water molecules due to hydrophobic salvation.

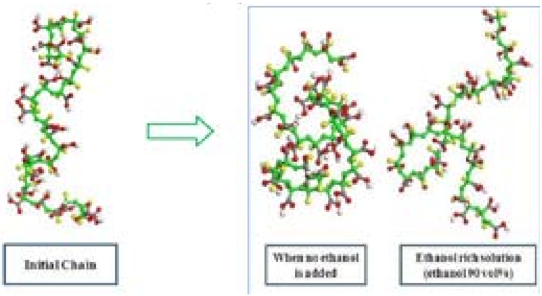


Figure 1. PMA Chain conformations influenced by mixture concentration.

References.
[1] Mandel, M.; Leyte, J. C.; Stadhouder, M. G.; *J. Phys. Chem.* 71(**1967**), 603.
[2] Dusek, K.; Patterson, D. *J. Polym. Sci: Part B: Polym. Phys.* 6(**1968**), 1209.
[3] Priel, Z.; Silberberg, A.; *J. Polym. Sci.* 8A-2(**1970**), 705.

PH8

Association studies of Poly(methacrylic acid) investigated by molecular dynamics simulations

Rajalakshmi Chockalingam and Upendra Natarajan
Molecular Simulation and Modeling Laboratory, Dept. of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036.
Emails: rajic.lingam@gmail.com; ch11d029@smail.iitm.ac.in; unatarajan@iitm.ac.in.
Ph. 91-44-22574184. Fax. 91-44-22574150, 22574152.

Self-association of *atactic* Poly(methacrylic acid) PMA chains in aqueous solution at 25^o C was studied via fully atomistic molecular dynamics (MD) simulations in explicit solvent. The effect of degree of ionization on self-association was investigated for multiple (3) chains of PMA in the range 0-100%. It was found that the association of PMA chains occurred only in the unneutralized (acid) form of PMA chains consistent with the experimental studies [1, 2]. This is due to the fact that the hydrogen bonding, which exists in the acid form of PMA, favors the association to occur, and due to the repulsive forces between the carbonyl groups of the PMA chains, association does not occur at the remaining degree of ionization other than the acid form. It is observed that, with an increase in degree of ionization causes an increase in Rg of multiple chains of PMA, similar to what has been observed [3] in very dilute single chain system. Hydrogen bond analysis has been done within the chains and between the chains and solvents. It is found that as degree of ionization increases, intermolecular hydrogen bonding increases and intra-molecular hydrogen bonding decreases. The intermolecular structure has been analyzed via radial distribution functions of chain with solvent molecules and counter ions. From our simulations, it is also observed that, with an increase in the concentration of the acid form of multiple PMA chains systems in going from dilute to semi dilute to highly concentrated,(i.e. from 0.00972 mol/l to 0.042 mol/l) the extent of intra-molecular hydrogen bonding increases and this makes the self association stronger, Additionally, chain conformational statistics (using torsion distributions) and interchain distances in these systems has been analyzed via our simulations.

References:

[1] Kogej, K.; Berghamns, H.; Reynaers, H.; Paoletti, S. *J. Phys. Chem.* 108 (**2004)** 18164
[2] Jerman, B.; Breznik, M.; Kogej, K.; Paoletti, S. *J. Phys. Chem.* 111 (**2007)** 8435
[3] Sulatha, M.S.; Natarajan, U. *Ind. Eng. Chem. Res.* 50 **(2011)** 11785

PH9

Influence of Host Preparation Method on the Structural Phase Transitions of Syndiotactic Polystyrene upon the Guest Exchange with n-Alkanes

P. Shaiju, Robbinson C. Jose, Baku Nagendra and E. Bhoje Gowd*
Material Science and Technology Division,
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Trivandrum, Kerala, India – 695019
bhojegowd@niist.res.in

The effect of host preparation method on the structural changes of syndiotactic polystyrene (sPS) upon the guest exchange process with a series of *n*-alkanes (n = 8, 9 and 10) was investigated by means of X-ray diffraction and Fourier transform infrared spectroscopy. For that purpose, we prepared sPS-solvent complexes using chloroform and toluene as guests starting with different thermal histories like amorphous, α and γ forms. The solvent exchange process was performed by dipping these samples in a series of n-alkanes (n-octane to n-decane) for 32 days. When the chloroform treated amorphous sample (δ_{chl}) is used for the guest exchange with n-alkanes, it is observed that the monoclinic δ_{chl} sample transformed in to the mixture of the δ form (triclinic) and the ε forms. On the other hand, chloroform treated α form samples (δ_{chl}) transformed into the triclinic δ form alone upon the guest exchange with n-alkanes. In another case, where chloroform treated γ form samples (δ_{chl}) were used, the δ_{chl} form transformed in to the ε form alone upon the guest exchange with n-alkanes. This research has clarified that the starting morphology of the samples used for the preparation of the sPS/chloroform complex influences the phase transitions of sPS upon the guest exchange process. On the other hand, toluene treated amorphous and α form samples (δ_{tol}) transformed into the triclinic δ form irrespective of the starting morphology, whereas the toluene treated γ form transformed back to the γ form upon the guest exchange process. It was also found that the degree of crystallinity of the starting sample plays an important role on the structural phase transitions upon the guest exchange process.

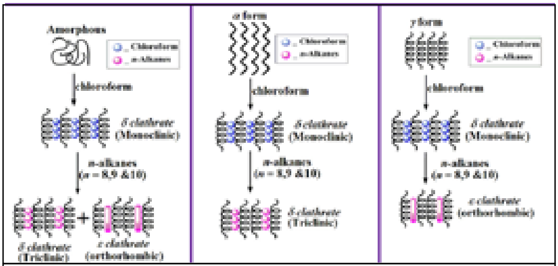


Figure: Schematic diagrams showing the guest exchange process of chloroform treated samples of sPS having different initial morphologies

References

[1] Gowd EB, Tashiro K, Ramesh C. *Prog. Polym. Sci.*, 34 **(2009)** 280
[2] Tarallo O, Schiavone M M, Petraccone V. *Polymer*, 52 **(2011)** 1426
[3] Gowd E B, Tashiro K. *Polymer*, 52 **(2011)** 822

PH10

Strong Confinement Induced Reduction In The Extent Of Entanglement Of Polymers And Its Effect On Enhancing The Dispersion Of Embedded Particles

Sivasurender Chandran, N. Begam and J. K. Basu*
[a]*Department of Physics, Indian Institute of Science, Bangalore, 560012, India*
** basu@physics.iisc.ernet.in*

Tube theory has caught the attention of the community and has taken the central stand because of its simple frame work in understanding the structure and dynamics of entangled polymer melts. The very nature of the theory gives rise to a length scale i.e., tube diameter, controlling the dynamics. But the key question about the theory remains still open i.e., what happens to the extent of entanglement when polymers are confined to the dimensions comparable to that of the tube diameter or molecular diameter? Though there are lot of reports on the subject, the findings are still inconclusive [1 – 4]. Herein, we report reduction in the electron density (Fig-1) of pure polymers, with confinement. We have spun casted pure atactic polystyrene films with the thickness ranging from 20 to 60 nm i.e., 2 to $8R_g$. The films were then annealed at high temperature under vacuum for long time to remove the effect of trapped solvent. The electron density at $8R_g$ is comparable to that of bulk where as the deviation becomes more vital at $2R_g$. This reduction in electron density (linearly scales with the mass density) suggests the increase in free volume, there by decrease in the extent of entanglement. We have also studied the dispersion of polymer grafted nanoparticles for different ratios of grafting (M_g) to matrix (M_m) molecular weights, which we define as miscibility parameter, f ($\sim M_g/M_m$). The studies are made for two different thicknesses of the films viz., 20 and 60 nm. To our knowledge for the first time, we have shown the enhancement in the dispersion of the embedded particles just by the effect of physical confinement. We have proposed a model to understand the observed enhancement in dispersion using the decrease in the extent of entanglement apart from the possible entropic contributions. In addition we have also constructed a phase diagram distinguishing the segregated and completely dispersed samples for different thickness (Fig-2). We believe that these findings will have a larger impact on the physics of polymers under confinement, self and driven assembly of particles &c., apart from the obvious applications in technology.

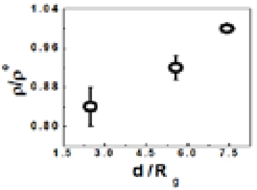


Figure-1.Electron density, ρ, of PS films normalized to the bulk electron density, ρ° as a function of reduced thickness (d/R_g). Decrease in the electron density with confinement

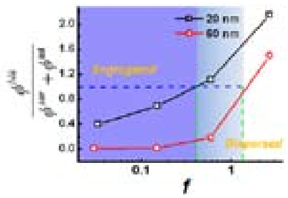


Figure-2. Ratio of the particles dispersed (φ^{blk}) to the particles segregated ($\varphi^{sur}+\varphi^{int}$) as a function of miscibility parameter, f. Enhanced dispersion with confinement could be witnessed.

References

[1] Mukhopadhyay, M, K.; et.al. *Phys. Rev. Lett*, 101 (**2008)** 115501.
[2] Wallace, W, E.; et.al. *J. Chem. Phys*, 108 **(1998)** 3798.
[3] Xu, S.; O'Connel, P, A.; Mckenna, G, B.; *J. Chem. Phys,* 132 **(2010)** 184902.
[4] Mayer, H.; et.al. *J. Phys. IV France,* 1 (**2008)** Pr1-1.

PH11

Surface vs Bulk In-Situ Polymerization for Oriented Transparent Conducting Polymers

Smita Mukherjee[a*], Rekha Singh[b], Anshu Kumar[b], Bikash K. Sikder[b], Sengottaiyan Thangapal[b] and Anil Kumar[a,]
[a]Centre of Excellence in Nanoelectronics, Indian Institute of Technology-Bombay, Powai-400076, Mumbai, India.
[b]Department of Chemistry, Indian Institute of Technology-Bombay, Powai-400076, Mumbai, India.
*Email:smita.mukherjee08@gmail.com

Polymers based on 3, 4-alkylenedioxythiophenes (ADOTs) are potential candidate for transparent conductors (TCs) [1], exhibiting high thermal and chemical stability as well as low band gap. Preparation of ultrathin films of oriented TC polymers (TCPs) is of utmost importance for device applications. Moreover, understanding their structure-property correlations has become an integral part for design of better TCs. However, realization of ultrathin films based on ADOTs and understanding their intrinsic process, viz. oxidative polymerization [2] is still a challenge. Our group aims at achieving the same by three different approaches, using surface and bulk in-situ polymerization.

The first approach, viz. Langmuir-Blodgett technique [3] provides an elegant way of understanding oxidative polymerization, along with preparation of ultrathin TCP films with molecular level control, which offers amplified sensitivity and real-time responses over bulk TCP. For this, surface pressure-molecular area (π-A) isotherms of mixed Langmuir monolayers of stearic acid (StA) and monomers based on 3,4-alkylenedioxythiophene (ADOTs), have been studied, both in presence and absence of ferric chloride as an oxidant. Preliminary results on area per molecule and phase changes of the mixed monolayers indicate strong interplay of hydrophobic and hydrophilic interactions at air-water interface, mediated through probable interaction with subphase ions and hydrocarbon chains. Moreover, results show existence of a concentration window for the monomer within which in-situ surface polymerization occurs (Fig. 1), and beyond which surfactant-monomer interactions become dominant. Ultrathin films transferred onto solid substrates from both concentration regimes show difference in their structures, as is evident from preliminary FTIR studies. Within the window region, the film shows strong evidence of interaction of the polymer with hydrocarbon chain of StA, thereby hinting at the possibility that polymer chains follow the ordering of the StA matrix. Although it is difficult to comment on the efficiency of these ultrathin films in the context of device application at this preliminary stage, it is worthwhile mentioning that the same appears to be promising candidate as ordered templates for bulk coated TCPs.

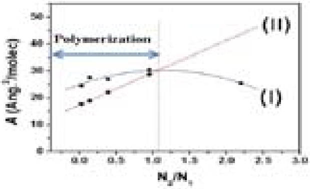


Figure 1: Observed (I) and expected (II) change in monolayer area/molec. with monomer/surfactant conc. ratio

The other two approaches undertaken essentially include bulk polymerization techniques. In one, thin films of PEDOT: PSS is treated with secondary additives [1, 4] to phase separate the PSS layer and align the PEDOT chains to obtain enhanced conductivity. In the other method, in-situ polymerization [5] is achieved by spinning alternate layers of oxidant and monomer in a layer-by-layer manner, yielding uniform films with enhanced transparency and conductivity. Both methods are promising except for factors like batch specificity of polymer used as well as poor thickness control. Work is underway to overcome these hurdles.

References

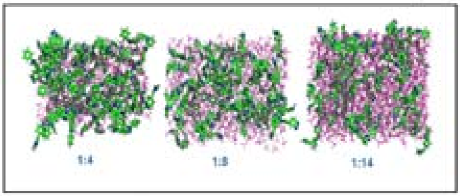
[1] Xia, Y.; Sun, K.; Ouyang, J.; *Adv. Funct. Mater.,* 24 **(2012)** 2436.
[2] Ha,Y. H.; Nikolov, N.; Pollack, S. K.; Mastrangelo, J.; Martin, B. D.; Shashidhar, R.; *Adv. Funct. Mater.* 14 **(2004)** 615.
[3] M.C. Petty, *Langmuir-Blodgett Films: An Introduction*, Cambridge University Press: Cambridge, 1996.
[4] Badre ,C.; Marquant ,L.; Alsayed ,A. M.; Hough, L. A.; *Adv. Funct. Mater.,* 22 **(2012)** 2723.
[5] McFarlane, S. L.; Deore, B. A.; Svenda, N.; Freund M. S.; *Macromolecules, 43* **(2010)** 10241.

PH12

Molecular Dynamics Simulation of Polybenzimidazole Mixed With Phosphoric Acid: A Potential Polyelectrolyte Membrane for Fuel Cell

Swagata Pahari and Sudip Roy*
Physical Chemistry Division, National Chemical Laboratory,
Pune-411008 INDIA

Polymer electrolyte membrane fuel cell (PEMFC) can generate power with high efficiency and minimal pollution and have various applications in aerospace, automobiles, portable devices, transportation etc [1]. Phosphoric acid (PA) doped polybenzimidazole (PBI) system is one of the promising polyelectrolyte membrane for high temperature (>100^{0}C) PEMFC [2]. The main function of the membrane is to conduct proton from cathode to anode in a PEMFC. The efficiency of the fuel cell is governed by the proton conductivity of the membrane. PBI has been experimentally observed to have high proton conductivity after doping with PA [3]. To get the structural insight and dynamical properties of the membrane, we have performed classical molecular dynamics simulation of the monomer (BI) of the PBI mixed with varied amount of PA [4]. Snapshots of the three simulation systems are shown in figure 1. From the structural analysis, we have predicted the arrangement of arrangement of PA near BI and different types of inter and intramolecular H-bonds in the system. We have examined the arrangement of BI among themselves and how it changes with varying amount of PA which gives us the favourable arrangement for efficient proton conduction. As a dynamic quantity imidazole ring flipping and diffusion of BI and PA have been calculated this shows intial drop and further increase in self-diffusion constant of both BI and PA with gradual increase in PA concentration. The origin of such anomalous diffusion has been identified. This is may be due to three different types of H-bonding arrangement of PA near BI (fig. 2) and H-bonding between PA molecules. The stability of the H-bonding network consisting of these different types of H-bonds between BI and PA has been calculated. Dynamic heterogeneity has been observed in the BI-PA system. We characterized the microscopic picture of dynamic heterogeneity by examining whether there is any correlation between dynamical heterogeneity and structural arrangement of the components in BI-PA system. Fast and slow PA molecules in the system have been observed due to coexistence of different types of H-bonds.



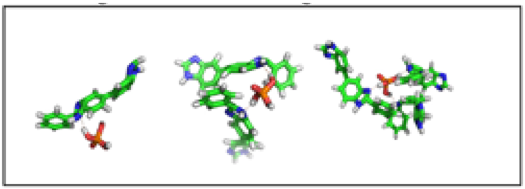


Figure 2. Different types of H-bonding arrangements

References:

[1] Hogarth, W. H. J.; Diniz da Costa, J. C.; Lu, G. Q. *Journal of Power Sources 142* (**2005**) 223.

[2] Wainright, J. S.; Wang, J. T.; Weng, D.; Savinell, R. F.; Litt, M. *Journal of The Electrochemical Society 142* (**1995**) L121.

[3] Li, Q.; He, R.; Berg, R. W.; Hjuler, H. A.; Bjerrum, N. J. *Solid State Ionics 168* (**2004**) 177.

[4] S. Pahari, C. K. Choudhury, P. R. Pandey, M. More, A. Venkatnathan, S. Roy, *J. Phys. Chem. B 116* (**2011**) 7357.

Polymeric gels and soft structures

Invited Talk

The Solvent in Physical Gelation: Polymers vs Organogelators

Jean-Michel Guenet
Institut Charles Sadron, CNTS-University of Strasbourg
23 rue du Loess, BP84047, F-67034 STRASBOURG Cedex2, FRANCE.
Jean-michel.guenet@ics-cnrs.unistra.fr

Physical gelation is a fascinating phenomenon which occurs in dilute or even very dilute solutions of "gelators" that can be polymers, biopolymers as well as small molecules [1,2,3]. On cooling these solutions form solid-like materials designated as "polymer thermoreversible gels", for polymers and biopolymers, or "organogels" for small molecules. The fraction of solvent can reach up to 99.9% of the weight fraction of the gel as is reported for biopolymers of the carrageenan type [4]. This fascinating situation arises from the gel morphology which basically consists of an array of randomly-dispersed fibrils possessing lengths in the micron range together with very thin cross-sections within the nanometer range. As a result, 3D connectedness can be achieved at very low "gelator" concentrations. While the fibrillar morphologies of polymers gels and of organogels are of different origins, they are in most cases indistinguishable [5] (figure 1). By simply examining AFM pictures "which is which" is a question hardly answerable. Is this simply fortuitous or due to a common gelation mechanism; this issue is not yet settled.

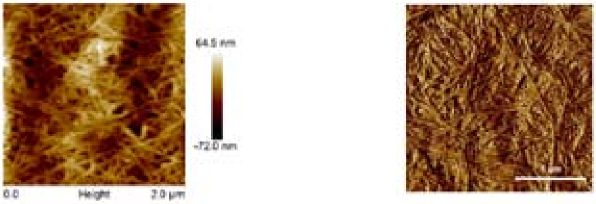


Figure 1. AFM picture of a polymer xerogel from syndiotactic polystyrene (left) and an organo-xerogel from oligo(phenylene vinylene gelators (right).

In the case of polymers, the prerequisite for obtaining fibrillar thermoreversible gels is the impediment of chain-folding. This occurs when polymers take on a worm-like chain conformation with a large persistence length. This property can be intrinsic to the polymer, such as agarose, or can be obtained by the occurrence of polymer-solvent molecular compounds, as is the case for stereoregular polymers[1,2].

Whether the solvent plays a similar role in organogels is an issue which is discussed in this talk. It is suggested that the main mechanism for producing fibrils involves the much faster growth of one face of the organogel crystal structure with respect to the other two, which can be enhanced via specific interactions with the solvent, something reminiscent of molecular compounds.

References

[1] J.M. Guenet, Thermoreversible Gelation of Polymers and Biopolymers (**1992**), Acad. Press, London; J.M. Guenet, Polymer-solvent Molecular Compounds (**2008**), Elsevier, London
[2] P. Terech, R.G. Weiss, Chemical Reviews, 97, (**1997**), 3133.
[3] A. Ajayaghosh, S.J. George, V. K. Praveen, Angew. Chem. Int. Ed. 42, (**2003**), 332
[4] A.H. Clark, S. B. Ross-Murphy, Adv. Polym. Sci. 83 (**1987**), 57
[5] J.M. Guenet Macromolecular Symposia 241, (**2006**), 45

Functional Supramolecular Materials based on Three Dimensionally-Designed π-Conjugated Molecules

Masayuki TAKEUCHI*
Organic Materials Group, Polymer Materials Unit,
National Institute for Materials Science, Sengen 1-2-1, Tsukuba 305-0047, Japan
** TAKEUCHI.Masayuki@nims.go.jp*

Self-assembly of organic molecules with functional properties is an active area of research, aimed at creating novel materials with potential applications in nanosciences and nanotechnology. Functionalities of such materials are significantly dependent on the supramolecular organization of the molecules and morphology of the resulting nanostructures. Through the control and modulation of molecular interactions, various kinds of self-assembled organic nanostructures with different morphologies such as fibers, tapes, wires, rods, tubes and particles have been reported. However, self-assembly of rationally designed molecular components into a prerequisite nanostructure, which enhances its functional properties, still remains a great challenge. Here we report on our three dimensional design of π-conjugated molecules, which leads to the creation of various functional organic materials with optimized optoelectronic properties. In addition, we will introduce a series of molecular machinery system whose function, properties, and morphologies can be controlled.

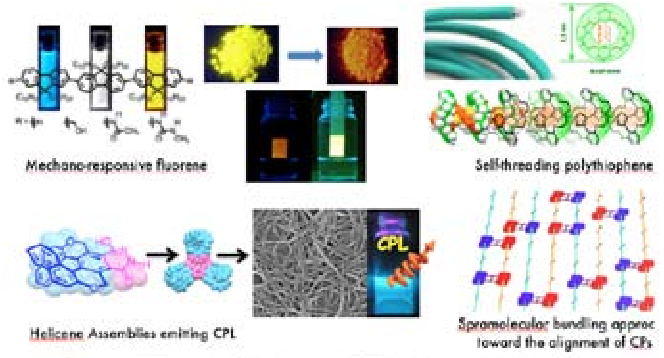


Figure 1. Functional Conjugated Molecules and Polymers

References

[1] Shibata, M.; Tanaka, S.; Ikeda, T.; Shinkai, S.; Ogi, S.; Takeuchi, M. *Angew. Chem. Int. Ed.* 52 (**2013**) 397-400.
[2] Ogi, S.; Sugiyasu, K.; Takeuchi, M. *ACS Macro Lett.* 1 (**2012**) 1199- 1203.
[3] Shomura, R. Sugiyasu, K.; Yasuda, T.; Sato, A.; Takeuchi, M. *Macromolecules* 45 (**2012**) 3759-3771.
[4] Balan, B.; Vijayakumar, C.; Ogi, S.; Takeuchi, M. J. Mater. Chem. 22 (**2012**) 11224-11234.
[5] Kaseyama, T.; Wakabayashi, R.; Shinkai, S.; Kaneko, K.; Takeuchi, M. *Chem. Eur. J.* 17 (**2011**) 1793-1797.
[6] Vijayakumar, C.; Sugiyasu, K.; Takeuchi, M. *Chem. Sci.* 2 (**2011**) 291-294.
[7] Sugiyasu, K.; Honsho, Y.; Harrison, R.; Sato, A.; Yasuda, T.; Seki, S.; Takeuchi, M. *J. Am. Chem. Soc.* 132 (2010)14754-14756.

Multi-component, Self-assembled, Functional Soft Materials

Uday Maitra
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012
maitra@orgchem.iisc.ernet.in

In recent years functional molecular gels have attracted considerable interest owing to their potential applications in various fields such as biomaterials, sensing, optoelectronics *etc*. We have been working on the aggregation of a variety of bile acid derivatives which form self-assembled fibrillar networks (SAFINs), eventually leading to the immobilization of solvent molecules around them.

In this talk, our efforts to develop functional, luminescent hydrogels through a self-assembly based approach using lanthanide cholates will be presented.

Observation of hexatic phases of achiral and chiral self-assembled polymers

Antara Pal, Santosh Prasad Gupta, Md. Arif Kamal and V.A. Raghunathan* ,
Raman Research Institute, Bangalore-560080 INDIA

The hexatic phase, characterized by short-range translational order and long-range bond-orientational order, was first proposed in the context of melting of two-dimensional crystals, as an intermediate between the crystalline and isotropic phases [1,2]. Later it was predicted that in three-dimensional liquid crystalline systems nematic order can coexist with bond-orientational order in the plane normal to the nematic director [3]. Influence of molecular chirality on the structure of this N+6 or line hexatic phase has been studied theoretically and two possible structures have been predicted, which have not been observed hitherto [4,5]. There have been two reports of a line hexatic phase in the literature [6,7]. However, many of the observed features, such as the phase sequence and the influence of molecular chirality on the structure of the line hexatic phase, do not agree with theoretical predictions.

We have observed a thermodynamically stable line hexatic (N+6) phase and its chiral analog in aqueous solutions of self-assembled polymer-like micelles of amphiphilic molecules. It occurs in between a nematic and two-dimensional hexagonal phases, as theoretically predicted. The structure of the chiral N+6 phase, obtained by doping with a chiral molecule, is different from that of its achiral analog and is consistent with the theoretically predicted Moire state consisting of polymer bundles, with bond-orientational order within each bundle twisted about an axis parallel to the average polymer direction [4]. Ordered line liquids also occur in many condensed matter systems, such as magnetic flux lines in superconductors, nematic polymers and electrorheological and ferro fluids [2]. Further, close-packing of chiral fibers is ubiquitous in biology [8]. Therefore, results of the present study are relevant in a variety of situations, in addition to confirming the predictions of fundamental theories of two-dimensional melting.

References:

[1]. Halperin, B. I.; Nelson, D. R. Phys.Rev. Lett. 41 (**1978**) 121
[2] Nelson, D. R**. 2002**. Defects and Geometry in Condensed Matter Physics, Cambridge University Press, Cambridge.
[3] Toner, J. Phys. Rev. A 27 (**1983**) 1157
[4] Kamien, R. D.; Nelson, D. R. Phys. Rev. Lett. 74 (**1995**) 2499
[5] Kamien, R. D.; Nelson, D.R. Phys. Rev. E 53 (**1996**) 650
[6] Podgornik, R.; Strey, H. H.; Gawrisch, K.; Rau, D. C.; Rupprecht, A.; Parsegian, V. A. Proc. Natl. Acad. Sci. USA 93 (1996) 4261
[7] Petukhov, A. V.; van der Beek, D.; Dullens, R. P. A.; Dolbnya, I. P.; Vroege, G. J.; Lekkerkerker, H. N. W. Phys. Rev. Lett. 95 (**2005)** 077801
[8] Weisel, J. W.; Nagaswamy, C.,; Makowski, L. Proc. Natl. Acad. Sci. USA 84 (**1987**) 8991

Porous PEG-PU Hydrogels: Synthesis, Characterization and Applications

Manohar V. Badiger*[a], B. L. V. Prasad[b], V. and V. D. Anumon[a]
[a]Polymer Science and Engineering Division,
[b]Materials Chemistry Division, National Chemical Laboratory (NCL)
Dr. Homi Bhabha Road, Pune – 411 008, India
e-mail:mv.badiger@ncl.res.in

Hydrogels have emerged as promising materials for engineering scaffolds and implants because of their biocompatibility, hydrophilicity and similarities to the native extra cellular matrix (ECM). Besides large number of applications in tissue engineering and controlled release technology, hydrogels have also shown potential in using them as matrices in embedding metal nanoparticles for catalytic applications. However, precise control of hydrogel properties, such as porosity, pore architecture and mechanical strength remains a challenge and play a significant role in cell survival, proliferation and nutrient diffusion to cells.

In our laboratory, we have worked on the synthesis of porous Polyethylene glycol-Polyurethane (PEG-PU) hydrogels using PEG-4000 as a soft segment, 4, 4'-methylenebis (cyclohexyl isocynate) as a hard segment. The degree of swelling in hydrogels was controlled by varying the amount of crosslinking agent namely, 1,6 hexane triol. The structural characterization of hydrogels was performed using ^{13}C solid-state NMR and IR spectroscopy. Investigations on the micro-structure of hydrogels by WXRD revealed the existence of crystalline domains of PEG. The SAXS studies on PEG-PU hydrogels indicated the possibility of an existence of lamellar micro-structures. The mechanical strengths of the hydrogels were evaluated by visco-elastic measurements. SEM and three-dimensional micro-computed tomography (μ-CT) imaging of hydrogels depicted the presence of inter-connected pores, which is an important property and has a great implication in tissue engineering applications. The MTT assay showed the ability of cells to proliferate in contact with the synthesized materials. We also demonstrated a simple and convenient method for generating and immobilizing gold NPs into these hydrogel matrices for catalytic applications.

Graphene –Conducting polymer Hybrids towards Photovoltaic Applications

S. Chatterjee[a]; R. K. Layek[a], A. K. Patra[b], A. Bhaumik[b], A.K. Nandi[a*]
[a]Polymer Science Unit,[b] Dept of Materials Science
Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700 032, INDIA
Email: psuakn@iacs.res.in

Amino-functionalized reduced graphene oxide (a-RGO) is used to change the morphology of polyaniline (PANI) and to increase the photocurrent in the PANI- a-RGO hybrid. The PANI morphology is changed from a nanotube to a flat rectangular nanopipe (FRNP) by the polymerization of aniline with a-RGO in acetic acid. Scanning (SEM) and transmission electron microscopy show the formation of FRNP morphology which varies by changing the PANI / a-RGO ratio in the hybrid. Time dependent SEM and Fourier transform infrared spectroscopy were used to investigate the mechanism of FRNP formation. Efficient (~500 times) improvement in photocurrent is observed in FRNP over PANI nanotubes on irradiation with white light. The photo response is quite reproducible even after several cycles with a time interval of 100 sec. and in both the negative and positive bias photocurrent increases. A donor-acceptor based 'electron-hole' pair mechanism is proposed for the photocurrent behavior of FRNP. Using the PANI-a-RGO FRNP hybrid a dye sensitized solar cell with Rose Bengal dye is constructed yielding a power conversion efficiency of 2.012%.[1]

TiO2 layer of the traditional dye sensitized solar cell (DSC) is replaced by a newly synthesized semiconducting poly[3-(2-hydroxyethyl)-2,5-thienylene] grafted reduced graphene oxide (PHET-g-rGO). TEM study indicates that pure PHET has fibrillar network morphology and in PHET-g-rGO the fibrous network morphology of PHET remains appended on the graphene surface making it a good electron transport promoter. FTIR study indicates co-valent binding of PHET and rGO. The diffuse reflectance spectra indicate that the absorption band of PHET at 374nm is red shifted to 383nm due to the co-valent bonding with rGO and this corresponds to a decrease of band gap from 1.86 eV in PHET to 1.38 eV in PHET-g-rGO. The photoluminescence (PL) intensity for pure PHET gets quenched and the emission peak gets red shifted by 13 nm due to grafting with rGO suggesting an efficient electron-hole pair separation. A stable photocurrent is produced after irradiation with white light (150 W Xenon lamp) in the PHET-g-rGO. The BET surface area for the PHET-g-rGO is 227.5 m2 g-1 and the respective pore volume is 0.19 cc g-1 which is very much comparable with the bare TiO2 surface area (typically ≈ 290 m2/g). By replacing the TiO2 used in traditional DSC for the first time with PHET-g-rGO the cell characteristics are as follows: the open circuit voltage equal to0.61V, photocurrent density = 7.5 mA/cm2 and the fill factor (FF) = 0.668 giving an overall power conversion efficiency η = 3.06 %.[2]

References

[1] Chatterjee, S.; Layek, R. K.; Nandi, A. K**.** *Carbon* , 52 **(2013),** 509
[2] Chatterjee S.: Patra, A. K.; Bhaumik A.; and Nandi, A. K. Communicated

Oral

Silica-polymer shake gels

Krishna Teja, Sai Prashanth and Basavaraja M Gurappa*
Department Chemical Engineering, Indian Institute of Technology Madras,
Chennai-600036 INDIA

Polymers are often added to colloidal dispersions as rheological modifiers either to increase viscosity or to create structured materials such that mixtures have controlled flow properties. Resulting colloid-polymer mixtures find applications as biological fluids, dirlling fluids, as well as in several food, pharmaceuitical and personal care industries [1]. When a solution containing certain colloids and polymers in a specic range of concentration of particles and polymers is shaken, the low viscosity solution transforms into a visco-elastic gel (see Figure 1). Such shear induced gels observed in colloid-polymer mixtures are popolarly called – "shake gels". These gels transform back into low viscosity fluid upon cession of flow. Such smart gels have potential applications in several fields – for example transportation of fluid-solid mixtures, as flow controllers and others.

Since the last decade research has been focussed on shake gels formed using disk shaped clay particles (Laponite) and Polyethylene oxide (PEO). We present an investigation of the formation of shake gel in silica-PEO and silica-PVP (Polyvinylpyrrolidone) mixtures. We construct a phase diagram representing the behavior of mixtures of polymers (PEO Mw = 300000 g/mol, 900,000g/mol, PVP Mw = 40,000 g/mol) and colloidal silica (varying sizes from 7 nm to 4 µm). A represenitive phase diagram for a mixture of silica (32 nm)-PEO (900 kDa) is shown in Figure 2. We use mcro-rheology, microscopy and conventional rheometry and presnet a study of flow behavior, mcrostructure and relaxation behavior of these complex materials. We estimation the critical shear rates, critical surface coverage values and other rheological properties.

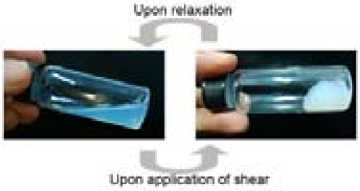


Figure 1. An aqueous Silica–PEO mixture before and after completion of shaking .

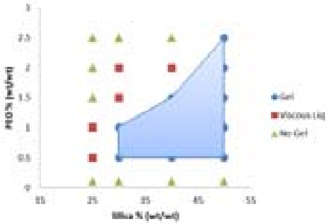


Figure 2. Phase behavior of Silica/ PEO 'shake-gels', formed by vigorous shaking. The molecular weight of PEO used is Mw = 900 000 g /mol and the size of silica particles is 32nm.

References:

[1] Zebrowski, J., Prasad, V., Zhang, W., Walker, L. M., & Weitz, D. A. (**2003**). Shake-gels: shear-induced gelation of laponiteÁ PEO mixtures, 213, 189–197.

Interaction of Cationic Random and Block Copolymers with Anionic Surfactants: Spontaneous Formation of Water-Soluble Nanostructures

Rakesh Banerjee, Debabrata Dey, Sujan Dutta, and Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur,
West Bengal-721302 INDIA

The complexation of polyelectrolytes with oppositely charged surfactants has been an active field of research in recent years, essentially because of their potential applicability in several industrial areas including biomedical and pharmaceutical industries, personal care and food products [1-3]. In search of newer polyelectrolyte-surfactant systems, we have synthesized random (RCPs) and block copolymers (BCPs) of similar compositions from poly(ethylene glycol) methyl ether acrylate (PEGMEA) and cationic monomer (3-(methacryloyl amino)propyl)trimethyl ammonium chloride (MAPTAC). While RCPs, synthesized using standard radical polymerization produced usual polydisperse sample, BCPs with controlled molecular weight and narrow polydispersity were synthesized using Reversible Addition Fragmentation Chain Transfer (RAFT) technique. The interaction behaviour of these cationic polymers with oppositely charged surfactants were studied using various physical and microscopic techniques, viz. fluorosence, DLS, zeta potential, and TEM. Depending on the polymer-surfactant combination these polymer surfactant complexes produced different nanostructures in aqueous solution with hydrophobic core. [4-5] Hence these water soluble nano-aggregates made using polymer and surfactant can be potentially useful to solubilize hydrophobic drug molecules more effectively. Importantly, the vesicles made from these BCP/AOT stoichiometric complexes were successfully utilized to reduce $HAuCl_4$ to gold nanoparticles. In the presentation the synthesis process, characterization and results will be presented and discussed.

References:

[1] K. Ksenija, *Advances in Colloid and Interface Science* 158, **(2010)**, 68-83.
[2] T. K. Bronich, M. Ouyang, V. A. Kabanov, A. Eisenberg, F.C. Szoka, A.V. Kabanov, *The Journal of American Chemical Society* 124, **(2002)**, 11872-11873.
[3] C. K. Nisha, P. Basak,. S. V. Manorama, S. Maiti, K. N. Jayachandran *Langmuir* 19, (**2003**), 2947-2955.
[4] R. Banerjee, S. Maiti, D. Dhara *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 395, (**2012**), 255-261
[5] R. Banerjee, S. Dutta, S. Maiti, D. Dhara *The Journal of Physical Chemistry B* **(2013)**, ASAP Article

Hydrogels from Grafting of Acrylic Acid on to Modified Chitosan

Renu Singh and C. N. Murthy*
Applied Chemistry Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara-390 001, Gujarat, India.

A novel hydrogel based on chitosan was prepared by graft copolymerization of acrylic acid on diamino derivative of chitosan i.e., 6-amino-6-deoxy-chitosan (6a6dC) [1]. This diamino chitosan was grafted with acrylic acid in an aqueous solution in contrast to acetic acid in the conventional method [2]. Hydrogen peroxide/L-ascorbic acid redox system was found to be an efficient initiator system for grafting reaction in an aqueous system at room temperature. The synthesized hydrogel, 6a6dC-g-PAA, was characterized by FTIR, TGA, SEM. Thermal studies showed that it is more stable than chitosan and 6-amino-6-deoxy-chitosan. This 6a6dC-g-PAA, also showed an appreciable water absorbing capacity which was confirmed from the observation of porous surface obtained by SEM measurement.

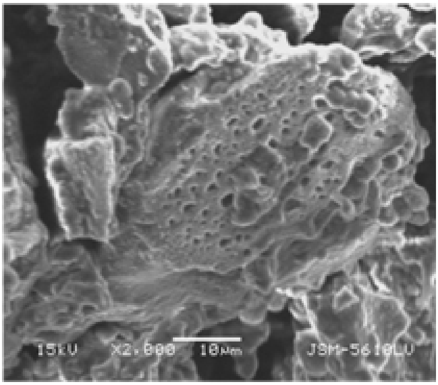


Figure 1. SEM Image of the hydrogel

References

[1] Satoh et al. *Carbohydrate Research,* 341 **(2006)** 2406-2413

[2] Shanmugapriya, A.; Srividhya, A.; Ramya R.; Sudha P. N. *International J of Environmental Sciences* 1**(2011)** 2086-2095

Mechanically Self-healing Hydrogel Composed of Metallo-Supramolecular Polymer with High Electrical Conductivity

Pradip K. Sukul, Dines C. Santra, Nabarun Hajra and S. Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata-700032, India

In recent years, the utilization of supramolecular interactions toward the design of new stimuli-responsive materials has achieved an extensive amount of interest. Reversible metal–ligand coordination is one class of non-covalent interaction that has been widely utilized to gain main-chain supramolecular polymers. Polymers with the ability to repair themselves after sustaining fracture could extend the lifetimes of materials utilized in many applications. Most reported approaches to healable materials require heating the fractured area. Here we prepared metallo-supramolecular polymers that can be healed automatically and rapidly by simply contacting the fractured surfaces together. Utilizing metal-ligand coordination bond, water soluble perylene bisimide (**GPI**) has formed supramolecular polymer (Fig. 1a) with Co^{2+} ion to give self healing hydrogel (Fig. 1b). Observation of strong bisignated cotton effect in the hydrogel indicates the induction of chirality in the self assembled perylene chromophores (Fig. 1c).This hydrogel potentially has been applied to demonstrate the healing efficiency with an LED in a series with a battery powered circuit.

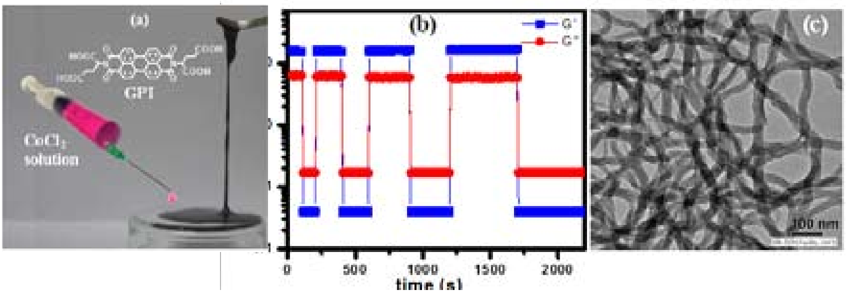


Figure (a) Stretchable self sustaining hydrogel. (b) Continuous step strain measurement ($\gamma = 0.1$ and 100 %). (c) TEM image of helical fibers.

References:

[1]White, S.R.; Sottos, N.R.; Geubelle, P.H.; Moore, J.S.; Kessler, M.R.; Sriram, S.R.; Brown, E.N.; Viswanathan, S. *Nature* 409 (**2001**) 794

[2]Pana, L.; Yu, G.; Zhaia, D.; Lee, H. R.; Zhao, W.; Liu, N.; Wang, H.; Tee, B. C.-K.; Shi, Y.; Cui, Y.; Bao, Z. *PNAS* 24 (**2012**) 9287

[3]Tee, B. C-K.; Wang, C.; Allen, R.; Bao, Z. *Nature Nanotechnology* **7** (**2012**) 825

[4]Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* 472 (**2011**) 334

[5]Phadke, A.; Zhang, C.; Arman, B.; Hsu, C.-C. Mashelkar, R. A.; Lele, A. K.; Tauber, M. J.; Arya, G.; Varghese, S. *PNAS* 109 (**2012**) 4383.

Transforming Soft Structures with Light: Ostwald Ripening of Organic Nanodots to Rods

Sankarapillai Mahesh [1,2] and Ayyappanpillai Ajayaghosh*[1]
[1]Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum 695019, India; Phone (Off): 0471-2515306; Fax: 0471-2491712, 2491585
[2] *Current Affiliation: Inspire Faculty, Department of Chemistry, Indian Institute for Space Science and Technology (IIST), Trivandrum-69554, India; Email: maheshs@iist.ac.in*
Phone (Off): 0471-2568537; Fax: 0471-2568541

Formation of shape persistent one-dimensional (1D) nano- and microstructures is a topic of current interest in the field of advanced materials research.[1] Ostwald ripening is one of the reasons to the formation of 1D nanostructures from nanoparticles of metals and semiconductors.[2] For example, CdTe, CdSe and ZnO nanoparticles have been shown to form nanorods by Ostwald type ripening process. Herein we report the light induced reversible morphology change from the initially formed nanodots of a *trans* azobenzene derivative to shape controlled rods.[3] For the self-assembly of π-systems to nano- and microrods with controlled aspect ratio, it is important to prevent the usually occurring spontaneous extended aggregation of molecules. π-systems derived from phenyleneethynylene units are appropriate for this purpose since they are known to form spherical or circular assemblies due to weak π-interaction. This method allows the preparation of organic supramolecular rods with controlled aspect ratio which can be assembled and disassembled by light of appropriate wavelengths. The new observation described here reveals yet another property of the versatile azobenzene chromophore which may encourage further studies enroute to stimuli responsive hierarchical structures with controlled morphological features.

References

[1] Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
[2] (a) Ostwald, W. *Lehrbuch der Allgemeinen Chemie*; part 1 ed.; Leipzig, Germany., 1896; Vol. 2; (b) Redmond, P. L.; Hallock, A. J.; Brus, L. E. *Nano Lett.* **2004**, *5*, 131.
[3] **S. Mahesh**, A. Gopal, R. Thirumalai and A. Ajayaghosh; *J. Am. Chem. Soc., **2012**, 134 (17), pp 7227–7230*

Poster

PG1

Supramolecular Polymerization of Coronene Bisimides (CBIs): Mechanistic Insights and Chiral Amplification

Chidambar Kulkarni,[a,b] and Subi J. George[a,*]
[a] *Supramolecular Chemistry Lab, New Chemistry Unit (NCU), JNCASR, Jakkur, Bangalore-560064, India*
[b] *Chemistry and Physics of Materials Unit (CPMU), JNCASR, Jakkur, Bangalore-560064, India*
** george@jncasr.ac.in*

Supramolecular polymers have gained immense interest in the past decade due to the non-covalent nature of the bonds holding the monomeric units together [1]. The presence of such non-covalent bonds manifests in properties like self-healing and reversibility, properties generally uncommon to covalent polymers [2]. Thus these materials are finding applications in fields like biomaterials and organic electronics. In spite of this, a precise control over the organization of molecules in the polymer or assembly remains a challenge. Studying the mechanism of the formation of these polymers gives insights into the organization and also aids in controlling the extent self-assembly. Two such well know mechanisms for one-dimensional supramolecular polymerization are cooperative and isodesmic pathways.

In the present study we have studied the supramolecular polymerization of π-conjugated coronene bisimides, a potential candidate for use in organic electronics and liquid crystals. Two derivatives of coronene bisimides bearing chiral and achiral 3,4,5-trialkoxy phenyl groups on the imide position is studied. The chiral derivative self-assembles mainly through π-stacking and van der Waals interaction in non-polar methylcyclohexane resulting in long one-dimensional fibrilar morphology and it follows an isodesmic mechanism. The thermodynamic parameters governing the self-assembly are detailed. The achiral derivative also shows similar self-assembly behavior as its chiral counter-part. The co-assembly of chiral and achiral derivatives shows a weak chiral amplification with the saturation at 50% of chiral derivative. This was further used to study the dynamics of the assembly.

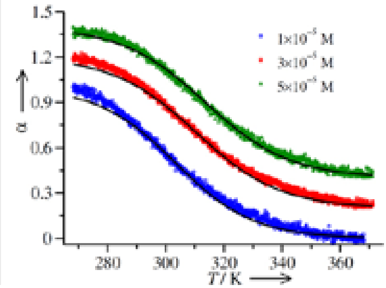


Figure 1. Mechanism of self-assembly of coronene bisimides. Fraction of aggregation (α) versus temperature at three different concentrations (c = 1×10^{-5} M, c = 3×10^{-5} M, c = 5×10^{-5} M) in MCH. The solid line for each curve shows the fit to the temperature-dependent isodesmic model. Each curve is displaced vertically by 0.20 from each other for clarity.

References:
[1] Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* 101 (**2001**) 4071
[2] Greef, T. F. A. de; Meijer, E. W.; *Nature* 453 (**2008**) 171.
[3] Greef, T. F. A. de; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* 109 (**2009**) 5687.

PG2

Hydrophobic Polymer Mediated Two Dimensional Self Assembly of Nanoparticles

Sarika.C.K* and Jaydeep Basu
Department of Physics, Indian Institute of Physics, Bangalore 560012, India
** sarika.sivadas@physics.iisc.ernet.in*

Hydrophobic interaction is a widely studied driving force of assembly first noted by Walter Kauzmann in 1959 [1]. In the case of hydrophobic polymers, they collapse from extended coil to a compact globule in presence of water [2]. In our study, Gold Nanoparticle (GNP) grafted with Polystyrene is synthesised by one phase grafting-to method [3]. These hybrid particles are dissolved in chloroform and spread onto air-water interface in Langmuir-Blodgett (LB) trough. The monolayer formed is then transferred onto substrate and examined by Atomic Force Microscopy. We observe a self assembly of GNPs to form spheroidal domains of definite size. A quantitative study reveals that the size of the domains scales up with concentration of GNP solution (Fig.1).

GNP dispersion inside the domains is studied using Transmission Electron Microscopy. The number of GNPs inside the domain and their interparticle distance can be tuned by using grafting polymer of different molecular weights (Fig.2).

The domain formation can be attributed to the hydrophobicity of the grafted polystyrene. When chloroform evaporates from the water surface, an attractive interaction is induced between polystyrene since they are in solvophobic condition. Attractive interactions bring the polymer chains together and they penetrate and coil to a form domains.

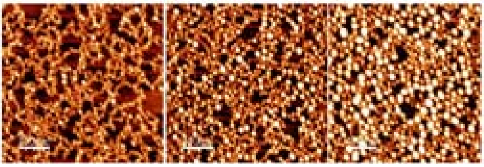


Figure 1. Domains size increases with concentration 0.25mg/ml, 1mg/ml, 2mg/ml from left to right

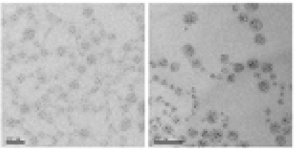


Figure 2. TEM images of domains with PS M_w 53K (left) and 3K (right)

References

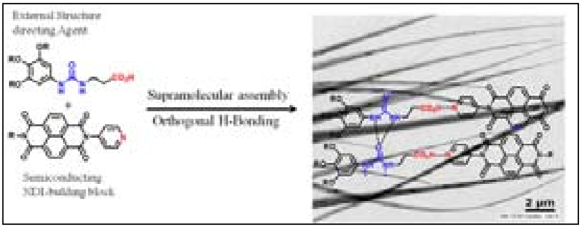
[1] Kauzmann, W. *Adv Prot. Chem.*, 14 (**1959**) 1-63.
[2] Wolde, P. R.; Chandler, D. *PNAS*, 99 (**2002**) 6539.
[3] Yee, C. K.; Jordan, R.; Ulman, A.; Henry, W.; Alexander, K.; Rafailovich, M.; Sokolov, J. *Langmuir*, 15 (**1999**) 3486.

PG3

Orthogonal H-Bonding Induced Gelation of Naphthalene Diimide (NDI) Building Block by an External Structure Directing Agent (ESDA)

Haridas Kar, Mijanur Rahaman Molla and Suhrit Ghosh*
Polymer Science Unit, Indian Association for the cultivation of Science, Kolkata-700032 INDIA
Corresponding author's email id- psusg2@iacs.res.in

Supramolecular-assembly of pi-conjugated chromophores is a promising approach to develop functional materials for optoelectronic applications. To understand nature of chromophore packing in solid state, often their association behavior and photophysical properties in highly non-polar medium are correlated where the chromophores remain in assembled form. However for generating aggregated structure and spectroscopic characterization in non-polar medium, one needs to ensure that a suitable derivative of the rigid chromophore remains soluble in that medium. For that purpose often a rigid pi-system is decorated with peripheral alkyl chains and H-bonding functional groups wherein the later components help in structure formation and alkyl chains provide solubility in non-polar medium. This approach suffers from that fact that self-assembly induced functional aspects cannot be fully realized because the structure-directing part often has detrimental effect on functional aspects. Primarily to address such issues, we envisaged a suitably designed External Structure Directing Agent (ESDA) would be worth investigating which can be decoupled from the functional pi-system once the structure-formation is achieved. Herein we demonstrate one such example where a pyridine-functionalized NDI-derivative could be assembled with long-range order by an ESDA containing two H-bonding functional groups operating in orthogonal directions. The ESDA contained a self-complimentary urea functional group and a carboxylic acid which is complementary for H-bonding to the pyridine group attached to the NDI. Indeed when they were mixed, spontaneous gelation could be noticed in a non-polar solvent methyl cyclohexane. Control experiments were done with a control ESDA without the urea group which was unable to produce gel (spherical morphology) revealing necessity of H-bonding interaction in orthogonal directions for effective self-assembly. Furthermore in *I-V* measurements, the electrical conductivity of the fibrillar gel was found to be appreciably higher compared to non-gelating mixture of control ESDA and NDI. Our recent results related to ESDA-based supramolecular-assembly of NDI chromophores [1] will be the topic of this presentation.



Reference

[1] H. Kar, M. R. Molla and S. Ghosh. *Chem. Commun*. **2013** (DOI-10.1039/c2cc36536g)

PG4

Unusual Thermoreversible Abrupt Gelation of Hydrophobically Modified Polymer

Ashish Lele[a], Indravadan Parmar[a], Manohar Badiger[a], Prakash Wadgaonkar*, Aarti Shedge[b]
Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India
* pp.wadgaonkar@ncl.res.in

Thermothickening polymers are amphiphilic stimuli responsive block co-polymers and show a gelation upon increasing temperature and liquefy upon cooling in the aqueous media [1]. In the literature, polymers which show an opposite behavior of gelation and liquefaction are less commonly encountered and all of them are naturally occurring polymers [2].

We have observed for the first time an abrupt gelation of aqueous solution of hydrophobically modified poly (N,N' dimethyl acrylamide-co-acrylic acid) upon cooling by imposing a low shear rate (0.5 Pa). A high molecular weight (5x 10^7 gm/mol) co - polymer was prepared by free radical co-polymerisation of N, N dimethylacrylamide (70 mol%) and of acrylic acid (30 mol%) and was subsequently modified by of dodecyl amine (10 mol%) as a hydrophobe. Structural elucidation of base co-polymer and hydrophobically modified polymer was performed by ^{1}H NMR and ^{13}C NMR spectroscopy.

Temprature rate ramp measurements

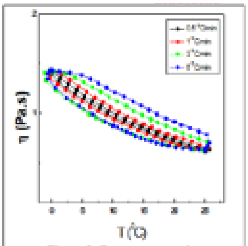


Figure 1. Precursor copolymer

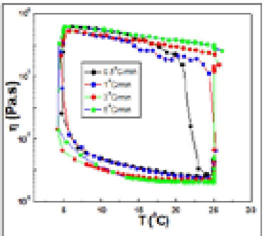


Figure 2. Hydrophobically modified polymer

The specific viscosities of the hydrophobically modified polymer was lower than that of precursor co-polymer. Critical concentration was decreased with decreasing temperature revealed from the dilute viscosity studies. Cooling a solution of the base copolymer at controlled rate and at low shear resulted in small amount of thickening (Figure 1.) whereas cooling a solution of hydrophobically modified copolymer at identical conditions resulted in an abrupt and large increase in viscosity at critical temperature (figure 2). Heating a solution of hydrophobically modified polymer at same rate of cooling showed an abrupt liquefaction at critical temperature.

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

PG5

Silver Nanoparticles Entrapped Fibrillar Hydrogel based Robust Nanoreactors

K.N. Rohini, K.N.Navya, T.Prasada Rao and J.D.Sudha*
Chemical Sciences and Technology Division, CSIR-NIIST, Thiruvananthapuram-695019 INDIA
*E-mail id - sudhajd2001@yahoo.co.in

Noble metal nanoparticles entrapped polymeric hydrogels are receiving importance due to the synergistic properties arising from tunable properties of stimuli responsive soft polymeric hydrogels and the specific optoelectronic properties of metal nanoclusters [1]. Hydrogels are three dimensional polymeric fibrillar networks which can imbibe large amount of water with stimuli responsive swelling and deswelling properties. Metal nanoparticles possess specific properties which make promising applications in photonic, electronic and sensor fields [2]. Apart from this, they have high catalytic activities for hydrogenation, hydroformylation, carbonylation etc [3,4]. In most cases, they would congregate during the catalytic process due to their van der Waals forces and high surface area. In this regard, surface modification using polymers, complex ligands or surfactants are frequently used to stabilize metal catalysts. Among these stabilizers, polymeric hydrogels with three dimensional fibrillar networks can entrap metal nanoparticles and serve as micro / nanoreactors. Here, the super hydrophilic fibrillar network can speed up the diffusion of metal ions through the fibrillar network and the charged backbone will facilitate the immobilization of metallic nanoparticles. Furthermore, the size and morphology of the metal nanoparticles can be tuned by varying the mount of monomer, crosslinker and functionality of the fibrillar networks. The standard preparation procedure involves the polymerisation of vinyl monomer using water soluble initiator in presence of metal salt and a cross linking agent.

In the present work, silver nanoparticles entrapped fibrillar networks of polyacrylic acid based hydrogel prepared by in-situ polymerization of acrylic acid and reduction of silver nitrate in presence of ammonium persulphate as intiator under ambient conditions using amidodiol as crosslinking agent. Silver nanoparticles entrapped fibrillar networks of hydrogel (SPAG) were characterized by ATR and UV visible spectroscopy. Crystalline phase of silver nanoparticles were studied by XRD and morphology by SEM and TEM. Results showed that shape, size of the silver nanoparticles in the fibrillar network could be controlled by varying the amount of silver ions in the system. Further, we envisaged the catalytic property of silver nanoparticles for the reduction of organic dyes such as methylene blue, rhodamine 6G and crystal violet [5,6]. Kinetics of reduction process was monitored periodically by measuring the decrease in the absorbance in UV-Vis spectrum. Results indicated that within 30 minutes, MB, CR and R6G with initial concentration of 19.16 mg L^{-1} can be reduced completely at ambient conditions and the catalytic activity is observed to be in the order CR > R6G > MB. Effect of temperature, pH on the reduction process was also studied. In addition, SPAG showed excellent reusability for ten successive cycles, with no appreciable decrease in catalytic effects. Thus, the prepared SPAG can be considered as a prospectable nanoreducer for purification of dye contaminated waste water.

References:

[1] Wang, C.; Flynn, N.T.; Langer, R. *Adv. Mater.*, 16 **(2004)** 1074.
[2] Li, S.J.; Gong, S. *Adv. Funct. Mater.*, 19 **(2009)** 2601.
[3] Xu, R.; Wang, D.; Zhang, J.; Li, Y. *Chem. Asian J.,* 1 **(2006)** 888.
[4] Subrata, K.; Madhuri, M.; Sujit Kumar, G.; Tarasankar, P. *J. Colloid Interface Sci.,* 272 **(2004)** 134.
[5] Jiang, Z; Liu,C.; Lu-Wei, S. *J. Phys. Chem. B,* 109 **(2005)** 1730.
[6] Zheng,Y.; Wang, A. *J. Mater. Chem.,* 22 **(2012)** 16552.

PG6

Shake gels: Shear induced gelation of silica-PEO mixtures

Krishna Teja, Sai Prashanth and Basavaraj M Gurappa*
Department of Chemical Engineering, Indian Institute of Technology Madras,
Chennai-600036 INDIA

In the recent years, there is a lot of interest in developing smart materials because of the range of application they offer. Shake gels are a subclass of these materials. These amazing fluids (Mixtures of a colloid and a polymer at specific range of concentrations) when shaken form a highly elastic gel. The rheology can change from a fluid which is just a little more viscous than water to that of chewing gum, simply on shaking. On leaving the material to rest the liquid like fluid reforms (Fig.1).

The very feature of shake gels "respond to forces applied on them by becoming firm" make a way to the tremendous applications of them in the industry like interesting possibilities in new separations technology [1], transportation of solids and micro channels.

Since the last decade, research has been focussed on shake gels formed using disk shaped clay particles (Laponite) and Polyethylene oxide (PEO). In our study we started with investigating the formation of shake gel using spherical colloidal silica particles with polymers PEO and Polyvinylpyrrolidone (PVP). Various experiments were performed on mixtures of polymers (PEO Mw = 300000 g/mol, 900,000 g/mol, PVP Mw = 40,000 g/mol) and colloidal silica (varying sizes from 7nm to 4μm) at different concentrations and a phase diagram (Fig.2) showing the resultant behaviour is developed. Till now the relaxation times of shake gels are measured visually [2], we made an attempt to qualitatively and precisely estimate them using the latest micro rheological technique, multiple particles tracking. Along with these, estimation of critical shear rates [3], critical surface coverage values [4] and other rheological properties are carried out and all the observations made, will be presented.

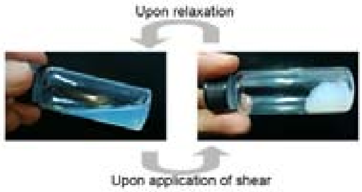


Figure 1. An aqueous Silica–PEO mixture before and after completion of shaking .

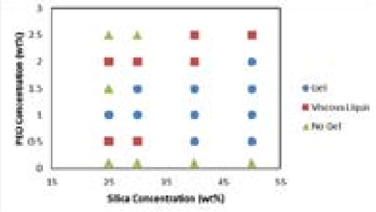


Figure 2. Phase behaviour of Silica-PEO 'shake-gels', formed by vigorous shaking. The molecular weight of PEO used is Mw = 900 000 g /mol and the size of silica particles is 22nm.

References:

[1] Pozzo, D. C., & Walker, L. M. (**2004**). Reversible shear gelation of polymer–clay dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *240*(1-3), 187–198.
[2] Zebrowski, J., Prasad, V., Zhang, W., Walker, L. M., & Weitz, D. A. (**2003**). Shake-gels : shear-induced gelation of laponiteÁ PEO mixtures, 213, 189–197.
[3] Fall, A., & Bonn, D. (**2012**). Shear thickening of Laponite suspensions with poly(ethylene oxide). Soft Matter, 8(17), 4645-465
[4] Can, V., & Okay, O. (**2005**). Shake gels based on Laponite–PEO mixtures: effect of polymer molecular weight. *Designed Monomers & Polymers*, *8*(5), 453–462.

PG7

Studies on the Fibrillar Network Formation in Cholesterol Carbonates of 3-Pentadecenyl Phenol based Organogelators

K. S. Neethu, S. Sivakala and J. D. Sudha*
Chemical science and Technology Division, CSIR-National Institute of Interdisciplinary Science and Technology, Trivandrum-695019 INDIA
*E-mail id: sudhajd2001@yahoo.co.in

Self-assembly of low molecular weight organic molecules form soft materials such as molecular gels and liquid crystals emerged enormous scientific and technological interest [1]. They find potential applications in the areas such as micro devices, molecular electronics, cosmetics, drug delivery systems, [2] corrosion protection coatings and so forth. The relationship between the self-assembled supramolecular architectures and their properties such as anisotropic strength, structural stability, material transport and opto-electronic properties should be better understood for their practical applications. Specific modes of packing within the three dimensional self assembled structure is determined by the balance among the weak physical interactions such as intermolecular hydrogen bonding, electrostatic forces, π- π stacking, electrostatic forces and London dispersion forces.[3,4]. There are many reports about various types of low molecular weight organogelators. It is challenging to understand transition from molecule to primary to secondary aggregates and their transitions from solutions to sols to gels. Initial nucleation, either spontaneous [5] or continuous nucleation, is decided by the molecule – solvent interactions, concentration, temperature etc. There have been several reports on cholesterol-appended chromophoric systems that self-assemble to form hierarchical structures which could modulate the morphological and optical properties.

Here, we present the studies of the role of unsaturation on self-assembling and specific modes of packing in cholesterol linked 3-pentadecylphenol and 3-pentadecenyl phenol molecules which differ in the presence of unsaturation in the side chain. 3- pentadecenyl phenol is a distilled product of cheap renewable resource based cashew nut shell liquid known as cardanol. Prepared compounds were characterized by elemental analysis, HRMS, FTIR, ^{1}HNMR and ^{13}C NMR spectra. Further, we have studied the effect of solvent, temperature and concentration on the self-assembling, nucleation and growth process by morphological observation using PLM, SEM, TEM and AFM. Variations in optical properties were studied using UV-Vis spectroscopy, emission spectroscopy and CD spectroscopy. Rheological properties [5] were studied by rheometry and changes in the packing studied by XRD. Both compounds exhibited solvatochromic effect in both absorption and emission spectra. Molecules with unsaturation in the side chain exhibited the formation of highly birefringent spherullites in toluene at low magnification with diameter of ~ 100μm. Later these spherullites entangle to form fibers and spreads through the whole sample volume. At higher magnifications, the highly branched networks of self-assembled networks with their junction zones become visible [1]. Whereas the saturated compound showed tubular /vesicular morphology which later transforms into sheet like structures or paper-like rolls of 1 μm diameter to several micrometer length. The different morphologies observed due to the variations in the specific mode of packing arising from the changes in the intermolecular hydrogen bonding, electrostatic forces, π- π stacking on varying the structure of the molecule, concentration, solvent, temperature.

References

[1]. Mathew, G.; Richard, G. W. *Accounts Chem. Res.*, 39 (**2006**) 489
[2]. Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev*. 34 (2005) 821
[3]. Terech, P.; Weiss, R. G. *Chem. Rev.* 97 (**1997**) 3133
[4]. Estroff, L. A.; Hamilton, A. D. *Chem. Rev*. 104 (**2004**) 1201
[5]. Huang, X.; Terech, P.; Raghavan, S. R.; Weiss, R. G. *J. Am.Chem. Soc.* 127 (**2005**) 4336

PG8

Caprolactone based Magnetic Copolymers for Biological Applications

Mutyala Naidu Ganivada[a], Pawan Kumar[a] and Raja Shunmugam[a]*
[a]*Polymer Research Centre, Department of Chemical Sciences,*
Indian Institute of Science Education and Research- Kolkata, India.
E-mail: sraja@iiserkol.ac.in

Well-defined caprolactone derived copolymers, with doxorubicin, magnetic particles and polyethylene glycol functionalities, are synthesised using ring opening polymerisation and click chemistry. All the polymers are characterized by ^{1}H NMR, FTIR, GPC and TGA techniques. The morphology of the copolymer nanocomposites are evaluated with DLS, TEM and AFM. The conjugated magnetic particles to the copolymers were monitored by FTIR. To prove the magnetic behaviour of nanocomposites, SQUID experiment is performed at room temperature. Newly designed copolymers having magnetic nature are expected to be magnetic resonance imaging (MRI) agent. Doxorubicin hydrazone linker is used to release the drug exactly at the mild acidic conditions resembling the pH of the cancerous cells.

References

[1] Kong, S. D.; Zhang, W.; Lee, J. H.; Brammer, K.; Lal, R.; Karin, M.; Jin, S. *Nano Lett.,* 10 **(2010)**, 5088.
[2] Vijaykameswara Rao, N.; Shivshankar, M.; Abhinoy, K.; Das Sarma, J*.; Shunmugam, R.* *Biomacromolecules***,** 13 **(2012)**, 221.

PG9

Guest Induced Self-Assembly: Chiral Expression, Dynamic Helix Reversal and Helical Memory in Supramolecular Polymer

Mohit Kumar, Subi J. George*
New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India-560064
* george@jncasr.ac.in

Expression of molecular chirality into its helical self-assembly has been a topic of great research in polymers for various technological applications. These polymeric materials are reported to show stimuli based helicity reversal and retain its helical organization even after removal of chiral information in so called "chiral memory" experiment.

Replicating the same phenomena in dynamic non-covalent polymers requires smart design. It is in this regard that we show specific guest binding induced supramolecular polymerization for induced chirality. For this purpose, we synthesized dipicolylamine derivatives of various chromophoric diimides. These achiral molecules assemble in presence of guests like ATP to form one dimensional nanostructures which show strong excitonically coupled circular dichroism signal due to induced helicity. We also see that replacing one guest by the other through competitive binding shows dynamic helix reversal of these supramolecular polymers. Finally removal of these guests from the assembly is seen to retain its chiral organization through chiral memory.

Through various spectroscopic methods, self assembly and chirality induction with memory will be presented. Microscopic studies giving insight into molecular reorganization will be shown as a useful tool to understand the system. Such systems will be utilized for investigating the enzymatic action of phosphatase and the process of ATP conversion in biological systems.

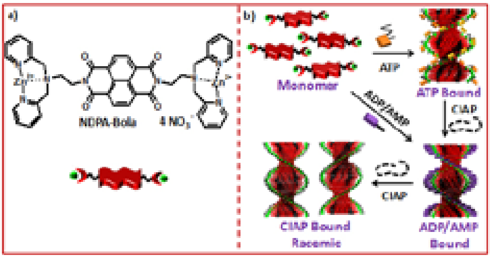


Fig. a) Dipicolylamine derivative of NDI and b) schematic representation of guest induced supramolecular helicity and enzyme action for chiral memory in these assembly.

References

[1] Yashima, E.; Maeda, K.; Okamoto, Y. *Nature,* 399 (**1999**) 449.
[2] Kumar, M.; Jonnalagadda, N.; George, S. J. *Chem. Commun.*, 48 (**2012**) 10948.
[3] Onouchi, H.; Maeda, K.; Yashima, E. *J. Am. Chem. Soc.,* 123 (**2001**) 7441.

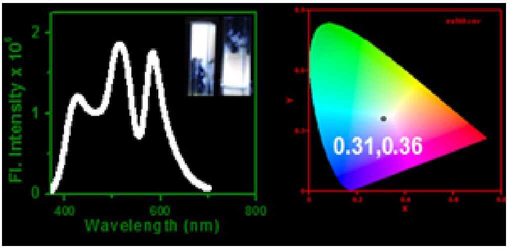
PG10

White Light Emitting hybrid Supramolecular Hydrogel of Melamine

Partha Bairi, Bappaditya Roy, Priyadarshi Chakraborty and Arun K. Nandi*
Polymer Science Unit, Indian Association for the cultivation of Science,
Jadavpur, Kolkata-700 032, INDIA

Fluorescence resonance energy transfer (FRET) from donor to acceptor molecules is a central footstep for construction of a light harvesting materials[1]. In this context supramolecular principle plays a vital role because it has provides a controlled molecular architecture which helps in the efficient excitation energy transfer from donor to acceptor molecules. Excitation energy transfer in the supramolecular gel scaffolds has played a significant role and Ajayaghosh and his co-workers has been reported several light harvesting materials with π- conjugated oligo(p-phenylenevinylene)[2] (**OPV**) molecule which acts as an efficient light harvesting antennae. With the help of partial fluorescence resonance energy transfer in a multi-component donor acceptor assembly one can tune the emission property and generate white light emitting materials. Many researchers have developed white light emitting materials using fluorescence energy transfer from donor to acceptor molecules either in the solution or in the solid state and very few reports are available in the supramolecular organogel[3] while in hydrogel system it's very rare until a recent report by S. J. George et. al[4].

I want to represents a hybrid white light (W-gel) emitting hydrogel which is composed by a co-assembled light harvesting hydrogel of melamine (M), 6,7-dimethoxy-2, 4[1H, 3H]-quinazolinedione (Q) with riboflavin (R) by mixing with the dye rhodamine B (RhB) in a requisite proportion.To study of FRET in solution phase we know that in a mixture of these three chromophores (Q, R, RhB) energy transfer occurs in the sequence of Q to R to RhB, respectively we also believe that this sequence also maintained in the gel sate. Hybrid gel having composition of M : Q : R : RhB = 100:100:0.5:0.02 with gives white light emission with CIE coordinates of 0.31 and 0.36 on excitation at 360nm; the values being very close to those of pure white light (0.33, 0.33).



Fluorescence spectra of W-gel excited at 360 nm and its corresponding CIE coordinates

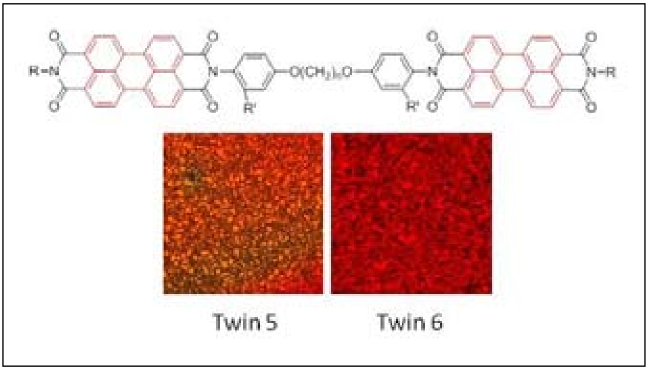
References:
[1]Pullerits, T.; Sundstrom, V. *Acc. Chem. Res.* 29 (**1996**) , 381.
[2]Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C. *Chem. Soc. Rev.* 37 (**2008**) 109.
[3]Vijayakumar C.; Praveen V. K.; Ajayaghosh, A. *Adv. Mater.*, 21 (**2009**) 2059.
[4]Rao , K. V.; Datta , K. K. R. Eswaramoorthy , M.; George,S. J. *Adv. Mater.,* DOI: 10.1002/adma.201204407

PG11

Unsymmetrical Perylene Bisimide Twin Liquid Crystals: Effect of Spacer Length on Odd –Even Oscillation and LC Properties.

Prajitha K. P. And S. K. Asha*
*Polymer Science and Engineering division, National Chemical laboratory, Pune.
E-mail: sk.asha@ncl.res.in

Conjugated liquid crystals (LC) have emerged as an interesting area of research since they provide improved ordering in the molecular level, which plays an important role in device performance. Perylene bisimides (PBI) are n-type semiconducting materials with high photo stability and high absorption coefficient in the visible region, making them a viable alternative for the poorly soluble fullerene derivatives. The rigid rod structure of the PBI core with the solubilising flexible alkyl chains at the imide position render the necessary structural requirements for inducing liquid crystallinity. However, the main challenge in this area is the attainment of mesogenicity in a temperature range that is adaptable on a device substrate; the clearing temperatures should be low and ideally the liquid crystalline phase should be retained at room temperature. This is achievable by rational design of the mesogen with careful choice of the length and position of flexible spacer segments attached to the PBI core. Here we present a novel design of twin liquid crystalline molecules based on two unsymmetrical PBI which are connected by a central polymethylene chain of varying spacer length (n: 2-12). The mesomorphic behavior and the phase transitions in twin liquid crystals are highly dependent on the number and parity of the carbon atoms in the spacer, known as the odd-even effect. All the twin molecules were structurally characterized using ^{1}H NMR and purity confirmed by mass and elemental analysis. The thermotropic characterization was carried out using Differential Scanning Calorimetric (DSC) studies combined with Polarized Light Microscopy (PLM) and variable temperature Wide Angle X ray Scattering (VT-WXRD). All the twin molecules exhibited thermotropic LC behaviour with most of them retaining the LC texture until room temperature. Energy minimized structures from DFT confirmed the bend core conformation for odd and zig- zag conformation for the even spacers.



Twin 5 Twin 6

[1] C. T. Imrie; P. A. Henderson. *Chem. Soc. Rev*., **2007**, *36*, 2096–2124.
[2] B. Jancy ; S. K. Asha. *Chem. Mater* , ***2008***, *20*, 169-181.
[3] A.Wicklein; M. Thelakkat. *JACS*, ***2009***, *131*, 14442–1445

PG12

Riboflavin - Poly (N-isopropylacrylamide) Hybrid Hydrogel: Temperature sensing, and development of Mercury sensor by *in situ* synthesis of Gel-Nano Composite

Priyadarshi Chakraborty, Partha Bairi, Bappaditya Roy and Arun K. Nandi*
Polymer Science Unit, Indian Association for the cultivation of Science
Jadavpur, Kolkata-700 032, INDIA

The present study dishes out preparation of Riboflavin(**R**) doped **PNIPAM** hybrid hydrogels(**R-PNIPAM**) and its myriad applications. The **R-PNIPAM** hydrogels were prepared in an effortless way using the free radical polymerisation technique [1]. The variation of fluorescent intensity of **R-PNIPAM** gels with temperature at different pH (fig.1) shows an increase in the intensity value in each pH reaching maxima at ~30^{0}C forming an inflection point After that it undergoes a sudden jump in the intensity value and then becomes almost constant. The initial increase of fluorescence intensity with temperature may be ascribed to the commencement of coil to globule transition of **PNIPAM** chains [2] leading to the formation of hydrophobic aggregates. The **R** molecules trapped inside those hydrophobic cores loose H bonding with water, diminishing quenching of excitons by solvent molecules and thus increase the fluorescence intensity. After 30^{o}C, owing to the phase transition of **PNIPAM,** the **R-PNIPAM** gel becomes turbid and the fluorescence intensity suddenly decreases due to scattering. This behaviour strongly recommends the **R-PNIPAM** gel to be used as an alarm type probe for detection of a specific temperature.

Silver nanoparticles were synthesised in the **R-PNIPAM** gels by immersing the slashed gel pieces in $AgNO_3$ solution. **R** acted as a reducing as well as stabilising agent. The **R** stabilized Ag nanoparticles provide alternate routes for the decay of excitons thus causing a quenching in the fluorescence intensity of **R-PNIPAM** gels. This condition is termed as "turn off" condition. On addition of Hg^{2+} ions, the fluorescent intensity is increased ~16 times than that of the **R-PNIPAM-Ag** hydrogel system and now we have termed this condition as the "turn on" condition. For all the other tested metal ions there is very small increase in the fluorescent intensity which in turn levels the nanocomposite as a selective sensor system.

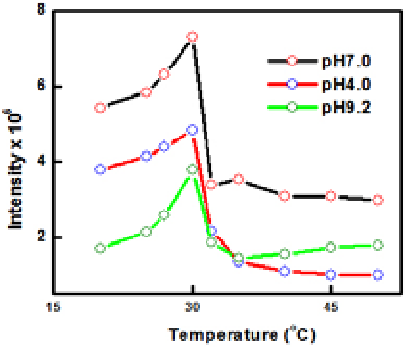


Figure 1.Variation of fluorescent intensity of **R-PNIPAM** gels with temperature at different pH.

References:
[1] Chen L.; Liu M.; Lin L.; Zhang T.; Ma J.; Songa Y.; Jiang L. *Soft matter* 6 (**2010**) 2708
[2] Heskins M.; Guillet J. E.; James E. J. *Macromol. Sci., Part A: Pure Appl. Chem.* 2 (**1968**) 1441

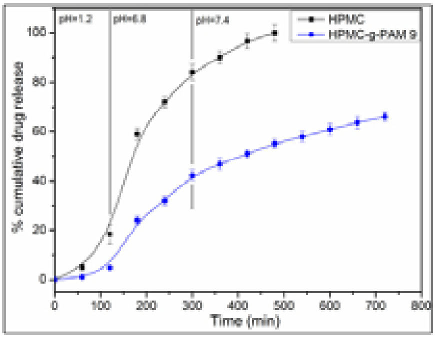
PG13

pH sensitive hydrogel composed of hydroxypropyl methyl cellulose and polyacrylamide: A novel matrix for colon specific delivery of ornidazole.

Raghunath Das, Sagar Pal*
Polymer Chemistry Laboratory, Department of Applied Chemistry, Indian School of Mines, Dhanbad – 826004 INDIA.

Hydrogels mainly based on polysaccharides/modified polysaccharides have significant advances in pharmaceutical and biomedical field for controlled release of drugs. More recently, *biopolymer-based* hydrogels have attracted ample of interest in tissue engineering and drug delivery applications [1]. Biopolymer-based hydrogels acquire various desired properties similar to their synthetic counter-parts and hence they were employed alone or with their modified forms in controlled drug release applications as they are biodegradable, abundant in nature, renewable, non-toxic, and relatively cheap. Finally, biopolymer-based or modified biopolymer-based hydrogels have high content of functional groups, like hydroxyl, amino, carboxylic acid groups etc., which are utilized in cross linking with additional functional cross linkers, as well as for further bioconjugation with e.g. cell targeting agents [2].

This study reflects the development of a novel polymeric hydrogel based on polyacrylamide grafted hydroxypropyl methyl cellulose (HPMC-g-PAM) under microwave assisted method and to use it as career for colon specific drug release of ornidazole. The developed hydrogel was characterized using various characterizations techniques. The equilibrium swelling ratio of hydrogels was recorded in different media and found to be maximum at pH 7.4. Results confirm that the prepared hydrogel showed good biocompatibility, being also able to effectively stimulate cell proliferation. The drug delivery results exhibited that HPMC-g-PAM hydrogel deliver ornidazole successfully in the colon region, without releasing the drug in stomach (Fig. 1), and may be a good candidate for orally administered drug delivery system. The release mechanism and kinetics of ornidazole from various hydrogels were determined using different mathematical models, which confirmed that non-Fickian diffusion as the principle mechanism of drug release. The release mechanism was further confirmed by calculating the exponents A and B derived from Kopcha model.



References:

[1] (a). Ortega, M. D. M.; Lorenzo, C. A.; Concheiro, A.; Loftsson, T. *International Journal of Pharmaceutics* 428 (**2012**) 152. (b) He, C.; Yin, L.; Tang, C.; Yin, C. *Biomaterials* 34 (**2013**) 2843.

[2] Oh, J. K.; Lee, D. I.; Park, J. M. *Progress in Polymer Science* 34 (**2009**) 1261.

PG14

Electroactive Polymer Gel as a Biomimetic Actuators

Rekha Saxena, Shikha Singh*,Dr Sumita Srivastava*
M.Tech 1st Year Student, Department Of Plastic Engineering, Central Institute Of Plastics Engineering and Technology, B-27, Amausi Industrial Area, Lucknow India
Email id rekha.saxena89@gmail.com, sumitas77@gmail.com

Many kinds of stimuli-responsive polymer and gels have been developed and applied to biomimetic actuators or artificial muscles. Gels exhibit a unique capability of undergoing spontaneous volume changes in response to oscillatory chemical reaction. For example, gels can undergo rhythmic swelling and shrinking in response to variations in the pH of the surrounding solution caused by an oscillating reaction. Electroactive polymers that change shape when stimulated electrically seem to be particularly promising. In all cases, however, the mechanical motion is driven by external stimuli, for example, reversing the direction of electric field. On the other hand, many living organisms can generate an autonomous motion without external driving stimuli like self-beating of heart muscles. Here we show a novel biomimetic gel actuator that can walk spontaneously with a worm- like motion without switching of external stimuli. The self motion of the gel is produced by dissipating chemical energy of the oscillatory Belousov-Zhabotinsky (BZ) reaction. The BZ reaction is the most commonly known oscillating reactions.

Figure 1. Conventional self-oscillating gel.

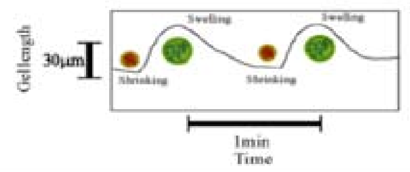
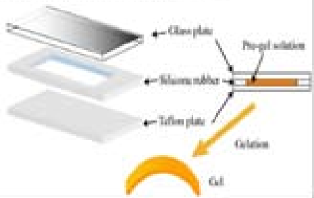


Figure 2. Preparation of the poly[NIPAAm-co-Ru(bpy)3-co-AMPS] gel undergoing anisotropic contraction. Reproduced from [25].



The change in the osmotic pressure inside the gel causes the swelling or shrinking of the polymer gel. The displacement of the self-oscillating gel is several dozen micrometers as shown in Figure 1. However, the mechanical displacement of the gel was too small to design the gel actuator. In order to make the gradient structure in the gel, we utilized the hydrophobic interaction between the Ru(bpy)32+ moieties and the casting mould during the polymerization. As a result, the large deformation of the self-oscillating gel was achieved [24]. During the polymerization, the monomer solution faces two different surfaces of plates: a hydrophilic glass surface and a hydrophobic, Teflon surface. as shown in Figure 2.

Although the gel is completely composed of synthetic polymer, it shows autonomous motion as if it were alive. The autonomous peristaltic motion of the gel would create a new design method for matter transport, micro or nano devices, etc

Keywords: polymer gel; polymer actuator; oscillating reaction.

References

[1] Maeda, S.; Hara, Y.; Yoshida, R.; Hashimoto, S. Peristaltic motion of polymer gels. Angew. Chem. Int. Ed. 2008, 47, 6690–6693.
[2] Hara, Y.; Yoshida, R. Self-oscillation of polymer chains induced by the Belousov-Zhabotinsky reaction under acid-free conditions. J. Phys. Chem. B 2005, 109, 9451–9454

PG15

Rheological view PPy based nanodispersions : Prospective Conductive Black Inks

Rupali Gangopadhyay*
Centre for Advanced Materials, Indian Association for the Cultivation of Science, Kolkata700 032
E mail of corresponding author : camrg@iacs.res.in

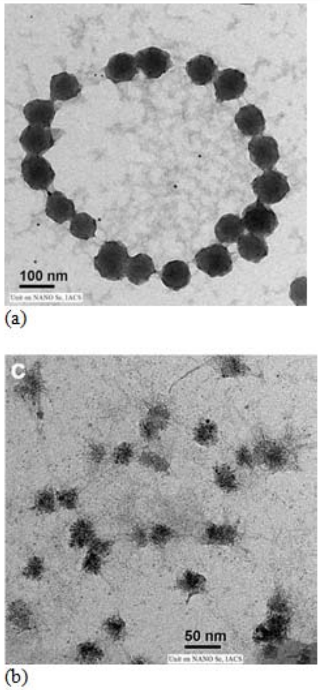


Fig.1. TEM images of (a) PPY-PVA and (b) PPY-SDS nanodispersion after 20-fold dilution

Chemical polymerization of pyrrole within aqueous solution of (a) SDS and (b) poly vinyl alcohol (PVA) gives rise to a series of nanodispersions with unique stability and monodispersity. All these dispersions, fundamentally different from simple polymeric solutions/ dispersions / blends / filled polymeric systems, have been explored in this work following microscopic, spectroscopic and rheological techniques. The PPy-PVA nanodispersion has shown uniform distribution of perfectly spherical ~110 nm (Fig. 1 a) PPy particles while PPy-SDS consists of clusters of finely dispersed spherical / elongated particles (10-20 nm) surronded by SDS micelles (Fig. 1 b) depending on the concentration of SDS, as seen from TEM, DLS. Both these systems possess high doping level (from UV-Vis analysis) and sufficient electrical conductivity (10^{-3} S/cm for PPy-SDS and 10^{-1} S/cm for PPy-PVA). Viscosity profile of both these systems have shown shear thinning property under steady shear as observed earlier for polyaniline based systems. Viscosity of the PVA based system was adjustable by dilution with water and observed shear thinning (under steady shear) was suitable for application in printing ink [1].

Dynamic mechanical studies have shown that both these dispersions behave like semidiluted single polymeric solutions and roughly follow Zimm model of viscoelasticity and do not exhibit a single relaxation time [2]. This behavior accounts for their unique stability and miscibility with water at any proportion without precipitation, until the micelle breaks for SDS based system. (We have diluted PPy-SDS with SDS solution of similar concentration). On drying or leaving the samples for seven days, partial crosslinking of PVA chains and SDS clusters take place via Fe^{3+} and after 15 days complete gelling occurs for PPy-SDS. Dynamic mechanical spectrum (G', G" vs frequency) of the aged dispersions (not gelled) have shown gel like behavior at terminal region (lower frequency) and a gel to sol transition at higher frequency. The PVA based dispersion forms uniform films on glass and metal surfaces that does not dissolve after complete drying; this observation encourages its application as ink or paint. Dried films of PPy-PVA have been used for EMI shielding application that have highlighted its importance as a conducting maerial.

References :

[1] Gangopadhyay Rupali, Mijanur Rahaman Molla *J. Polym Sci. Pt B : Polym. Phys.* 49 (**2011**) 792-800

[2] Gangopadhyay Rupali, J Appl Polym Sci., (**2012**) DOI: 10.1002/APP.38218

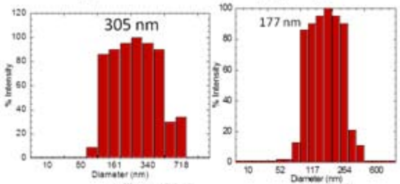
PG16

Stimuli Responsive Hyaluronan Hydrogel/Nanogel *via* Click Chemistry for Biomedical Applications

Sharad K Pasale and Gaio Paradossi*
Department of Chemical Science and Technolody,University of Rome 'Tor Vergata', 00133 Rome, Italy
Email- *gaio.paradossi@uniroma.it*

Before adding catalyst After added catalyst

Hyaluronic acid (HA) is a natural linear high-molecular weight charged polysaccharide, composed of disaccharide repeating units. It can be extracted from synovial fluids of articular joints of mammalians. Due to its excellent biocompatibility, biodegradability, as well as its ability to bind the specific receptor of CD44, a trans-membrane protein over-expressed by many tumour cells, HA can be considered as a good candidate molecule to enhance the targeting properties of synthetic micro/ nano polymer-based devices. In this contribution we have used HA for the fabrication of hydrogels and nanogels focussing on cancer treatment. The objective of the study is to impart ionic, temperature and pH-sensitive capabilities to hyaluronan based hydrogels and nanogels so that they can change their swelling properties upon external stimulation. We have developed a general and efficient method for end group modification of controlled molecular weight p(NiPAAm) samples involving "click" reaction. Mechanical properties can also be tuned using appropriate molecular chain length of polymer. HA-p(NiPAAm)-HA Hydrogels exhibited a high swelling ratio, 3000-4000% at room temperature. The swelling ratio increased at pH values higher than 3 according to the dissociation of carboxylic group. Due to the presence in the network of hyaluronic acid, these hydrogels and nanogels can be biodegraded by the action of enzymes as hyaluronidase. Coupling temperature-and pH responsivities allows a flexible control over the polymer phase behaviour, resulting in multi-functional smart materials. These HA-p(NiPAAm)-HA cross-linked hydrogels and nanogels may represent a promising material for biomedical applications.



swelling at 20 °C at 45 °C.

References:
[1] Yang, X.; Kootala,S.; Hilborn, J.; Ossipov,D.A. *Soft Matter* 7 (**2011**) 7517
[2] Xu, X.; Jha, A.K.; Harrington, D. A.; Farach-Carson, M.C.; Jia. X. *Soft Matter* 8 (**2012**) 3280
[3] Kupal, S. G.; Cerroni, B.; Ghugare, S. V.; Chiessi, E.; Paradossi. G. *Biomacromolecules* 13 (**2012)** 3592
[4] Ghugare, S. V.; Chiessi, E.; Fink, R.; Gerelli, Y.; Scotti, A.; Deriu, A.; Carrot, G.; Paradossi. G. *Macromolecules* 44 (**2011**) 4470

PG17

Effect of Silicone on the Surface Characteristics of the Hydrogels

Bindu Manchanda,[b] Shreedhar Bhat, Anubhav Saxena,*, [a] Laxmi Samantara, [a] Debarshi Dasgupta, [b]Deeksha Gupta, [b]Jacob Josemon [b] Veena Choudhary[b]
[a]Global Research & Development Centre, Momentive Performance Materials Pvt. Ltd; Survey # 9, Electronic City West (Phase-1), Hosur Road, Bangalore-560100; India
[b]Centre for Polymer Science, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India
** anubhav.saxena@momentive.com*

Since its invention, hydrogels have been one of the most discussed polymeric materials that has attracted both scientific and industrial world [1]. Hydrogels are polymeric systems, physical or chemical, that can absorb water from 10 to about 1000 times its weight without any dissolution. Hydrogels are popular in adsorbent, textile, coating, agriculture, personal care, wound care and health care industries and thus demands greater R&D developments [2]. By adding silicones in to conventional organic hydrogels enhance the mechanical property, the gas permeability and reduces bioactive residue build up [3, 4]. Silicone hydrogels use silicones as the media through which the oxygen is transferred thus gas permeability is probably up to 5 times better than the conventional gels. The major challenge here is to compatibilize the hydrophobic silicone molecules in the hydrophilic organic co-monomer additives used in the formulation and control desired surface topography.

Our silicone hydrogel designs are based on TRIS (3- tris(trimethylsiloxy)silyl propyl methacrylate) as the silicone monomer, HEMA (2-hydroxyethyl methacrylate) as the organic monomer, and EGDMA (ethylene glycol dimethacrylate) as the cross-linker. We led efforts to understand the relationship between the structure at the interface, formulation and preparation techniques. The cross-linking density was found to play a key role in the formulation by which hydrogel properties can be manipulated. When cross-linking density was increased tensile modulus of the material went up and water content decreased along with increase in the surface water contact angle. The effect of cross-linking density on the hydrogel property was nearly two fold for silicone hydrogels when compared to organic hydrogels. This enhance seen could be only realized if we consider favourable neighbouring group interaction due to which the silicone like-like domains are being created when cured. The details of this work will be presented in the poster.

References

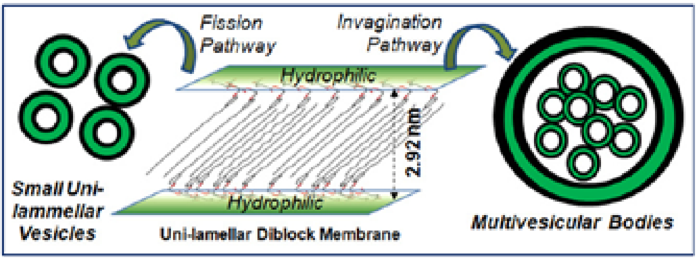
[1] Jagur-Grodzinski, J. *Polymers for Advanced Technologies*, 21 (**2010)** 27.
[2] Rybtchinski, B. *ACS Nano*, 5 (**2011)** 6791.
[3] Peng, C.-C.; Burke, T. M.; Chauhan, A. *Langmuir*, 28 (**2012)** 1478.
[4] Chhabra, M.; Prausnitz, J. M.; Radke, J. C. *Ind. Eng. Chem. Res.*, 47 (**2008)** 3540.

PG18

Design and Development of A B-Diblock Thermo-responsive Assemblies and Polymeric Vesicles

SmitaKashyap and M. Jayakannan*
Department of Chemistry , Indian Institute of Science Education & Research (IISER-Pune)
Dr.HomiBhabha Road, Pune 411008, Maharashtra, INDIA

Polymeric vesicles represent a newly emerging research area and have attracted increasing scientific interest due to their various potential applications such as controlled drug delivery and nanoreactors for controlled chemical reaction[1]. Here, the present work is designed to form vesicular carriers utilizing naturally available renewable resources based hydrophobic units (PDP) and commercially available flexible hydrophilic polyethylene glycols (PEG).The formation of uni-lamellar layer-like self-assemblies due to existence of strong inter-molecular interactions was proved by resolving single crystal structures. These amphiphilic AB diblocks produced small uni-lamellar vesicles (SUVs) or multi-vesicular bodies (MVBs), by undergoing selective vesicular fission. Based on theoretical models, self-organization parameters such as relative volume ($\nu_{e)}$ and reduced area difference (Δa_o) were determined for MVBs and SUVs. Their fluorophore encapsulation pathways as well as their dye encapsulation capabilities were studied by encapsulating pyrene. MVBs were found to be more efficient in encapsulating the dye as it was distributed uniformly throughout its hydrophobic layer. The introductions of amide linkage in the above synthetic AB diblocks lead to the thermo-responsive properties. These AB diblocks undergo phase transition when the temperature is raised above their lower critical solution temperature (LCST). The LCST of the AB diblock with shorter PEG was found to be 42 ^{0}C (very close to body temperature). While the diblock with longer PEG chain LCST value increases. Due to this unique property of phase separation above LCST, these thermo-responsive polymers are currently applied as stimuli responsive smart materials for drug delivery.



Reference:
[1] Hie, J.; Tong, X.; Tremblay, L.; Zhao, Y.*Macromolecules***2009**, *42*, 7267-7270.
[2] SmitaKashyap and M. Jayakannan, *J. Phys. Chem. B*, **2012**, *116*, 9820-9831.

PG19

Electrochemical Properties of Rectification Device Using TEMPO-containing Polymers

Hiroshi Tokue, Takashi Sukegawa, Kenichi Oyaizu and Hiroyuki Nishide*
Dept. of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan
E-mail: semth12raph7tud@ruri.waseda.jp; nishide@waseda.jp

Organic electronic devices have attracted much attention because of inherent advantages over the conventional inorganic-based materials, such as lightness, flexibility, and non-toxicity. Radical polymers containing densely populated robust radical groups were studied for electrode-active materials of rechargeable organic batteries [1]. We reported their rapid charge transportation in electrolyte and revealed its mechanism composed of electron self-exchange reaction between redox sites [2]. In this report, we utilized the excellent charge transportation in wet condition and anisotropic charge transfer corresponding to the difference of redox potentials between p-type and n-type redox polymers. The wet-typed pn-junction (Fig. 1) and transistor were fabricated and their electrochemical properties were investigated.

TEMPO-substituted polynorbornene **1** was employed as p-type redox polymer. We fabricated single-layer device by laminating **1** and Pt layers on a glass substrate and controlled potentials of both electrodes by cyclic voltammetry. The magnitude of the current increased sharply at the redox potential and achieved diffusion limited current comparable to the theoretical value. From this result, we concluded that charge transport was based on redox behavior and ideal concentration gradient of redox species. Polyviologen was employed as n-type redox polymer and the pn-junction composed of **1** and polyviologen was fabricated by laminating both polymers and Pt layers on a glass substrate. The pn-junction indicated rectification derived from the difference of redox potentials at the dissimilar polymer interface and charge transportation corresponding to two-step redox behavior of viologen. A single-layer device performed transistor property by using one electrode as both source and gate, and another as drain. Possibility of such electrochemical devices and their future prospects will be discussed.

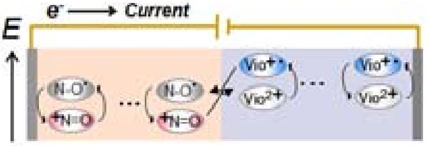


Figure 1. Schematic representation of pn-junction using p-type and n-type redox polymers.

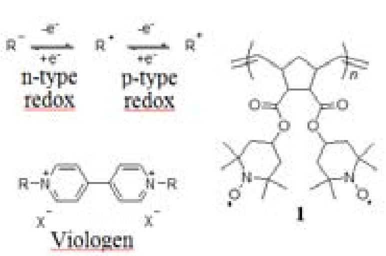


Figure 2. The p-type and n-type redox behaviors of radical species and a structural formula of viologen and TEMPO-substituted polynorbornene.

References:

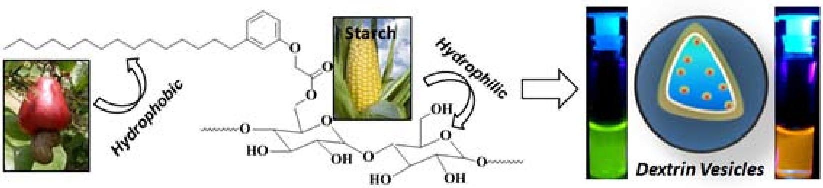
[1] Nishide, H.; Oyaizu, K. *Science.* 319 (**2008**) *737*
[2] Nakahara, K.; Oyaizu, K.; Nishide, H. *Chem. Lett.* 40 (**2011**) *222*

PG20

Design and Development of Dextrin Vesicles and Their Encapsulation Capabilities

Uma Sridhar and M. Jayakannan*
Department of Chemistry
Indian Institute of Science Education and Research (IISER), Pune,
Dr. Homi Bhabha Road, Pune-41100, Maharastra, India

Polymer based drug delivery approaches are emerging as an important tool for administrating drug to cancel tissues. Among the various polymer structures, polysaccharide based scaffolds have been explored for drug delivery applications due to their better efficacy against resistant tumour cells and fewer side effects and so on. This present approach emphasizes a facile method of preparing dextrin (starch derivative) amphiphiles using a renewable hydrophobic units such as 3-pentadecylphenol as the hydrophobic moiety. Dextrin amphiphiles with different degree of substitutions were synthesized and their structures were characterized by NMR and FTIR techniques. The self assembly of the newly synthesized amphiphiles were investigated using dynamic light scattering, electron microscope (SEM and TEM) and atomic force microscopic techniques. The critical vesicular concentrations (CVCs) were determined using pyrene as fluorophore. Further, the encapsulation capabilities of the dextrin scaffolds were investigated using hydrophobic and hydrophilic dye molecules. The results proved that dextrin with 7 % hydrophobic substitution stabilizes the Rhodamine-B (Rh-B) in the vesicular scaffold. On the other hand, higher incorporation of hydrophobic content fails to show any encapsulation. The in-vitro release characteristics of Rhodamine-B loaded dextrin vesicles were studied under physiological conditions. Esterase enzyme was employed as stimuli to breakdown he vesicular scaffolds and delivers the encapsulated cargo at much faster rate. The study gives an insight into role of the hydrophobic unit in the self assembly and the forces that are responsible for giving rise to these structures at the molecular level. The scaffolds, thus synthesized could be used for the loading and delivery of hydrophobic as well as hydrophilic anticancer drugs which are currently investigated in detail.



PG21

Effect of Layered Fillers in Interpenetrating Polymer Matrices for Vibration Damping Applications

V. G. Jayakumari, Rahna K Shamsudeen, S. Kusumakumari, R. Rajeswari, T. Mukundan*
Naval Physical & Oceanographic Laboratory, Thrikkakara, Kochi-682021, Kerala, India
** ms_npol@yahoo.in*

Vibration damping gels were developed and characterised for their application as damping material for underwater applications. In the present work, a polydimethyl siloxane (SIL) based jelly material and its interpenetrating polymer network (IPN) with epoxy/polyurethane were prepared and characterized. Interpenetrating networks offer systems with molecular interpenetration and a broad glass transition between those of individual homopolymers providing better damping [1]. In addition, effect of micron sized fillers with layered structure such as graphite, mica and clay were studied on varying compositions [2,3].These materials were characterised using vibration transmissibility measurement in 50 Hz to 4000 Hz range. Viscoelastic properties of the gel material were studied using Stress Rheometer.

A series of gel compositions with PDMS gel, PDMS-PU IPN and PDMS-Epoxy IPN were made and various layered fillers such as graphite, mica and clay were incorporated into this in varying percentages and studied their effectiveness in reducing the vibration transmissibility. The set up used for vibration transmissibility (VT) measurements are shown in fig.1. A 250 mm tube was filled with the gel and mounted on a shaker table. Two accelerometers, one at the bottom and another at the top of the tube were pasted for measuring the transmissibility. The specified sine profile was swept and used for measurement. It was observed that PU-PDMS IPNs were more effective in damping region and epoxy-PDMS IPNs are more effective in the vibration isolation region. Epoxy based IPNs (EP-SIL) with 10 phr graphite as filler reduced the VT to - 70 dB compared to - 30 dB of PDMS (SIL) alone (fig.2). Rheological properties measured showed a stable behaviour from -70 to + 120° showing their suitability for low temperature applications (fig.3).

Figure1. Set up for vibration transmissibility measurement

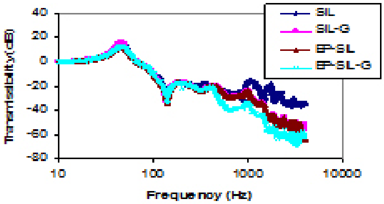


Figure 2. VT results for SIL, silicone gel with graphite filler (SIL-G), EP-SIL, EP-SIL with graphite filler

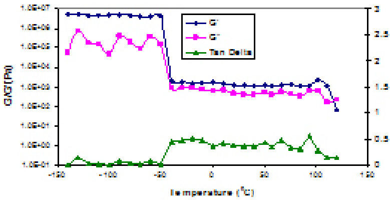


Figure 3. Rheological property of EP-SIL graphite filler

References

[1] L. H. Sperling, Interpenetrating Polymer Networks and Related Materials, Plenum Press, New York, 1981
[2] Agarwal, S. K; Delong, N. S. Bhatia, S. K.; Tew, G. N. Bhatia, S. R. *Langmuir*, 26 (2010) 17330
[3] Luo X, Chung, D. D. L.; *Carbon*, 38 (2000) 1499

PG22

Biosynthetic Copolymer Hydrogels as Carrier for For Long-Term Cell Growth

G. T. Finosh, M. Jayabalan*
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Polymer Science Division, BMT Wing,
Thiruvananthapuram – 695 012, Kerala State, India.
**Fax:0091-471-234814; Tel: 0091-471-2520212;E-Mail. muthujayabalan@rediffmail.com*

Growing demand for tissues and organs for transplantation and the inability to meet this need has led to the rapid development of tissue engineering as an alternative. Cardiac tissue engineering aims to replace or facilitate the re-growth of damaged or diseased tissue by applying a combination of biomaterials, cells and bioactive molecules. Biosynthetic polymers have been used for the fabrication of tissue growth scaffold owing to the favorable influence on the three dimensional growth of cells and extracellular matrix. In the present study a biosynthetic polymeric hydrogel scaffold based on copolymer of hydroxyl terminated polypropylene fumarate (HT-PPF) and alginate was prepared and evaluated for cardiac applications.

The biosynthetic PPF-alginate copolymer resin (PA) was synthesized by reacting HT-PPF with alginate under acidic conditions. A chemically croslinked hydrogel, PA-P was prepared by free radical and ionic crosslinking of PPF-alginate (PA) resin with polyethylene glycol diacrylate (PEGDA) and Ca^{2+} ions. PA-P was further modified by reacting with acrylic acid to get modified hydrogel, PA-PA. The physiochemical characterization were carried out by ATR spectral analysis, swelling efficiency and water holding capacity, contact angle measurements, DSC analysis, surface morphology. The biological evaluations to assess hemocompatibility, cytotoxicity and apoptosis were carried out [1]. The long term cell penetration was quantified by a modified MTT assay. In order to enhance the long term viability of cells in hydrogels, unidirectional porosity was introduced to the hydrogels by controlled dynamic stretching in aqueous conditions.

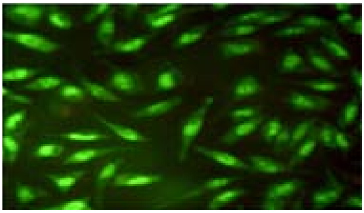


Figure-1. Live/dead assay showing healthy being of cells in PA-PA hydrogel

The water contact angle (PA-P 38.94 ± 3.99, PA-PA43.42 ± 2.42) of the water swelled hydrogels revealed that both these hydrogel surface possess amphiphilic character. The equilibrium water holding capacity (PA-P 61.12 ± 1.79, PA-PA73.36 ± 1.77) and swelling of the scaffold (PA-P 157.48 ± 11.94 %, PA-PA273.35 ± 22.29%) is favorable for the growth of different cell types for cardiac tissue formation. DSC thermal evaluation of hydrogels revealed endothermic peak corresponding to the melting of freezing-free water which provides a suitable microniche for the cells to penetrate and to proliferate. PA-PA was found to be hemocompatible and supports the healthy being of the cells as evident by MTT assay and direct contact assay. The live/dead assay showed these cells were non apoptotic (**Figure 1)** [2]. The quantification of infiltration of L929 fibroblasts for 18 days showed that it can promote and provide long term viability in the interstices of PA-PA. The unidirectional porosity induced by the controlled stretching of PA-PA imparted characteristic changes in the surface morphology as evident by ESEM. The cell penetration was found to be increased to a greater level than the unstretched samples. All these qualities promote PA-PA to be a good scaffold for cardiac tissue engineering applications for the treatment of end stage cardiac complications.

References

[1] Finosh, G. T.; Jayabalan, M.; Vandana S.; Raghu, K. G. *Colloids Surf., B*, 107 (**2013**) 137.
[2] Taylor, E.L.; Megson, I. L, Haslett, C.; Rossi, A. G.; *Cell Death Diffe,r* 10 **(2003)** 418.

Polymer processing

Invited

Shielding and de-shielding of hydrogen bonding motifs; from synthetic to bio-polymers

Sanjay Rastogi, Yogesh S. Deshmukh, Jules Harings, Maurizio Villani, Esther Vinken
Department of Materials, Loughborough University, Loughborough, England (UK)
Department of Bio-Materials, Maastricht University, The Netherlands
Department of Complex Fluids, National Chemical Lab., Pune, India
e-mail: s.rastogi@lboro.ac.uk

During the spinning process in spiders and silkworms ions are amongst several other parameters crucial for mediating the transition from the solubilized random coil and/ or helical conformation to crystalline β sheets. Prior to the assembly into β sheets, which give rise to a unique combination of properties, ions inhibit the interchain hydrogen bonding. In this presentation we will show that under specific conditions water can be a good solvent for a range of hydrogen bonded aliphatic polymers including polyamides. Depending on the presence of monovalent or divalent ions and their ionic strength, the dissolution temperature of polyamides can be suppressed to the extent that the amorphous polyamides can be obtained at room temperature. These amorphous polyamides can be oriented, and restoration of hydrogen bonding in the oriented structures can be perceived with the successful removal of the ionic motifs. With the help of dynamic NMR, FTIR spectroscopy and X-ray diffraction the dissolution process of polyamides, shielding and de-shielding process of hydrogen bonding is investigated. Different states of water molecules and their interaction with the polyamides will be also discussed.

References:

[1] Self-organization of Oligopeptides Obtained on Dissolution of Feather Keratins in Superheated Water; Jie Yin, Sanjay Rastogi, Ann E. Terry, and Crisan Popescu; *Biomacromolecules* 2007, 8, pp 800-806

[2] Dissolution of Hydrogen-Bonded Polymers in Water: A Study of Nylon-4,6; S Rastogi, AE Terry, E Vinken; *Macromolecule*s 2004; 37(24) pp 8825 – 8828

[3] The Influence of Hydrogen Bonding on the conformaational Changes, the Brill Transition, and Lamellae Thickening in (Co) polyamides, Vinken, E., Terry, A.E., Koning, C.E. and Rastogi, S., *Macromolecules*, 39, 2006, pp 2546-2552.

[4] Vinken, E., Terry, A.E., van Asselen, O., Spoelstra, A.B., Graf, R. and Rastogi, S., "Role of Superheated Water in the Dissolution and Perturbation of Hydrogen Bonding in the Crystalline Lattice of Polyamide 4,6", *Langmuir*, 24, 2008, pp 6313-6326

[5] Jules A. W. Harings, Yefeng Yao, Robert Graf, Otto van Asselen, Rene Broos and Sanjay Rastogi; "Erasing Conformational Limitations in *N*,*N*′-1,4-Butanediyl-bis(6-hydroxy-hexanamide) Crystallization from the Superheated State of Water" ; *Langmuir*, 25(13), 2009, pp 7652-7666

[6] PhD thesesTU Eindhoven ; Esther Vinken (2008); Jules Harings (2009); Maurizio Villani (2012) and Yogesh S. Deshmukh (2012)

Effect of Confinement and Viscosity Ratio on Droplet Coalescence in Sheared Polymer Blends

Pieter De Bruyn, Ruth Cardinaels and Paula Moldenaers*
Soft Matter, Rheology and Technology, Department of Chemical Engineering, KU Leuven, Willem de Croylaan 46, BE-3001 Leuven, Belgium
**Paula.Moldenaers@cit.kuleuven.be*

The properties of an immiscible polymer blend strongly depend on the morphology, which is the result of a balance between droplet breakup and coalescence. Currently, technology improvement has led to a continuous trend towards smaller scales. When two-phasic fluids such as polymer blends are processed in microfluidic devices, the droplet size can become comparable to the dimensions of the channels, which will cause wall effects (confinement) on the droplet dynamics [1].

In the present work, the effect of geometrical confinement on the coalescence of sheared droplets is systematically studied. A home-built counter rotating parallel plate device, equipped with a microscope, is used to visualize two interacting droplets in shear flow. Generally, coalescence requires very weak flows, associated with low capillary numbers. In our previous study it was observed that confinement extends the range of capillary numbers for which droplets coalesce [2]. Hence, confinement can promote droplet coalescence. However, this study was limited to a viscosity ratio of one and a single initial relative position of the droplets. The previous study is now extended by studying the effect of confinement on droplet coalescence for viscosity ratios below and above one. Furthermore, for the first time the effect of confinement on droplet coalescence is studied for a wide range of initial relative positions of the two droplets. One of the interesting results is the occurrence of reversing trajectories for confined droplets with a very limited initial centertocenter distance in the velocity gradient direction. Consequently and unlike in bulk conditions, in confinement there is a lower boundary for this distance, below which there is no coalescence. The value of this lower boundary depends on the viscosity ratio. On the other hand, the vertical center-to-center distance up to which coalescence is possible, is larger in confinement as compared to bulk conditions. In addition, the coalescence angles are smaller in confinement. These differences in the dynamics of colliding droplets in unconfined and confined conditions can be explained on the basis of trajectory analysis, 2D numerical simulations and investigation of the rotation speed of the droplet doublets.

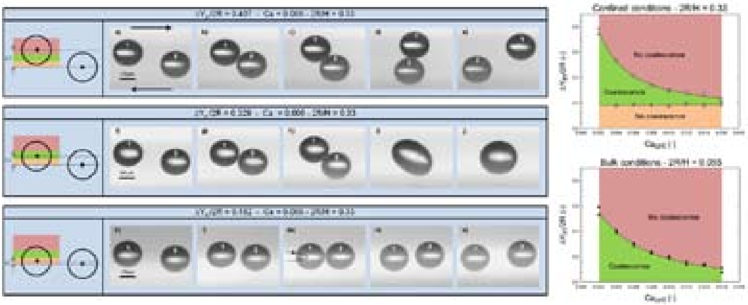


Figure 1. Typical droplet behaviour of interacting droplets in shear flow with different initial offsets $\Delta Y_{in}/2R$ (=dimensionless distance between the droplet centers in the velocity gradient direction) for bulk and confined conditions (droplet diameter 2R / gap spacing H = 0.055 and 0.30)

References

[1] Van Puyvelde, P.; Vananroye, A.; Cardinaels, R.; Moldenaers, P. *Polymer*, 49 (**2008**) 5363.
[2] Chen, D.; Cardinaels, R.; Moldenaers, P. *Langmuir*, 25 (**2009)** 12885.

Viscoelastic Phase Separation Process and the Development of Micro and Nanomorphologies in Epoxy Based Blends for Super Toughness

Sabu Thomas*
[a]*Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Priyadarshini Hills P. O.*
Kottayam, Kerlala, India -686 560
Email.sabuchathukulam@yahoo.co.uk

Phase separation in general could be either by diffusion or by diffusion and hydrodynamic flow. A new model has been suggested recently to follow the phase separation process in dynamically asymmetric mixtures composed of fast and slow components. This new model is often called the ***viscoelastic phase separation process*** due to the fact that viscoelastic effects play a dominant role in the phase separation process [1-6]. The dynamic asymmetry can be induced by either the large size difference (mol.wt) or the difference in glass-transition temperature between the components of a mixture or blend. The mol.wt difference often exists in complex fluids, such as polymer solutions, polymer blends, micellar solutions, colloidal suspensions, emulsions, and protein solutions. The Tg differences, can exist in any mixtures. In dynamically asymmetric mixtures, phase separation generally leads to the formation of a long-lived `interaction network' (a transient gel) of slow-component molecules (or particles), if the attractive interactions between them are strong enough. Because of its long relaxation time, it cannot catch up with the deformation rate of the phase separation itself and as a result the stress is asymmetrically divided between the components. This leads to the transient formation of network like or sponge like structures of a slow-component-rich phase and its volume shrinking [4]. In the present talk we present our new results on the viscoelastic phase separation process in epoxy/SAN and epoxy/ABS blends [1-4]. Epoxy resin is often blended with high molecular weight thermoplastics to generate micro structured morphologies for the better impact performance. These systems are very ideal to follow the viscoelastic phase separation process on account of their mol.wt and Tg differences. We have looked at the phase separation process in these blends by various techniques such as optical microscopy, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and small angle laser light scattering. The dynamics of phase separation has been carefully followed by optical microscopy and laser light scattering. In most cases the system undergo spinodal decomposition and the viscoelastic phase separation was prominent at higher concentration of the thermoplastic phase where phase inversion occurs[1-6]. The particle in particle morphology (secondary, ternary and quaternary phases), IPN type of structures and unusual shrinkage have been examined as a result of the viscoelastic phase separation process [1, 4]. All these phenomena have been carefully quantified and co-related with the viscoelastic phase seapration process.

References

[1] Jyotishkumar, P; Pionteck, J; Ozdilek, C; Moldenaers, P; Cvelbar, U; Mozetic, M; Thomas, S. *Soft matter*, 7(2011) 7248.
[2] Jyotishkumar, P; Ozdilek, C; Moldenaers, P; Sinturel, C; Janke, A; Pionteck, J; Thomas,S. *J. Phys. Chem. B.*,114 (2010) 13271.
[3] Jyotishkumar,P; Koetz, J; Tierisch, B; Strehmel,V; Häßler,R; Ozdilek,C; Moldenaers, P; Thomas,S. *J. Phys. Chem.B.*, 113 (2009) 5418.
[4] Jose,J; Joseph,K; Pionteck,J; Thomas,S; *J. Phys. Chem. B.*, 112 (2008) 14793.
[5] Zhong,x; Liu,Y; Su,H;Zhan,G; Yu,Y; Gan,W. *Soft Matter*, 7(2011) 3642.
[6] Tanaka,H; *Adv Mater.*,21(2009) 1872.

Carbon Nanotubes based Polymer Composites: Processing, Structure and Properties

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) incorporated polymer composites have gained enormous research interest in the academic as well as industrial community due to the unique properties associated with CNTs. However, the 'aggregated' dispersion of CNTs in the polymer matrix along with inadequate interfacial interaction between the CNTs and the polymer matrix make it a challenge to achieve outstanding properties associated with CNTs. In this context, multiwall carbon nanotubes (MWNTs) have been exfoliated with the help of an organic modifier; Na-salt of 6-amino hexanoic acid (Na-AHA). Na-AHA modified MWNTs have been shown to exhibit a lower electrical percolation threshold in various polymer matrices, which include polyamide 6 (PA6), polypropylene (PP) and various binary and ternary blends of PP, PA6 and acrylonitrile butadiene styrene copolymer (ABS) [1-5]. The talk will focus on the 'processing-structure-property' relationship studies in these composites, which may serve as the basis for the development of MWNTs based polymer composites for industrial application.

[1] P. V. Kodgire, A. R. Bhattacharyya, S. Bose, N. Gupta, A. R. Kulkarni, A. Misra, *Chem. Phys. Lett.,* **2006,** 432, 480-485.
[2] S. Bose, A. R. Bhattacharyya, P. V. Kodgire, A. R. Kulkarni, A. Misra, *J. Nanosci. Nanotech.,* **2008,** 8, 1867-1879.
[3] S. Bose, A. R. Bhattacharyya, R. A. Khare, A. R. Kulkarni, P. Pötschke, *Macromol. Symp.,* **2008,** 263, 11-20.
[4] S. Bose, A. R. Bhattacharyya**,** R. A. Khare, A. R. Kulakarni, T. U. Patro, P. Sivaraman, *Nanotechnology,* **2008,** 19, 335704.
[5] S. Bose, A. R. Bhattacharyya, A. R. Kulkarni, P. Pötschke, *Comp. Sci. Tech.,* **2009,** 69, 365-372.

Squeeze flow analysis of polymeric resins through porous fabrics

Akankshya Mazhi and Abhijit P. Deshpande*
Department of Chemical Engineering, Indian Institute of Technology Madras,
Chennai - 600036 INDIA
*abhijit@iitm.ac.in

The permeation and imbibition characteristics of different fluids in porous media are important in various polymer and composite processing operations. Polymeric composite processsing involves flow of polymeric resins through fibrous beds. In this work, constant velocity squeeze flow experiments were carried out with different fluids on bare surface and fabric surfaces. Polyester, epoxy and polyol were some of the model fluids used, while aluminum and glass farbrics were some of the substrates used. Normal force variation with squeezing gap was analyzed for different combinations of the types of fluid, temperature, squeezing velocity and the substrates. Three distinct regions could be identified; Region 1 (in the beginning when contact of the fabric with the fluid starts), Region 2 (squeeze flow occurs) and Region 3 (towards the end of the squeeze flow experiment, when the fluid film is very thin). Each region was then analysed in detail and attempts were made to compare results with a suitable model.

Advanced Material Preparation with Co-rotating Twin-Screw Extruders

Babu Padmanabhan, Don Robert Roden*
STEER Engineering Pvt. Ltd.
290, 4th Main, 4th Phase, Peenya Industrial Area
Bangalore, Karnataka, India 560 058
* robert.roden@steerworld.com

Neat Polymer resins cannot provide performance characteristics that are needed in the present day advanced applications. Plastics compounding attempts to present a solution by modifying one or more resins with additives, fillers and reinforcements. While some resins and modifiers are highly stable to shear and temperature, some are highly sensitive. The use of bio-plastics, bio-fillers and other sensitive polymers such as PLA is on the rise. Certain polymers such as PET and others such as PP although more stable suffer from molecular weight loss if not handled carefully. Applications in information technology grew sharply with the improvement in the process capability of the CPU. Likewise, applications in material technology are influenced by the process capability of the Extruder Processing Zone (EPZ) of the co-rotating twin-screw compounder. A ten-fold improvement in EPZ process capability accompanied by precise control of shear rates, kneading cycles and stirring rates can usher rapid growth of applications in plastics technology.

Figure 1: Using melting and mixing elements designed for specific tasks can significantly improve processing efficiency (DSE mixing elements)

Plastics compounding efficiency can be significantly improved by utilizing special elements within the EPZ designed for specific tasks such as kneading or promoting laminar flow. By using such melting/mixing elements that are designed to deliver a specific response it is possible to reduce or eliminate ineffective and unintentional energy consumption. With more effective and predictable melting and mixing it is possible to reduce the required length of the EPZ and free up energy which can result in higher throughput, lower process temperatures, and better product quality. Since fewer barrel sections and shorter screw shafts will be required savings can be realized in capital expenses as well, and the smaller footprint of the extruder will require less floor space.

Co-Rotating Twin Screw Extruders are increasingly being used to replace continuously stirred tank reactors, offering a continuous manufacturing option with many advantages over batch reactor methods. Examples include: Very uniform and controlled energy input, uniform residence time in a high energy mixing environment, fully self-wiping design, small working volume, on-line quality assurance, environmental containment, etc. With a nearly infinite availability of process configurations, twin screw compounders can perform many mixing functions to increase and control reactions rates and significantly improve product quality and manufacturing productivity. The narrow residence time in which materials reside within a mixing/reaction environment can result in a significant reduction in the polydispersity of the reacted product. Examples of reactive extrusion include preparation of reactive blends, grafting vulcanization (TPV), chemical modification, and polymerization.

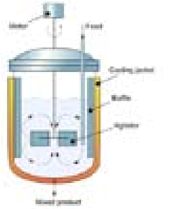


Figure 2: Continuously stirred tank (batch) reactor

This paper presents a 21st century outlook to high performance twin-screw compounding which can also lead to more cost effective and scientific compounding.

PE-CPE Blends and their Graphene Oxide Nanocomposites: Properties and Reduced Low Temperature Brittleness

Vikas Mittal[a,*], A. Chaudhry[a], Gisha Luckachan[a], Nadejda Matsko[b]
[a]*Chemical Engineering Department, The Petroleum Institute, Abu Dhabi, UAE*
[b]*Graz Centre for Electron Microscopy, Graz, Austria*
**Vikas Mittal, vmittal@pi.ac.ae*

Graphene-based nanocomposites were generated by solution mixing of the graphene oxide filler with chlorinated polyethylene compatibilizers followed by melt mixing of the solution mixed masterbatches with high density polyethylene. Compatibilizers with two different chlorination contents were used in different amounts in order to analyze their effect on the morphology and properties of resulting nanocomposites. Peak melting point as well as overall crystallinity was affected by graphene oxide as well as compatibilizers. Compatibilizer with higher chlorination content also interacted with polar graphene oxide surface more effectively thus leading to better filler dispersion in the composites. The addition of compatibilizers to the composites resulted in their shear and processing stability at higher angular frequencies and temperature, which otherwise was not possible for pure polymer as well as composites without compatibilizer. The mechanical performance of the nanocomposites at ambient conditions was also affected by the factors like filler delamination, plasticization of the matrix, compatibilizer content as well as their chlorination level and amorphous/semicrystalline nature. An increase of 16% in tensile modulus and 21% in strength of the composites with 5 wt% of 25% chlorinated compatibilizer at 0.5 wt% graphene oxide content was observed. The graphene oxide platelets were also observed to be covered with harder phase in AFM which was concluded to have resulted due to stronger nucleating action of graphene clusters along with alignment or ordering of CPE phase at the interface with filler. The filler and the CPE phases were observed to have chemical interaction during solution mixing which enhanced during melt mixing of CPE- graphene oxide masterbatch with PE matrix. Majority of the Cl atoms in the CPE chains were observed to be depleted during chemical reaction or thermal degradation at melt compounding temperature, thus, resulting in chlorine free materials. The semi-crystalline CPE (CPE25) compatibilizer did not induce viscoelastic behavior at temperatures lower than the glass transition temperature of PE, whereas the amorphous CPE (CPE35) had completely different behavior. The samples with CPE35 could not be sufficiently hardened even at -180^{0}C and remained too soft for cryo-sectioning.

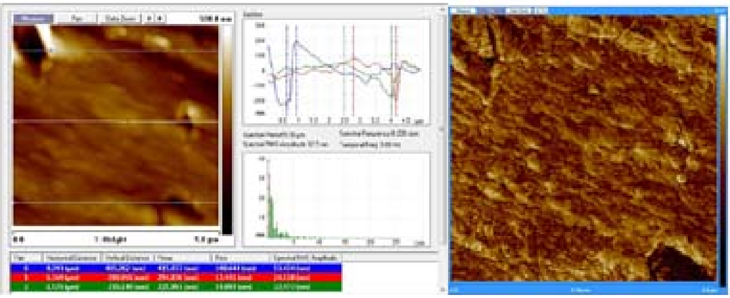


Figure 1. Height corrugation (left) and phase (right) analysis of the block faces sectioned at -180^{0}C for PE+G+5%CPE35 nanocomposite.

Oral

Effect of In Process Fiber Orientation on the Melt Rheological Behavior of a Short Aramid Fiber Reinforced Thermoplastic Elastomer

Shibulal G S and Kinsuk Naskar*
K.Naskar (knaskar@rtc.iitkgp.ernet.in)
Rubber Technology Center
I.I.T Kharagpur
West Bengal-721302

The effect of fiber loading and its orientational changes on the melt rheological properties of a short aramid fiber reinforced ethylene-octene copolymer was explored as a function of dynamic strain and frequency using a Rubber Process Analyser (RPA). The viscoelastic responses such as the storage modulus and complex viscosity to a dynamic strain sweep and linear viscoelastic (LVE) frequency sweep in several cycles were performed to probe the orientational changes of the short fiber within the sample. An enhanced elastic shear modulus was observed at the low strain regime with a few cycles of strain sweeps and level off thereafter [Fig 1]. This can be attributed to the orientational changes of the short fiber from its initial random orientation to a well-ordered continuous fiber string and the string-string packing with repeated oscillatory shear strain. The complex viscosity measured at all the frequency sweep cycles shows similar values which are not subjected to any pre strain history. But very interestingly the complex viscosity measured as a function of LVE frequency sweep having the influence of a pre strain, which is responsible for the fiber string formation was also found to increases in first few cycles [Fig 2]. The optical microscopic images of the samples before and after the RPA analyses also support the fiber orientations and their subsequent packing with repeated strain sweeps.

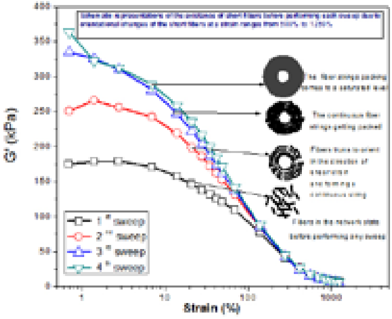


Figure 1 Variation of G' of a 5 phr short fiber filled composite with repeated strain sweeps from 0.7% to 1250% at 80°C and 0.3Hz

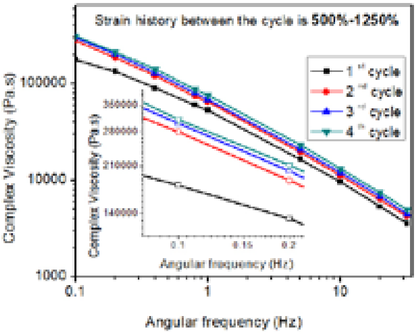


Figure 2 Variation of complex viscosity of the composite with repeated frequency sweep from 0.1Hz to 33 Hz at a constant strain of 1% at 80°C involved with a pre strain history 500% to 1250%

Electrospinning: production of fibers due the presence of small amounts of high molecular weight polymer in polydisperse and low concentration solutions

Naveen K. Reddy[a], *Siddarth Srinivasan*[b], *Ljiljana Palangetic*[a], *Robert E. Cohen*[b], *Gareth H. McKinley*[c] *and Christian Clasen*[a]
[a] Department of Chemical Engineering, KU Leuven, B-3001, Belgium
[b] Department of Chemical Engineering, MIT, Cambridge, MA 02139, United States
[c] Department of Mechanical Engineering, MIT, Cambridge, MA 02139, United States

Fiber-spinning has become one of the major topic of research in recent year due to its ability to produce micro to nano meter thick fibers using polymer solutions at room temperatures and to form thick non-woven fabrics. These fabrics have potential applications in areas such as non-wetting and breathable clothing, wound dressing and template for growing artificial skin etc. Many techniques have been invented or rediscovered for making micro to nano meter thick fibers; examples are electro-spinning, spray-spinning, forced-spinning etc. During fiber production depending of the conditions, there can be only beads (without fibers), beads with fibers or just fibers. The control parameters that are important in producing only fibers (or predominantly fibers) are still not clear. A review of literature on this topic shows different parameters to be important. A few of these control parameters are the concentration (C) of polymer solution should be above the overlap concentration (C*), solution must have certain number of entanglements, should show extensional thickening, solution should be capable of forming a network etc. It is well know in literature that a polydisperse polymer solution gives fibers at concentrations well below C*. Recently we have shown, fibers can be produced by blending high concentration low molecular weight (Mw) polymer with low concentration high Mw polymer such that the effective Mw is similar to the polydisperse sample[1]. This experimental evidence points that the extensibility averaged molecular weight (M_L) and the extensibility averaged C_L* might be a major factor that controls the fiber formation. In this talk we will discuss the results in terms of some of the above mentioned control parameters on fiber formation using a well-characterized PMMA solution.

References

[1] Siddarth Srinivasan, Shreerang S. Chhatre, Joseph M. Mabry, Robert E. Cohen, Gareth H. McKinley, *Solution spraying of poly(methyl methacrylate) blends to fabricate microtextured, superoleophobic surfaces*, Polymer **52** (2011) 3209-3218

Melt-Processed LLDPE/EVA/PANi-MDSA Conducting Composites

Sneh Bharti*, Anup K. Ghosh and Josemon Jacob
Centre for Polymer Science and Engineering, Indian institute of Technology Delhi, Hauz Khas, Delhi 110016, India
** Sneh Bharti, sbhartiiitd@gmail.com*

The field of polymers was revolutionized in 1977 by the discovery of conductivity in iodine-doped polyacetylene which was followed by discovery of many more conducting polymers such as polyaniline (PANi), polypyrrole, polythiophenes, poly(p-phenylene), and poly(p–phenylene sulfide). These polymers can conduct electricity due to their unique molecular structure and are called intrinsically conducting polymers (ICP). All these ICPs are associated with limitations in their processability and mechanical properties. Several strategies have been used to solve these limitations. The authors have recently developed methanedisulfonic acid doped PANi (PANi-MDSA) with thermal stability up to 315 ˚C [1], thereby, enabling blending with general polymer matrix. The resultant composite has higher electrical conductivity and better mechanical properties simultaneously.

The composite of linear low density polyethylene (LLDPE) and PANi was found to be very attractive because of its excellent processability, low cost and desirable mechanical properties which can be used in preparation of antistatic materials. There is large difference between the polarity of LLDPE and PANi which leads to lack of compatibility between the two and results in phase separation and low conductivity. Phosphoric acid-esters [2-3] and ethylene-acrylic acid [4-5] copolymer were used by the authors to increase the compatibility between LLDPE and PANi. Excess of DBSA (dodecylbenzenesulfonic acid) in PANi-DBSA was also used to address the compatibility issue [6-8]. In this work, ethylene vinyl acetate has been used to increase the polarity of the matrix. Various composites of LLDPE/EVA/PANi were prepared by melt processing. The electrical, mechanical, rheological properties and morphology of composite were investigated. An increment of up to four orders of electrical conductivity of LLDPE/EVA/PANi-MDSA was obtained compared to that of LLDPE/PANi-MDSA.

References

[1] S. Bharti, J. Jacob and A. K. Ghosh, *Polymer International*, DOI:10.1002/pi.4365 (2012).
[2] J. P. Yang, P. Rannou, J. Planès, A. Proń and M. Nechtschein, *Synthetic Metals*, **93**, 169-173 (1998).
[3] J. Laska, A. Proń and S. Lefrant, *Journal of Polymer Science Part A: Polymer Chemistry*, **33**, 1437-1445 (1995).
[4] G. Wang, Z. Shen, X. Li and C. Li, *Journal of Applied Polymer Science*, **98**, 1511-1516 (2005).
[5] C. Su, G. Wang, F. Huang and X. Li, *Polymer Composites*, **29**, 1177-1182 (2008).
[6] O. T. Ikkala, J. Laakso, K. Väkiparta, E. Virtanen, H. Ruohonen, H. Järvinen, T. Taka, P. Passiniemi, J. E. Österholm, Y. Cao, A. Andreatta, P. Smith and A. J. Heeger, *Synthetic Metals*, **69**, 97-100 (1995).
[7] A. J. Heeger, *Synthetic Metals*, **57**, 3471-3482 (1993).
[8] N. Kuramoto and E. M. Geniès, *Synthetic Metals*, **68**, 191-194 (1995).

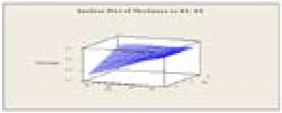
Effect of Speed Ratio and Cycle Time on Thickness of LLDPE Products in Rotational Moulding Process

[a] PL. Ramkumar *, [b]D.M. Kulkarni and [c]Sachin D. Waigaonkar
[a, b & c] Department of Mechanical Engineering, Brila Institute of technology and Science Pilani-Goa Campus,
Zuari Nagar, Goa -403726, India
*Email: ramkumarpl@goa.bits-pilani.ac.in , plramkumarno1@gmail.com
*Mob no: 9823256780.

Rotational moulding is a polymer processing technology used for producing hollow seamless articles by heating, melting and subsequent sintering of powders in bi-axially rotating moulds, followed by cooling the melt for solidification [1- 4]. It is used to produce hollow parts at a lesser production cost. The parts produced by rotational moluding process are relatively stress free compared to other moulding process like injection moulding or blow moulding, since in rotational moulding plastics are not forced to take up a shape that is not natural for it. Rotational moulding process is extensively reviewed by Crawford [5, 6] in terms of structure, properties, material and processibility studies. He has identified that out of all polyethylenes', linear low density polyethylene (LLDPE) has a unique melt flow property which makes it suitable for rotational moulding process. However, a proper control over the process parameter is required before embarking on tightly controlled production schedule to yield desired thickness, shape, surface finish etc. which is considered as quality measures of the product. The two important process parameters that govern the thickness of the product are: Speed Ratio (X_1), Cycle Time (X_2) (Ref. table for process parameters and their levels based on D.O.E- Full factorial design).

A number of investigations have been carried out to study the effect of these variables on mechanical properties and quality of rotationally moulded products. Effect of thickness for various speed ratios and cycle time is the biggest challenge in this process. Moulders have to depend heavily upon trial and error methods as well as experience of the operator to predict the thickness for a particular speed ratios and cycle time. In this work, an attempt has been made to investigate the thickness of the rotational moulded parts for different speed ratios and cycle time using experiments and statistical techniques .Experimental runs followed by analysis of variance (ANOVA) have revealed that thickness of the part is severely affected by both of these process parameters.

Process Parameters	Unit	Designation	Lowest level (-1)	Highest level (+1)
Speed ratio	rpm	X1	3:1	5:1
Cycle time	minutes	X2	32	42



Regression equations have been derived to predict the part thickness in terms of above process parameters within the regime of experimentation (i.e., -1 to +1). Thickness variation with respect to both the process parameters are shown using surface graphs (fig).

References:

[1] Brent strong, A.**2006**.Plastics Materials and Processing, Pearson Education Inc, p. 571. New Jersey: United States.
[2] Crawford, R.J.; James, L.T.**2002.**Rotational Molding Technology,William Andrew Publishing, p.1.Norwich, England**.**
[3] Antonio, G.; Alfonso, M. *J. Appl. Polym. Sci* .92 **(2004**) 449
[4] Bharat, I.C.; Elizabeth, T.; John, V. *J. Polym. Eng. Sci*. 41 (**2001**) 1731
[5] Spence, A.G.; Crawford, R.J. *J. Polym. Eng. Sci*. 36 (**1996**) 993
[6] Crawford, R.J. *J. Mater. Process. Technol.* 56 (**1996**) 263

Low Temperature Cure Epoxy Adhesive with High Temperature Performance

Ranajit Pal*, Rohit Sharma, Suraj S., V. Lakshmana Rao
Polymers and Special Chemicals Division
Vikram Sarabhai Space Centre, Thiruvananthapuram-695022.
** Corresponding author, Email: ranajitp@gmail.com*

Room temperature (RT) curing epoxy adhesive system with high service temperature upto 120° C is of great importance in the area of aerospace, automobile and avionics industries for structural applications [1-2]. Conventional polymeric adhesive system cannot withstand the high temperature (HT) environments since the polymer loses its property above the glass transition temperature (Tg). In order to achieve satisfactory performance at ambient and HT, polymeric systems must be modified suitably [3-4].

The present work outlines the synthesis of a urethane-oxazolidone modified epoxy resin that achieves the required cross link density at room temperature upon curing with a polymeric aromatic amine that is derived from reaction product of meta-xylylenediamine and epichlorohydrin and a phenolic tertiary amine. The study also was extended to evaluate the effect of loading of crystabollite silica (CBS) on the adhesive properties at RT and HT. The maximum adhesive strength was achieved as 25 to 26 MPa at RT (Fig. 1.a) and 7 to 8 MPa at 120° C (Fig. 1.b). CBS improved the adhesive properties initially quite rapidly. Beyond 5 parts per hundred ratio (phr) loading of CBS, the effect was less pronounced. The high temperature property is attributed to high Tg of the cured system.

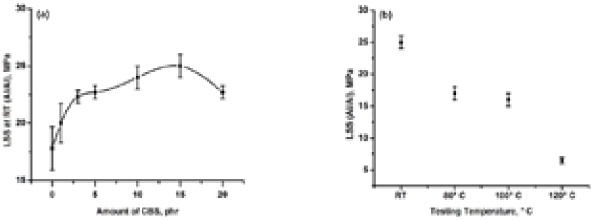


Fig. 1: (a) Effect of amount of CBS on lap shear strength and
(b) Effect of temperature on lap shear strength

Key words: epoxy, high temperature performance, crystabollite etc.

References

[1] Dodiuka, H.; Keniga, S.; Lirana, I. *J. Adhes*., 22 (**1987**) 227.
[2] Dodiuka, H.; Keniga, S.; Lirana, I. *J. Adhes*., 31(**1990**) 203.
[3] Dodiuka, H.; Keniga, S.; Lirana, I. *Composites*, 22 (**1991**) 319.
[4] Ungarish, M.; Joseph, R.; Vittoser, J.; Keniga, S. *Composites*, 21 (**1990**) 481.

Poster

PR1

Studies of Surface Modification of Silica by Silane Coupling Agent for Improved Properties in Rubber/Silica Composites

Bharat Kapgate and Chayan Das*
Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur, Maharashtra, India-440010
*Email: chnds@rediffmail.com; chayandas@hotmail.com

Silica filled rubber composites are of great importance in different fields like tire industry, packaging, footware, food industry to name a few due to improved tensile strength, abrasion resistance, tear strength, lower rolling resistance etc. However, the agglomeration of silica and it's poor compatibity with rubber matrix put together a barrier to achieve rubber composite with desired properties. In this context, surface modification of silica by bifunctional silane coupling agent plays a significant role in achieving improved composite properties. Silane coupling agents in one hand reduces interparticle interaction of silica leading to better dispersion into rubber matrix and on the other hand contributes to the crosslinking in the rubber structure via it's organofunctional group containing sulfur. In this work, the role of γ-mercaptopropyltrimethoxysilane (γ-MPS), a silane coupling agent, as a surface modifier of silica in improving the ultimate properties of the composites has been studied. Surface modification of silica by γ-MPS has been done at different stages of composite preparation viz. pre-modification of silica before external mixing with rubber, modification of silica during external mixing with rubber and modification along with in-situ silica generation into rubber matrix. Morphology, mechanical properties and visco-elastic properties of silica filled composites obtained from different routes have been studied and compared with unmodified silica composites. These studies indicate that surface modification results in better filler dispersion, improved mechanical properties and enhanced rubber-filler interaction.

Polymer processing

References:

[1] Murakami, K.; Iio, S.; Ikeda, Y.; Ito, H.; Tosaka, M.; Kohjiya. S. *J Mater Sci* , 38 **(2003)** 1447
[2] Das, A.; Jurk, R.; Stockelhuber, W.; Heinrich, G. *J Macromol Sci Part A: Pure Apllied Chem,* 45 **(2008)** 101
[3] Wu, Y. P.; Zhao, S. Q.; Zhao, S. H.; Zhang, L. Q. *J Appl Polym Sci,* 108 **(2008)** 112
[4] Nasir M.; Poh, B. T.; Ng, P. S. *Eur Polym J,* 24 **(1998)** 961
[5] Ten Brinke, J. W.; Debnath, S. C.; Reuvekamp, L. A. E. M.; Noordermeer, J. W. M. *Compos Sci Technol*, 63 **(2003)** 1165

PR2

Biocomposites Synthesized from Castor Oil based Bio-Polyurethane and Polylactic acid (PLA)

Gurunathan T, Smita Mohanty*, Sanjay K. Nayak
LARPM, Central Institute of Plastic Engineering and Technology, Bhubaneswar - 751024, India
*Corresponding Author: Phone: +91-674-2740173; fax: +91-674- 2740463
E-mail: larpmcipet@gmail.com

The present study describes the effect of bio-based NCO terminated polyurethane (PU)-PLA copolymers synthesized employing a systematic two-step process. In the first step, isocyanate terminated PU prepolymers were prepared by reacting soft segments such as epoxidized polyols (Castor oil) with hard segments like methylene diisocyanate (MDI) with NCO/OH ratio 2:1. In addition, the biocomposites and the resulting particle properties are investigated by means of FTIR, NMR, TGA, DSC, SEM, and XRD. The effects of the PU content and its crosslink density on the mechanical properties and the toughness of Bio-PU/PLA blends were investigated. Maximum toughness of Bio-PU/PLA blends, an order of magnitude higher than that of pure PLA, could be achieved by the use of a proper amount of PU and a proper extent of cross-linking.

Keywords: Biocomposites; Polylactic acid (PLA); Polyurethane (PU); mechanical properties;

PR3

Curing Behaviour and Curing Kinetics of Epoxy–Imidazole Systems by Dynamic Differential Scanning Calorimetric Method

K Leena*[a], P B Soumyamol[b], Monisha Baby[a], Dhanya S Mohan[a], S Suraj[a] and R Rajeev[b],
[a]Polymers and Special Chemicals Division &
[b]Analytical Spectroscopy Division
Vikram Sarabhai Space Centre, Thiruvananthapuram-695022, Kerala, India
*leenakarthi@yahoo.co.in

Imidazoles are tertiary amines that are often used as hardeners in a variety of epoxy resin systems to initiate the homopolymerisation of epoxy compounds [1]. The objective of the present investigation is to study the cure behaviour and cure kinetics of a tetra functional epoxy resin N,N,N',N'-tetraglycidyl-4,4'diaminodiphenylmethane (TGDDM) with three different imidazole curing agents, viz, 1-methyl imidazole(1-MI), 2-methyl imidazole(2-MI) and 2-ethyl 4-methyl imidazole(2E4MI) . The cure profile was studied by dynamic Differential Scanning Calorimetric method at four different heating rates of 5, 10, 15 and 20°C/minute.

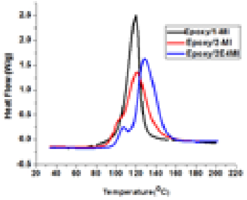


Fig. 1. DSC curves for epoxy cured with 1-MI, 2-MI and 2E4MI

Fig.1 depicts a comparison of the DSC cure curves of the three imidazole systems at a heating rate of 5°C/minute. The epoxy/1-MI system shows a single exothermic peak which corresponds to the formation of a 1:1 adduct between the epoxy and the imidazole which propagates by the polyetherification of epoxy [2]. The epoxy/2-MI and epoxy/2E4MI systems give an additional small peak at a lower temperature in the DSC cure profile. This is attributed to the 1:1 and 1:2 adduct formation proposed in the curing mechanism of 1, 3- unsubstituted imidazoles with epoxies [3]. However it was observed that as the heating rate increases, the two stages of curing merge together for epoxy/2-MI system, whereas for epoxy/2E4MI system, it remains distinct indicating a different mechanism.

The activation energy and pre-exponential factor for the curing of three systems were calculated using Kissinger equation [4]. A complete accession of activation energy throughout the entire conversion was done using isoconversional method [4] as depicted in Fig.2. It is observed that for epoxy/1-MI and epoxy/2-MI systems, the activation energy systematically decreases with degree of conversion. For epoxy/2E4MI system, it decreases sharply up to 25% conversion and then suddenly shoots up to a high value and remains more or less constant for further conversion. The initial phase may be due to adduct formation and the second phase corresponds to the polyetherification reaction at which, the steric hindrance offered by the ethyl and methyl groups increases the activation energy.

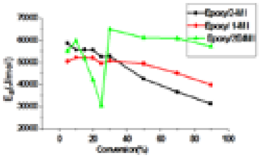


Fig.2. Activation energy (Ea) vs. % conversion for three epoxy imidazole systems.

References

[1] Farkas,A.; Strohm,H.M. *J.Appl.Polym.Sci.*, 12 (**1968**) 159.
[2] Dearlove, T.J. *J.Appl.Polym.Sci.*, 14 (**1970**) 1615.
[3] Barton,J.M.; Hamerton,I.; Howlin,B.J.; Jones,J.R.; Liu,S. *Polymer,*10 (**1998**) 1929.
[4] Lee,J.Y.; Shim,M.J.; Kim,S.W, *Thermochimica Acta*, 371 (**2001**) 45.

PR4

Phase transition temperatures in weakly dynamic asymmetric blends in presence of multiwall carbon nanotubes

Keshav Sharma, Maya Sharma, Suryasarathi Bose*
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, India
sbose@materials.iisc.ernet.in*

Liquid-liquid phase separation in weakly dynamic asymmetric blends of poly (methyl methacrylate)/poly (styrene-co-acrylonitrile) (PMMA/SAN) in presence of functionalized multiwall carbon nanotubes (MWNTs) were investigated systematically using melt rheology. The MWNTs were incorporated in the homogeneous mixture by melt mixing and the phase transition temperatures of near critical compositions were determined *in-situ* rheologically. As both the concentration fluctuation and interfacial driven elasticity is often masked in weakly dynamic asymmetric blends, different rheological measurements like isochronal temperature sweeps, time temperature superposition, cole-cole and the onset of gel-point were employed. The phase transition temperatures (T_{rheo}) were evaluated using various fingerprint regions and the spinodal decomposition temperature (T_s) in the blends were derived using the mean field theory. There was a considerable difference in the absolute values of T_{rheo} as obtained from different techniques and we assign these differences to the weak dynamic asymmetry in the blends. It was observed that small amounts of MWNTs in PMMA/SAN blends altered the T_{rheo} to a moderate extent however, the T_s to a larger extent. This effect was also supported by a decrease in the thermodynamic interaction parameter (χ) in the blends in presence of MWNTs. Thermodynamics that led to phase separation further paved way for selective localization of MWNTs in the blends as supported by atomic force microscopy.

PR5

Effect of Various Solvents on Thiophene Derivative Electrospun Structures

Khadija Kanwal Khanum, Ranjith K and Praveen C. Ramamurthy*
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012
** praveen@materials.iisc.ernet.in*

The electrospinning is attractive technique to generate fibers in sub micron range [1]. In this process polymer solution is drawn through the nozzle by applying high voltage between nozzle tip and collector. It has gain popularity due to the possibility of having wide control over fiber diameter and morphology, by studying and fine-tuning various process parameters like applied voltage, flow rate, tip to collector distance, deposition time, viscosity [2] and solvent utilized [3]. If polymer used has an insuffcient viscosity it leads to breaking of jet and as the viscosity decreases breaking of jet increases, which leads to just spraying on collector, which is known as electrospraying [4].

In this study, a thiophene derivative (7, 9-di (thiophen-2-yl)-8H-cyclopenta[a]acenaphthylen-8-one) (DTCPA) solution synthesized in lab [5], having donor acceptor architecture is electrospun by changing the solvent and keeping all other process parameters same to study the solvent effect on the structure formed. Chloroform and chlorobenzene were used to electrospun the fibers and the scanning electron microscope (SEM) were used to study the formed structure. Fig.1, indicate that electrospraying has occurred. Spiked sphere structure (diameter of ~ 5-10 µm) was observed when chloroform was used as the solvent and short individual elongated crystal structures were observed when chlorobenzene was used as the solvent. The effect of this change in morphology due to the solvent on the electronic properties of the final material structure is studied.

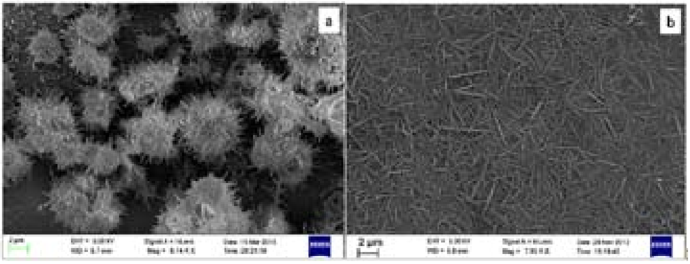


Figure 1. SEM images of electrosprayed DTCPA using solvents (a) chloroform (b) chlorobenzene

References
[1] Bhardwaj N.; Kundu S.C.; *Biotechnology Advances*, 28 **(2010)** 325.
[2] Deitzel J.; Kleinmeyer J.; Harris D.; Beck Tan N. *Polymer*, 42 **(2001)** 261.
[3] Luo C.J.; Nangrejo M.; Edirisinghe M. *Polymer*, 51 **(2010)** 1654.
[4] Shenoy S.L.; Bates W.D.; Frisch H.L.; Wnek G.E. *Polymer*, 46 **(2005)** 3372.
[5] Swathi S.K.; Ranjith K.; Kumar P.; Ramamurthy P.C. *Solar Energy Materials and Solar Cells*, 96 **(2012)** 101.

PR6

Direct HPILC Analysis on Cellulose Depolymerization in Ionic Liquids

Kosuke Kuroda,[a,b] Yukinobu Fukaya,[b] Hiroyuki Ohno[a,b]*
[a]*Department of Biotechnology, Tokyo university of Agriculture and Technology, 2-24-16, Koganei, Tokyo JAPAN*
[b]*Functional Ionic Liquid Laboratories, 2-24-16, Koganei, Tokyo JAPAN*
** ohnoh@cc.tuat.ac.jp*

Cellulose is the most abundant biomass in the world and has attracted much interest as a sustainable energy resource. However, insolubility of cellulose is a great issue to be solved for its energy conversion. Recently, many reports have been published about ionic liquids (ILs), organic salts with melting points below 100 °C, which can dissolve cellulose under mild conditions. To convert cellulose into energy in ILs, there are three essential processes: extraction of cellulose from biomass, hydrolysis of cellulose into glucose or cellobiose, and energy conversion *via* alcohol fermentation or in biofuel cells. In spite of developments in biomass processing using ILs, there are few reports on analytical methods to detect profiles of cellulose dissolved in ILs. Especially, there has been no method for dynamic analysis of cellulose in ILs during hydrolysis. For this end, HPLC with ILs as eluents (HPILC) is a method for tracing cellulose hydrolysis in polar ILs in view of the molecular weight distribution (MWD) without pretreatment. We have reported HPILC with 1-ethyl-3-methylimidazolium methylphosphonate ([C$_2$mim][(MeO)(H)PO$_2$]) as an eluent.[1] Here we analyzed time depending change of the MWD of cellulose in [C$_2$mim][(MeO)(H)PO$_2$] using HPILC.

Results and discussion

As a preliminary study, we analyzed hydrolyzed cellulose by cellulase in water. Before HPILC measurement, the medium of hydrolyzed cellulose was exchanged from water to [C$_2$mim][(MeO)(H)PO$_2$] to dissolve the hydrolysate completely. As shown in the chromatogram (Figure 1), MWD of cellulose was changed depending on reaction time. First, rapid decrease of cellulose was observed and subsequently generation of cellobiose was found. Second, cellobiose decreased with increasing glucose. In the retention volume from 3.5 to 4.0 ml, no peak was observed indicating that oligosaccharides except for cellobiose were scarcely generated. These observations correspond to catalytic feature of enzymatic hydrolysis. These results show that HPILC can investigate the change of MWD of cellulose.

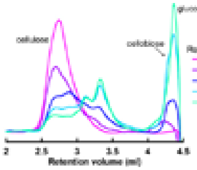


Figure 1. Chromatograms of hydrolyzed cellulose in water with cellulase at different reaction times.

Depolymerization of cellulose in ILs was analyzed without pretreatment. For depolymerization, we utilized ultrasonication, which does not change the composition of the sample solutions. The cellulose/[C$_2$mim][(MeO)(H)PO$_2$] solutions were ultrasonicated, and the resulting samples were injected directly into our HPILC system. Figure 2 shows change in the profile of depolymerized cellulose as the function of ultrasonication time. The peak for cellulose shifted to higher retention volume side as the ultrasonication time increased. This indicates that the average molecular weight of cellulose gradually decreased with ultrasonication. Peak for low molecular weight saccharides as seen in Figure 1 was not detected in this profile. From this change in the chromatograms, the depolymerization of cellulose by ultrasonication was confirmed to occur in random. It is clearly found that HPILC is a powerful tool for the analysis of cellulose depolymerization in ILs.

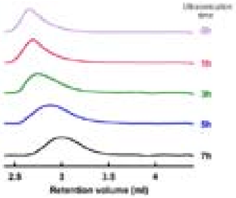


Figure 2. Chromatograms of cellulose depolymerized by ultrasonication at the different ultrasonication time.

References

[1] Fukaya. Y; Tsukamoto. A; Kuroda, K.; Ohno. H; *Chem. Commun.*, 47 (**2011**) 1994.

PR7

Water Dispersible Polyurethanes from butadiene diols: Morphology and Self-cleaning Properties

Malkappa Kuruma and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad 500 046
E-mail: tjscuoh@gmail.com

The aim of this research work is to study the synthesis and characterizations of stable aqueous dispersion of hydroxyl terminated polybutadiene (HTPB) and modified HTPB based polyurethanes. Two dinitrochloro benzene (DNCB) molecules are covalently attached at the terminal carbon atoms of HTPB in case of modified HTPB (HTPB-DNCB) [1]. We prepared series of water born polyurethanes (PUs) with varying hard segment content [2]. This PUs are characterized by infrared spectroscopy (IR), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), transmission electron microcopy (TEM), atomic force microscopy (AFM), universal testing measurement (UTM) and contact angle measurement. From IR-spectroscopy we conformed that complete formation of polyurethane and disappearance of isocyanate peak. In this PUs dimethylol propionic acid (DMPA) used as cross linker and it is act as internal emulsifying agent. From UTM study we clearly observed that with increasing hard segment content tensile strength increases and elongation decreases [3]. Compare to HTPB-PUs, HTPB-DNCB-PUs shows more tensile strength in all hard segment content of PUs, because of DNCB moiety (Figure 1). From TEM (Figure 2) we observed that morphology of all the water dispersed PUs and we measured the average surface roughness of the polymer films using AFM. With increasing hard segment content water contact angle increases in both cases but compare to HTPB-PUs, HTPB-DNCB-PUs shows more contact angle because of $-NO_2$ functional groups. It may be possible that in case of HTPB-DNCB, all hydrophilic groups are inside hence the surface is hydrophobic [4, 5].

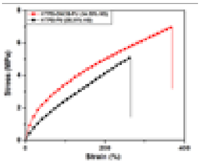


Figure 1. Tensile plots of PU

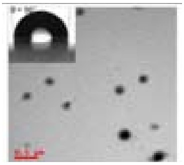


Figure 2. TEM Image and contact angle of PU

References

[1] Shankar R. M.; Roy T.; Jana T. *Journal of Applied Polymer Science, 114 (***2009)** 732
[2] Yongshang Lu.; Richard C. Larock. *Biomacromolecules , 9 (***2008)** 3332
[3] Lixin Yang.; Jizheng Wei.; Lesan Yan.; Yubin Huang.; Xiabin Jing. *Biomacromolecules,* 12 (**2011**) 2032
[4] Shengyang Yang.; Lifang Wang.; Cai-Feng Wang.; Li Chen, and Su Chen. *Langmuir,* 26 (**2010**) 18454
[5] Mitra Yoonessi.; John A. Peck.; Justin L. Bail.; Richard B. R.; Bradley A.; Lerch.; Michael A. *ACS Appl. Mater. Interfaces*, 3 (**2011**) 2686

PR8

Effect of functionalized MWNTs on the crystallization induced phase separation in PVDF/PMMA blends.

Maya Sharma*, Keshav Sharma, Dr. Suryasarathi Bose
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012
*maya.sharma89@gmail.com

Effect of differently functionalized multiwall carbon nanotubes (amine and carboxyl acid functionalized MWNTs) on crystallization induced phase separation in PVDF/PMMA (poly vinylidene fluoride/poly methyl methacrylate) blends, was systematically investigated by melt-rheology, polarizing optical microscopy, dielectric spectroscopy and electron microscopy. Functionalized MWNTs were observed to act as hetero-nucleating agents while only amine functionalized MWNTs (a-MWNTs) manifesting in an increase in the crystallization temperature. The latter augmented the phase separation temperature in the blends. On the other hand, carboxyl functionalized MWNTs (c-MWNTs) were observed to decrease the crystallization temperature of the PVDF phase thereby delaying the phase separation temperature of the blend. The presence of specific interactions between a-MWNTs and PVDF was inferred from FTIR analysis. Such interactions induce β-phase in PVDF, which was also confirmed by wide angle XRD analysis. SEM and selective etching was used to confirm the localization of MWNTs in the PVDF phase of the blends. Dielectric spectroscopy studies were conducted to detect changes in conductivity and dielectric relaxation behavior of polymer chains in presence of functionalized MWNTs.

PR9

Influence of Selective Dispersion of MWCNT on Electrical Percolation of *In-Situ* Polymerized Styrene-Acrylonitrile (SAN)/ MWCNT Nanocomposites

Nilesh K. Shrivastava*, Supratim Suin, Sandip Maiti and Bhanu B. Khatua
Materials Science Centre Indian Institute of Technology, Kharagpur
Kharagpur 721302, India
Email: 10ms9402@iitkgp.ac.in

The electrical conductivity of an insulating polymer can be altered by adding conducting particles like carbon black [1], carbon fibers [2], metallic fillers [3], conducting polymers [4] and carbon nanotube [5],as a second phase into matrices. These conducting composites have an extensive range of applications in various fields such as in electronics, aerospace, military, flexible electronics, electromagnetic induction (EMI) shielding, electrostatic dissipation, and sensors. The remarkably higher performance of the CNTs in polymer composites has led to a considerable amount of research being devoted to develop polymer/CNT nanocomposites with the potential of the CNTs as electrically conductive filler. Compared to the conventional conductive fillers such as carbon black [6] high electrical conductivity can be achieved with low loading of CNT, but the dispersion of the CNT in the matrix has to be effective. The low loading of filler leads to cost-effective production of electrically conductive composites with unhindered processability.

In this work we reported a novel processing technique that involves in-situ bulk polymerization of styrene and acrylonitrile monomers mixture in the presence of multi-walled carbon nanotubes (MWCNT) and commercially available styrene-acrylonitrile (SAN) beads. The nanocomposites prepared by this new method shows extremely low electrical percolation threshold (i.e. 0.032 wt % MWCNT) with critical exponent $t = 2.76$. With increase the concentration of MWCNT in these composites from 0.0 to 0.5 wt % of MWCNT , a considerably increases in DC conductivity value was observed , from 1×10^{-11} to 1.33×10^{-3} Scm^{-1},which is best to our knowledge, highest value of DC conductivity ever reported for SAN/MWCNT nanocomposites at such low level of MWCNT loading. Nanocomposites prepared by this method shows DC conductivity of 1.33×10^{-3} Scm^{-1} at 0.5 wt % MWCNT loading, whereas, nanocomposites prepared by (with same polymer and MWCNT) conventional solution casted and melt mixing process is required 2 wt % and 3 wt % MWCNT respectively to achieve the same level of electrical conductivity. This technique demonstrates the formation of a more continuous network structure of the MWCNT in SAN matrix. The scanning and transmission electron microscopy studies revealed the dispersion of MWCNT selectively in the in-situ polymerized SAN phase of nanocomposites.

References

[1] Connor, M. T.; Roy, S.; Ezquerra, T. A.; Balta Calleja, F. J. *Phys. Rev. B* 57 (**1998)** 2286.
[2] Lozano, K.; Bonilla, R. J.; Barrera, V. *J. Appl. Polym. Sci.* 80 (**2001)** 1162.
[3] Kar, P.; Khatua, B. B. *Polym. Engg. Sci.* 51(**2011**) 1780
[4] Cassignol, C.; Cavarero, M.; Boudet, A.; Ricard, A. *Polymer* 5 (**1999**) 1139.
[5] Nilesh K. Shrivastava, N. K.; B.B. Khatua, B. B. *Carbon* 49 (**2011**) 4571
[6] Spitalskya, Z.; Tasisb, D.; Papagelisb, K.; Galiotisa, C. *Prog. Polym. Sci.* 35 (**2010)** 357.

PR10

Dyeing of Polyester and Polyamide Using Solvent Crazing Technique

R.D. Kale*, Usha Sayed, Ashis Banerjee and Prabhat Shobha Bansal
Department of Fibers and Textile Processing Technology
Institute of Chemical Technology, Matunga, Mumbai-400019, INDIA
Dr. Ravindra D. Kale, Email: rd.kale@ictmumbai.edu.in, ravikale73@gmail.com

Partially oriented yarns (POY) of Polyester (PET) and polyamide (PA) of two different deniers were dyed while drawing on the melt spinning unit at room temperature and just above their corresponding glass transition temperature (T_g) using *solvent crazing* technique [1,3]. Crazing of polymer is a type of nonelastic plastic deformation. It takes place in three stages namely craze formation stage, craze growth stage and craze expansion stage [6] as shown in figure 1.

Crude disperses dyes of three different energy levels dissolved in solvent Benzyl Alcohol (BA) were taken for dyeing of synthetic fibres with solvent crazing technique. The same yarns after converting them into fully drawn yarns (FDY) were dyed by conventional methods with commercial disperse dyes [2, 3, 5].

The depth of dyeing obtained by *solvent crazing* technique was more than the dyeing of yarn done by conventional method, without any adverse effect on the fastness and mechanical properties [4]. The depth of the shade did not change even after running of the yarn for 600 meters. Hence, indicating that thousands of meters of these yarns could be uniformly dyed while manufacturing without any variation in the shade [2, 3].

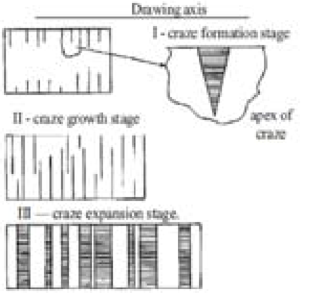


Figure 1: Schematic illustration of the individual stages of crazing of polymer

The proposed process can be used to reduce the consumption of energy as well as saving of cost that is incurred during manufacturing of commercial disperse dyes. Moreover, this whole process can be carried out on the same existing equipment for drawing polymer fibres after insignificant modifications which is a very important factor [4, 5]. This phenomenon of extremely slow release of non-volatile liquid component into surrounding space is of definite practical interest in the field of drugs release etc. Also, since the solvent used is recovered on completion of the process along with ultra-filtration of the dye solution at molecular level which reduces the cost incurred in effluent treatment plant. Further scope in this process which is yet to exploit is in the field of combined processing with incorporation of thermally unstable and incompatible additives.

References:

[1] [1]. Volynskii, A.L.; Bakeev, N.F.; *Studies in Polymer Science*, Amsterdam **(1995)**
[2] [2]. Moncrieff, W; *Man-Made Fibre Butterworth and Co. Ltd.*, London **(1975)**
[3] [3]. Burkinshaw, S.M.; *Chemical Principles of Synthetic Fibre Dyeing*, Glasgow **(1995)**
[4] [4]. Thompson, A.B.; Hearle, J.W.; Peters, R.H.; *Fiber structure*, London **(1963)**
[5] [5]. McCabe, W. L.; Smith, J. C.; *Chemical Engineering operations*, New York **(1999)**
[6] [6]. Ullmann, F; *Ullmann's Encyclopedia of Chemical technology,* Vol 10, Berlin **(2000)**

PR11

Metal ion adsorption by chelating resin containing an 'O'N' donor schiffs base

P.S.Kulkarni*, S.V.Lonikar,
Department of Chemistry , Solapur University , Solapur – 413 255 , India.
S.E.S Polytechnic College, Solapur , India.

A new chelating polymer was synthesized from chloromethalated polystyrene (2% DVB cross linked) and a chelating ligand , derived from salicylaldehyde and 4 , 4'- diamenodiphenyl ether and evaluated for adsorption of CO(II) and Ni(II).The complex formation of the resin ligand with Co(II) and Ni(II) was studied under the optimum conditions which were first determined by using a low molecular weight analogue of the resin ligand. Adsorption capacity, rate of adsorption , effect of eluent on desorption , effect of various electrolyte were studied .

The resin should remarkably high adsorption capacity for Co(II), 0.594 m mol/g at pH 9. Maximum adsorption was observed for Co(II) in presence of 0.5 M NaCl and for Ni(II) in presence of I M NaCl .The adsorbed metal ion could be easily and rapidly stripped by using 2 M HCl . The resin was stable to acidic medium of stripping and was recyclable.

PR12

Synthesis and Characterization of New Polyimide containing 1, 2, 3-Triazole by Click Reaction

R.Balasubramanian , M.Sarojadevi*
Department of Chemistry, Anna University, Chennai-600025
E-mail: chemsubbu@gmail.com

A new kind of 1, 2, 3 triazole containing polyimdes were synthesized by the Cu (I) – catalysed 1, 3 dipolar cycloaddition by click reaction. An alkynyl –oxy terminated diimide was synthesized using dianhydride (3, 3′, 4, 4′-Benzophenonetetracarboxylic -3, 3′, 4, 4′-dianhydride and pyromellitic dianhydride) and aminophenyl propargyl ether by polycondensation reaction. The polyimide containing 1, 2, 3-triazole was synthesized by reacting diazide and diimide by step growth polymerization. The chemical structures of the resulting polytriazoleimides were characterized by Fourier transform infrared and nuclear magnetic resonance spectroscopy. Polymerization behavior and thermal properties of polymers were characterized by differential scanning calorimetry and thermo gravimetric Analysis.

Keywords: Polyimide-triazole- click reaction- thermal properties

References

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

PR13

Synthesis and Characterization of Optically Active Polyimides

S.Balaji and M.Sarojadevi*
Department of Chemistry, Anna University, Chennai-600025
E-mail: bal_jichem@yahoo.co.in

Structurally varied polyimides have been synthesized in recent decades for their thermal, mechanical, and dielectric properties. In this study a new optically active diamine monomer (RS) (1-phenyl 3,4-dihydrolisoquinolinyl) (3,5-diaminophenyl) methanone was successfully synthesised using 1-phenyl 1,2,3,4 tetrahydroisoquinoline as starting material and polymerized with different aromatic tetracarboxylic dianhydrides such as BTDA and PMDA via thermal imidization method to produce different chiral polyimides. The synthesized diamine and polyimides were characterized by Fourier transformer infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR). Imidization process of polyimides were monitored by FTIR and DSC at different temperatures. The thermal properties of the novel polyimides were investigated by TGA.

References:

[1] Mousa Ghaemy*,Raouf Alizadeh, Hossein Behmadi European Polymer Journal 45(2009) 3108- 3115
[2] Guey-Sheng Liou ,* Sheng-Huei Hsiao and Hwei-Wen Chen J.Mater.Chem., 2006, 16, 1831-1842
[3] Der-Jang Liawa,*, Kung-Li Wangb, Ying-Chi Huanga, Kueir-Rarn Leec, Juin-Yih Lai c, Chang-SikHad Progress in polymer Science 37(2012)907-974
[4] Zuolin Wu, Baochun Han, Chunhua Zhang, Danyang Zhu, Lianxun Gao, Mengxian Ding, Zhenghua Yang* Polymer 53 (2012) 5706-5716

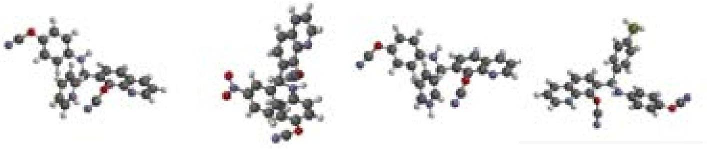
PR14

Synthesis, Characterization and Curing Studies of Cyanate Esters Using Microwave and Conventional Heating Sources

Sakthi Dharan C P [a, b], Sarojadevi M [a], Sundararajan P R [b*]
[a] Department of Chemistry, CEG, Anna University, Chennai, India – 600 025
[b] Department of Chemistry, Carleton University, Ottawa, Canada – K1S 5B6
[*] Corresponding author sundar@carleton.ca

Thermosetting polymers based on dicyanate esters offer highly desirable physical, electrical, thermal, and processing properties required of an ideal matrix resin. These properties are further tunable through backbone structure and/or by blending with other polymeric materials such as epoxy resin, bismaleimide and benzoxazines[1]. In this work, five different diols were synthesised from 4-amino phenol, aromatic aldehyde and 8-hydroxyquinoline using Betti condensation method. Cyanate esters were synthesised by treatment of prepared diols with cyanogen bromide in the presence of triethyl amine.

The cyanate ester was cured by heating with or without catalyst (e.g. zinc naphthenate) [2]. While curing dicyanate ester forms triazine network. The curing of dicyanate ester was carried out by conventional (multi step curing and post cure) and a one-step curing. With multi step curing, using a conventional heating source, temperatures of 100, 150, and 200 °C were used with dwell times of 30 minutes at each temperature and the post cure was performed at 250 °C (30 min). With microwave curing, the dwell time was 20 minutes, and the post cure was done at 225 °C. Complete curing was achieved by a single step curing at 200 °C for 90 minutes using conventional heating, and in 45 minutes at 225°C with microwave heating. We show that use of microwave as the source of heating leads to a reduction in the time as well as temperature required for complete curing.



Dicyanate esters synthesized in this study

References

[1] H. C. Chang, H. T. Lin and C. H. Lin, *Polym. Chem.*, **2012**, *3*, 970-978; [2]J. T. Reams et al, *Appl. Mater. Interfaces* **2012**, *4*, 527–535.

This work was supported in part by a Commonwealth Scholarship from the Government of Canada, Natural Sciences and Engineering Research Council of Canada and University Grants Commission (UGC) of India.

PR15

Mechanical transition in Random polymer composites

Sambit Bapari*, Atul H. Chokshi
Department of Materials Engineering, Indian Institute of Science,
Bangalore-560012 INDIA
**sambit@platinum.materials.iisc.ernet.in*

Mechanical properties of random composites are of great interest because of possible universality[1]. Mechanical properties include factor such as elastic modulus, strength and viscoelasticity. In this work we focus on the transition in strength of random composites, with polyvinyl chloride (PVC) matrix and inclusion of nickel (Ni) particles. The random but homogenized composite morphology is tricky to achieve experimentally, because of segregations and porosity, especially when the volume fraction of the added inclusion is as high as 0.5. A processing technique has been developed to reduce segregations and porosity at a very high volume fraction of inclusions.

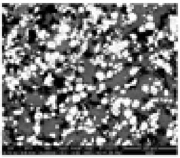


Figure1. Micrograph of PVC+0.5 volume fraction of Ni

Rigid PVC powder, having spherical particle of size 130 μm, was mixed with spherical nickel particles of 40 μm in a ball milling machine. Then, the solid powder mixer was hot pressed at a temperature (150°C), above the T_g (85°C) of PVC, to get a compact. The compaction process requires high flowability of the polymer under load through the interstices between Ni particles at the chosen hot pressing temperature. The microstructure suggests that the polymer has flowed reasonably well under the given conditions (fig.1).

Figure 2. Yield points with different volume fractions of Ni

Samples for mechanical testing were made from the compacted pellets. The results from compression tests show a transition in the strength of the composites near a volume fraction of 0.4 (fig.2). we are investigating possible explanations of the observed behavior including rigidity threshold as well as possible changes in the matrix due to different processing conditions to achive dense compact.

References

[1] S. Torquato. *Applied mechanics reviews*, **44 (1991).**

PR16

Phase Transformation and Effect of Tensile Strain on Electrical Properties in PVDF/BTPC Films

Saurabh K.Tiwari[a], Ashok Misra[b], Devang V. Khakhar[a]*
[a]*Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai, 400076, India*
[b]*Intellectual Ventures, No. 701 Raheja Paramount, 138 Residency road, Bangalore 560 025, India*
* khakhar@iitb.ac.in

Polyvinylidene fluoride (PVDF) is a melt processable fluoro polymer which has excellent electrical property. PVDF exhibits four crystal forms (α, β, γ, δ), the phase transformation in PVDF depends on the processing parameters such as temperature, pressure with addition of nanoclay and stretching in unidirectional or in bidirectional. The β phase of PVDF crystal is polar and has very good piezoelectric properties as compared to the non polar α phase. PVDF and different amount of BTPC (0.5 - 3%) were melt mix in twin screw extruder and film has been prepared by single screw extruder. Addition of small amount of BTPC confirms the formation of β phase crystal, the film containing 3% BTPC gave highest fraction of β phase crystal (87%). Small angle light scattering results showed the size of spherulitic decreases with increase in the weight fraction of BTPC. Dielectric properties of these blends before and after stretching were studied at wide range of frequency from 10-10^6 Hz. The result showed change in the dielectric constant, dielectric loss and conductivity after stretching at higher temperature. Significant change has been observed in piezoelectric constant (Figure 1) and breakdown voltage after stretching of PVDF/BTPC films.

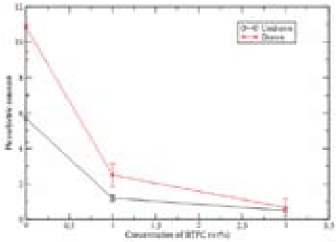


Figure 1. Dependence of piezoelectric constant on concentration of BTPC before and after stretching

Keywords:
[1] PVDF/BTPC, blends, piezoelectric, SALS, FTIR, WAXD.

PR17

Synthesis and Characterization of Fluorinated Polybenzoxazines

A. Shakila Parveen, M. Sarojadevi*
Department of Chemistry, Anna University, Chennai – 600025
E-mail: shakilaasraf@gmail.com

A large variety of polymers has been proposed for use as materials with low dielectric constants for applications in microelectronics. In this study, fluorinated polybenzoxazines have been synthesized by incorporating mono, di and trifluoro aniline groups into the monomer and its structures have been characterized by Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (^{1}H NMR, ^{13}C NMR and ^{19}F NMR). The curing reaction was investigated by Differential scanning calorimetry (DSC) at different heating rates.
These fluorinated compounds were found to have decreased dielectric constant because of small dipole and low polarizability of the C-F bond and possess high thermal stability, which makes it a suitable candidate for interlayer dielectrics.

Keywords: Fluorinated polybenzoxazines, interlayer dielectrics.

References

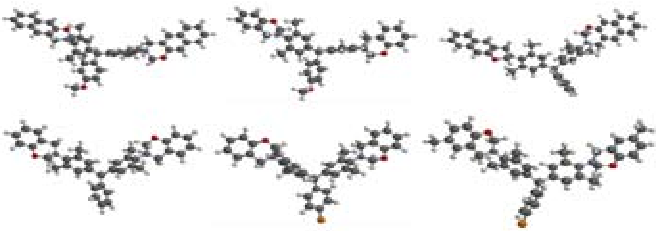
[1] [1]. Rimdusit, S.; Ishida, H. Polymer 41 (2000) 7941-7949
[2] [2]. Maier, G. Prog. Polym. Sci. 26 (2001) 3-65
[3] [3]. Yi-Che Su; Feng-Chih Chang. Polymer 44 (2003) 7989–7996
[4] [4]. Yi-Che Sua; Wan-Chun Chena; Kai-lin Oua; Feng-Chih Chang. Polymer 46 (2005) 3758–3766

PR18

Thermal Polymerization of Aryldiamine based Benzoxazine Using Conventional and Microwave Heating Sources

Sudha V [a, b], Sarojadevi M [a], Sundararajan P R [b*]
[a] *Department of Chemistry, CEG, Anna University, Chennai, India – 600 025*
[b] *Department of Chemistry, Carleton University, Ottawa, Canada – K1S 5B6*
[*]*Corresponding author sundar@carleton.ca*

Diamine-based benzoxazine monomers were prepared using three different diamines, formaldehyde, and various phenol derivatives (including phenol, p-cresol, β –naphthol). New diamines were prepared by reacting 2,6 dimethyl aniline and benzaldehyde,4-methoxy benzaldehyde and chloro benzaldehyde in presence of concentrated hydrochloric acid. The materials were characterized using FTIR, NMR and differential scanning calorimetry. Thermal curing led to ring opening polymerization. The curing of benzoxazine monomers was carried out by conventional heating as well as using microwave source. Two different heating protocols were examined: (1) multi step curing followed by post curing and (2) direct one-step curing. For (1), using a conventional heating source, temperatures of 100, 150, and 200 °C were used with dwell times of 30 minutes at each temperature and the post cure was performed at 250 °C (30 min). With microwave curing, the dwell time was 20 minutes, and the post cure was done at 225 °C. For (2), complete curing was achieved by a single step curing at 200 °C for 90 minutes using conventional heating, and in 45 minutes at 225°C with microwave heating. We show that using the microwave source leads to a reduction in the time as well as temperature required for complete curing. Further studies will be carried out to determine the minimum temperatures and times required for curing with the microwave source.



Benzoxazine monomers synthesized in this study

This work was supported in part by a Commonwealth Scholarship from the Government of Canada, Natural Sciences and Engineering Research Council of Canada and the Department of Science and Technology (DST) India.

PR19

Effect of Strain Rate on Mechanical Behaviour of PDMS and Copper Powder Filled PDMS Composites

Sudhi Oberoi and Praveen Kumar*
Department of Materials Engineering, Indian Institute of Science, Bangalore, India
**praveenk@materials.iisc.ernet.in*

High strain rate sensitivity of polymers enables polymer matrix composites as a material of choice for shock absorption and damping applications [1, 2]. Here, we present effects of inclusion of micrometre sized copper particulates, Cu(p) into polydimethylsiloxane (PDMS) on the mechanical behaviour of PDMS based composites. Monolithic PDMS and 5 vol. % Cu(p) - PDMS composite were cyclically loaded to a strain of 30% at strain rates ranging from 10^{-3} to 1 s^{-1} for several number of loading-unloading cycles; representative stress-strain behaviour of PDMS and 5 vol% Cu(p) - PDMS composite for the first 5 cycles are shown in **Figure 1**. The loading-unloading cycles showed the stress-strain hysteresis indicating accumulation of irrecoverable microstructural damages during the cyclic deformation.

Figure 2 summarizes the effects of Cu addition on the peak stress and the total strain energy absorbed during the first cycle of monolithic PDMS and Cu(p)-PDMS composite. The Cu(p)-PDMS composite, as compared to the monolithic PDMS, shows not only superior load bearing capacity, but also significantly higher energy absorption per unit volume during a loading-unloading cycle. Interestingly, the performance of the composite improves at high strain rates. Rheological study showing the effect of Cu addition on the storage and tangent moduli of the composite as well as a mechanistic model addressing the reasons for the aforementioned differences will also be presented.

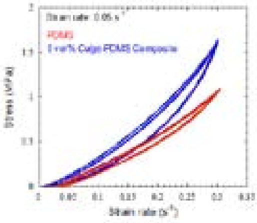


Fig. 1: Representative stress-strain behaviour of monolithic PDMS and Cu(p)-PDMS composite up to 5 loading-unloading cycles.

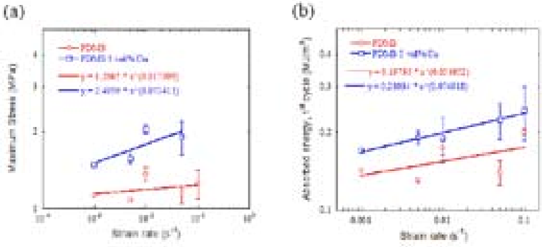


Fig. 2: Effect of the strain rate on the (a) peak stress, and (b) energy absorbed per unit volume during the first loading-unloading cycle.

References

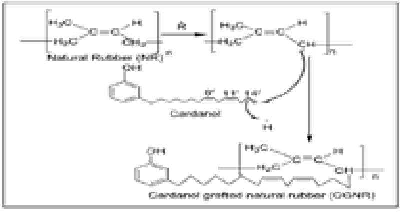
[1] Hogg, P. *Science*, 314 (**2006)** 1100.
[2] Sarva, S.; Deschanel, S.; Boyce, M.; Chen, W.; *Polymer,* 48 (**2007)** 2208.

PR20

Cardanol Grafted Natural Rubber As a Substitute to Oil Plasticized Natural Rubber

Sunita Mohapatra and Golok Bihari Nando*
Rubber Technology Centre, Indian Institute of Technology Kharagpur, West Bengal, India-721302
**Corresponding author e-mail id: golokb@rtc.iitkgp.ernet.in*

The use of aromatic oils as a plasticizer and a process aid in the rubber industry is prevalent for more than a century. However, in recent years its use is almost limited due to the growing concern on its carcinogenic effect on health and environment because of the presence of polycyclic aromatic hydrocarbons within it. Therefore, there is a need to substitute these hazardous aromatic oils. Cardanol (m-pentadecenyl phenol), 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 the recent years. Menon et al. [1] have reported that natural rubber modified with phosphorylated cardanol are superior to those obtained by di-ethyl-hexyl-phthalate plasticizer in terms of higher tensile properties, better flame retardancy and resistance to thermo-oxidative decomposition Also, phosphorylated cardanol has been proved to be an effective plasticizer for ethylene-propylene diene rubber [2] , polychloroprene and polybutadiene rubber [3], and LLDPE/EVA copolymer blends [4]. Alexander et al. [5, 6] have also reported superiority of cardanol over aromatic oil in natural rubber containing HAF black. It has been also reported by Menon et al. [7] that cardanol and its derivatives on incorporation into the rubber as a plasticizer is tedious and a time consuming process. In addition, it causes cure-retardation due to absorption of activators by the plasticizer and thus needs additional doses of ZnO activator. Vikram et al. [8] have reported grafting of cardanol onto NR backbone by solution technique.



The present study highlights the grafting of cardanol on to natural rubber in the latex stage which is economically viable and eco-friendly. The grafted natural rubber is characterized by FTIR and NMR spectroscopy. The cardanol grafted natural rubber (CGNR) is found to have lower Mooney viscosity, lower Wallace plasticity number and higher cure rate as compared to the unmodified natural rubber. The physico-mechanical properties of the CGNR vulcanizates have been found to be at par or better than the unmodified natural rubber vulcanizates. The CGNR vulcanizates show lower compression set, higher rebound resilience and higher abrasion resistance. The rheological properties of CGNR and the ungrafted natural rubber have also been investigated and it is shown that the extent of disentanglement is higher in the grafted rubber as a result of the plasticizing effect of the long aliphatic side chain present in the cardanol. Differential scanning calorimetry and dynamic mechanical analysis show lowering of the glass transition temperature for the CGNR in comparison with the ungrafted natural rubber which confirms the plasticization effect of the cardanol grafted onto the natural rubber backbone. Cardanol is found to act as a cure promoter, in addition to its plasticizing effect.

References:

[1] [1] A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *Eur. Polym. J.*, 34,**(1998)** 923.
[2] [2] A. R. R. Menon, *Iran. Polym. J.*, 12,**(2003)** 305.
[3] [3] A. R. R. Menon and L. L. Y. Visconte, *J. Appl. Polym. Sci.*, 102,**(2006)** 3195.
[4] [4] A. R. R. Menon and C. K. S. Pillai, *Iran. Polym. J.*, 11,**(2002)** 85.
[5] [5] M. Alexander and E. T. Thachil, *J. Appl. Polym. Sci.*, 102,**(2006)** 4835.
[6] [6] M. Alexander and E. T. Thachil, *Progress in Rubber, Plastics and Recycling Technology*, 26,**(2010)** 107.
[7] [7] A. R. R. Menon, C. K. S. Pillai and G. B. Nando, *J. Appl. Polym. Sci.*, 73,**(1999)** 813.
[8] [8] T. Vikram and G. B. Nando, *J. Appl. Polym. Sci.*, 105,**(2007)** 1280.

PR21

Effect of nanoclay dispersion in the vapor sorption properties of EVA/clay nanocomposites

Runcy Wilson[1], Anil Kumar S[2] and Sabu Thomas[3*]
1School of Chemical Science, Mahatma Gandhi University, Kottayam, Kerala, 686560, India.
2Center for Nanoscience and Nanotechnology, Mahatma Gandhi University, P.D Hills, Kottayam, Kerala, 686560, India.
3Department of Chemistry, N.S.S College, Ottapalam, Kerala, 679103, India.

Corresponding authors: runcy21@gmail.com, anugraha_anil@yahoo.com, sabupolymer@yahoo.com

Poly (ethylene-co-vinyl acetate) (EVA) / clay nanocomposites containing two different organoclays with different clay loadings were prepared. The vapor transport through the composite membranes was investigated and the results were compared. These studies revealed that the incorporation of nanoclay in the polymer increased the efficiency of the membranes towards barrier properties. Due to the aggregation of nanoclay at higher loadings, it was found that the permeability of the vapor increased. The morphology of the nanocomposites was studied by scanning electron microscopy, transmission electron microscopy and X-ray scattering. SAXS results showed significant intercalation of the polymer chains between the organo-modified silicate layers in all cases. Better dispersed silicate layer stacking and more homogeneous membranes were obtained for Cloisite® 15A based nanocomposites compared with Cloisite® 10 A samples. SEM and TEM observations were also agree with this result. The dispersion of clay platelets seemed to be maximized for 3 wt% of clay and agglomeration increased with higher clay loading. The effect of free volume on the transport behavior was studied using positron annihilation spectroscopy. The permeability results have been correlated with Bhardwag model.

Key words: Vapor sorption, Permeability, nanocomposites, SAXS.

Polymeric biomaterials

Invited

Improvement of Mechanical Properties of PVA Hydrogels for Artificial Cartilage

Atsushi Suzuki*, Taegu Noh, and Saori Sasaki
Department of Materials Science and Research Institute of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501 Japan.
*Corresponding author: asuzuki@ynu.ac.jp.

To achieve the artificial joints based on bionic design, the hydrogels with material properties similar to natural articular cartilage have long been desired. In the literature [1], PVA(poly(vinyl alcohol)) hydrogel is one of the most promising candidate materials of artificial cartilage, which shows excellent lubricity and enhancement of fluid film formation in joint simulator test and numerical analysis. For practical applications of PVA gels in artificial cartilage, however, there are several essential properties required: biocompatibility, low friction, high wear resistance, suitable water content, and high mechanical strength, i.e., stiffness, fracture toughness, fatigue resistance.

Physically crosslinked PVA gels prepared by a repeated freeze-thawing method (FT gel) have been extensively studied [2] for biomedical and pharmaceutical applications. A new type of physical PVA gels prepared by a cast-drying method (CD gel) has been recently investigated [3,4]. Although the network nanostructures of both gels are similar to each other, the CD gels are transparent and elastic, while the FT gels are opaque and less elastic. The CD or FT gel is not able to satisfy all required properties alone. Among the requirements for the practical uses, the mechanical strength and wear resistance of both gels are not necessarily high comparing with natural systems, and further achievements are desired. Moreover, physical gels show the elution and erosion phenomena in general [5,6], where polymers in gels are partially released from the gel into the outer solvent. These phenomena are important problems that remain to be solved.
In this study, new preparation methods of PVA gels were examined using the following two methods. One was a lamination method to control the network nanostructures at the interfaces. The other was a novel freeze-thawing method to control the network microstructures. The mechanical behaviors of the gels were investigated using a tearing test and a linear reciprocating sliding test. In addition, the elution of polymers from gels and the abrasion loss by friction were quantitatively estimated by measuring the total carbon in the solvents. On the basis of the experimental results, possible mechanisms underlying the tear propagation, the reciprocating friction, and the elution and sliding wear behaviors will be discussed in terms of the multiscale network structures, characterized by the microcrystallites formed at gelation.

References

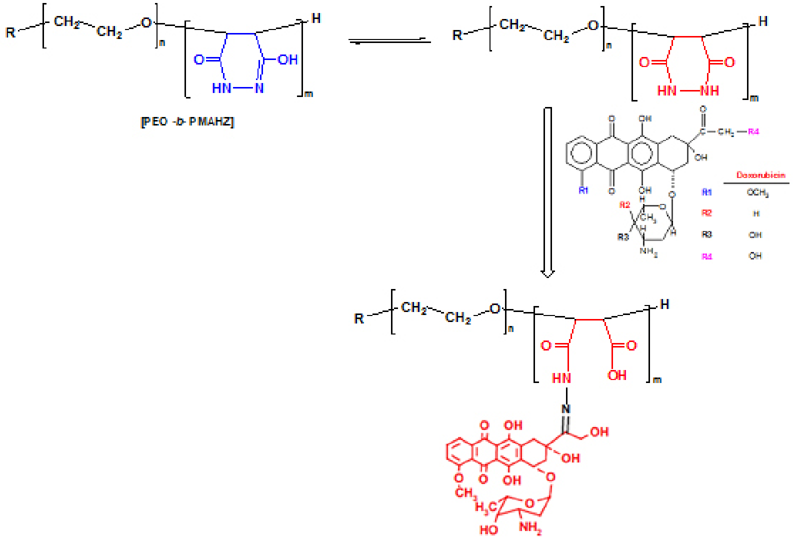
[1] T. Murakami, H. Higaki, Y. Sawae, N. Ohtsuki, S. Moriyama, Y. Nakanishi, *Proc. Inst. Mech. Eng. Part H: J. Eng. Med.,* 212 (**1998**) 23-35.
[2] C.M. Hassan, N. A. Peppas, *Adv. Polym. Sci.*, 153 (**2000**) 37-65.
[3] E. Otsuka, A. Suzuki, *J. Appl. Polym. Sci.,* 114 (**2009**) 10-16.
[4] E. Otsuka, S. Sasaki, K. Koizumi, Y. Hirashima, A. Suzuki, *Soft Matter,* 6 (**2010**) 6155-6159.
[5] S. Sasaki, E. Otsuka, Y. Hirashima, A. Suzuki, *J. Appl. Polym. Sci.,* 136 (**2012**) 233-241.
[6] S. Sasaki and A. Suzuki, *React. Funct. Polym.*, (**2013**) in press.

Synthesis of Smart Polymeric Pro-drugs exhibiting Stimuli-responsive Behavior

Abu B. Siddique, Jae Hyeok Lee, Yoon Kim, Sera Yang, Jungahn Kim*
Department of Chemistry, Kyung Hee University, Seoul 130-701, Korea
(E-mail: jakim05@khu.ac.kr)

A variety of polymers have been developed as basic materials in several fields for a long time. Among them, biocompatible polymers have received a great attention in the biomedical field. Specifically, poly(ethylene glycol) (PEG) approved by FDA has been utilized not only for modification of water-insoluble drugs or medicines but also for manufacturing drug-nanocarrier in the drug delivery system to get the enhanced permeation and retention (EPR) effect. In this study, I will discuss the applications and the importance of PEG derivatives in relation with the synthetic methodology as well as the incorporation of the functional groups into the polymers bearing a Schiff base linkage to get a high efficacy for modification of drugs as shown in *Scheme 1*. Especially, a 'smartness' of the resulting polymeric pro-drugs may be discussed in the application point of view.

Scheme 1



In this presentation, the preliminary results for the synthesis of block copolymers exhibiting pH-sensitive Dox-releasing behavior and the formation mechanism will be discussed.

References

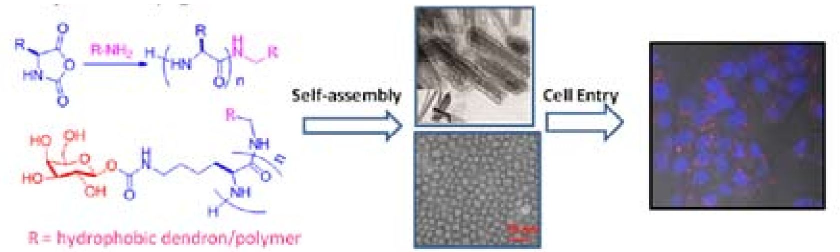
[1] Kim, J.; Lee, S.; Nam, J. H.; Cho, Y. J.; Kim, J.; Lee, J. Y.; Kang, H.-J.; Kim, S.; Kim, H. T.; Park, H. M.; Kim, J. *Macromol. Res.* **2011,** *19,* 716.

Glycopolypeptides and their Self-assembled Nanostructures as Possible Drug Delivery Vehicles

Sayam Sen Gupta
National chemical laboratory, Pune, India
ss.sensgupta@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 biomolecular recognition events such as cellular recognition, adhesion, cell growth regulation, cancer cell metastasis, and inflammation. The interaction between carbohydrate binding protein lectins and carbohydrates is weak but may be greatly enhanced through polyvalency. Since glycopolypeptides are typically polyvalent, they present a platform for which multiple copies of a carbohydrate can be presented simultaneously, thus enhancing their affinity and selectivity for lectins many folds. We have reported the facile synthesis of high molecular weight water soluble *O*-glycopolypeptide polymers by the ring opening polymerization of their corresponding N-carboxyanhydride (NCA) in very high yield.[1] The synthesized water soluble glycopolypeptides (with mannose side chain) were found to be α-helical in aqueous solution and their binding study with the lectin Con-A displayed a polyvalency of 15-36 folds.[2]

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 synthesized. 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 tune the morphology of the nanostructures from rods to micelles to vesicles.[3] All the assemblies were found to be bioactive as was demonstrated by the interaction of mannose-functionalized nanorods/micelles with the lectin ConA. Finally, we also show that glycopolypeptides having a β-galactose side chain can be used for selectively targeting the liver cancer cell line HepG2 which is known to over-express receptors for β-galactose.



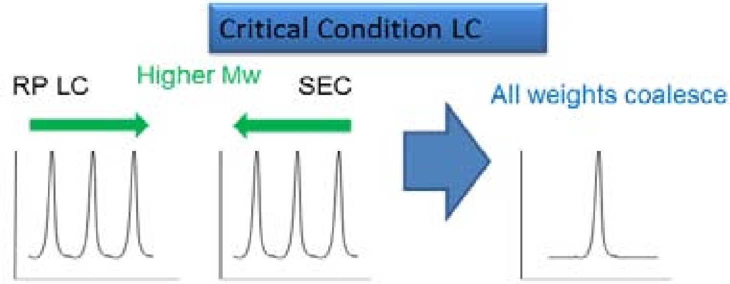
References

[1] D. Pati et al *Polymer Chemistry*, 2011, **2**, 805.
[2] D. Pati et al *Biomacromolecules*, **2012**, 13, 1287
[3] D. Pati et al *J. Am. Chem. Soc*, **2012**, 134, 7796

Activated methoxy poly(ethylene glycol) ''mPEG" and polymers for drug delivery

Prodip Sarker
Dr. Reddy's Laboratories, Chirotech Technology Centre, 410 Science Park, Cambridge CB4 0PE
p.sarker@drreddys.com

Dr. Reddy's Laboratories is one of the leading manufacturers and suppliers of activated methoxy poly(ethylene glycol) "mPEGs" for the conjugation of biopharmaceuticals (PEGylation) such as proteins, antibody fragments and peptides. PEGylation improves the stability and the pharmacokinetic properties of biologic drugs. Key properties of pharmaceutical grade activated mPEGs are low poly-dispersity and low diol content. Dr. Reddy's manufacturing technique for the synthesis of mPEG-alcohol (mPEG-OH) embodies these attributes by optimisation of conditions and careful control of the water content. The mPEG-OH is then converted to activated mPEGs under good manufacturing practices (GMP) for use in clinical trials or commercial sale, with batch sizes from 100's g to 10's Kg. The analysis of activated mPEGs is challenging, both in terms of functionality and molecular weight distribution. We have developed analytical methods in the areas of HPLC under critical conditions and mass spectrometry. There are 11 launched PEGylated drugs and many more in clinical trials. My talk will review this growing area, and highlight other uses of polymers for drug delivery.



Reference:

[1] Polyethylene glycol compounds and process for making, Patent No. US 7,199, 193 B2
[2] Method for analysing polyethylene glycol compounds, Patent No. US 7,824,919 B2

Hyaluronic Acid- A Versatile Biopolymer in Biomedicine and Biosurgery

Pradeep K. Dhal*, Bo Chen, Diego Gianolio, and Robert J. Miller
Polymer & Biomaterial R&D, Sanofi-Genzyme R&D Center, Genzyme Corporation – A Sanofi Company, 270 Albany Street, Cambridge, MA,02139, USA
*Pradeep.dhal@genzyme.com

Hyaluronic acid (HA) is a naturally occurring biopolymer. HA is biodegradable, highly biocompatible, and contains functional groups like carboxylic acid, hydroxyl, and acetamido groups along its backbone. The glycosaminoglycan polymer exhibit interesting physico-chemical and biological properties. For example, as a ligand for cell surface receptors, HA can modulate various signaling event in specific cells. These characteristics of HA make it a promising biomaterial for medical device and bioengineering applications as well as an attractive carrier for targeted and sustained delivery of (bio)therapeutic agents. In recent years, numerous approaches have been developed to prepare conjugates of HA with small molecule drugs and biologics. The pharmacokinetic, pharmacodynamics, and biodistribution of these HA conjugated therapeutic agents have been carefully modulated by appropriate chemical modification. This talk will provide an overview of recent developments in the chemistry and biology of HA derivatives as new generation of human therapeutic agents.

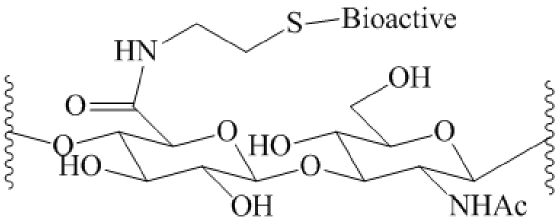


Figure 1. Schematic illustration of a HA conjugated bioactive agent.

References

[1] Dhal, P. K. ; Gianolio,D. A.; Miller. R. J. *J. Macromol. Sci., Part A* 48 (**2011**) 994.
[2] Chen, B.; Miller, R. J.; Dhal, P.K. *J. Biomed. Nanotechnol.* (in press)

Polymer Based Approaches for Novel Antithrombotic and Infection Resistant Surfaces

Jayachandran N. Kizhakkedathu
Centre for Blood Research and Department of Pathology and Laboratory Medicine, University of British Columbia, Vancouver BC, Canada; Department of Chemistry, University of British Columbia, Vancouver BC, Canada.
**E-mail: jay@pathology.ubc.ca*

Modern medicine is greatly benefited by the advancement in biomaterials. The design and development of novel therapeutics and novel materials for the replacement of natural tissues and organs influenced the health care of millions of people. Synthetic polymers have played critical roles in the success of biomaterial applications and are widely used for drug delivery, implants, contact lenses, vascular grafts, cardiovascular stents and dental materials. Objectives of my research program are to understand molecular level interactions of tailored synthetic polymers with biological systems for the design of novel biomaterials. We take an integrative and interdisciplinary approach with an understanding of the pathophysiology of diseases: advanced polymer synthesis in combination with well designed biological assays and animal models for the discovery of novel polymers and technologies for biomedical and clinical use.

In this talk, I will describe the design of novel antimicrobial and antithrombotic coatings based on polymer brushes on implant surfaces to address implant associated infections. We use surface initiated atom transfer radical polymerization (SI-ATRP) approaches for the development of functional polymer brushes on surfaces towards blood compatible surfaces. Functional polymers are selected from a group of N-substituted acrylamide polymers and are functionalized with specially designed short antimicrobial peptides to generate antithrombotic and antimicrobial activity. Studies are performed to understand the relation between the blood compatibility, cell adhesion, antimicrobial activity and biofilm resistance to structural properties of the functional brushes and to optimize the design. Optimized surface coatings are tested in animal models to demonstrate the antithrombotic and antimicrobial activity against clinically relevant bacterial strains.

References:

[1] Gao et al *Biomacromolecules* **2011**, 12(10):3715-27.
[2] Gao et al *Biomaterials* **2011**,*32, 3899-3909.*
[3] Gao et al *Chemistry & Biology* **2012,**19, 199-209.
[4] Lai et al *Biomaterials* **2010**, *31*, 6710-6718.
[5] Yu et al *Adv Healthc Mater*. **2012**, 1, 199-213.

Biosynthetic Novel Copolymer Hydrogels – Studies On Hydrogel-Cell Interaction.

G. T. Finosh, M. Jayabalan*
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Polymer Science Division, BMT Wing,
Thiruvananthapuram – 695 012, Kerala State, India.
*Fax:0091-471-234814; Tel: 0091-471-2520212;E-Mail. muthujayabalan@rediffmail.com

Cardiac tissue engineering approach is to design novel therapeutic strategies to minimize the myocardial necrosis and to enhance the cardiac repair following myocardial infarction. Hydrogels have drawn great deal of interest as tissue engineering scaffolds especially for cardiac applications mainly due to their excellent biocompatibility. In the present study we prepared a biosynthetic hydrogel from the novel polymer poly(sebacate-co-fumarate-co-manitol) (SFM) by co-polymerization with alginate and studied the hydrogel-cell interaction.

Oligomeric SFM resin was prepared by the condensation polymerization of sebacic acid, maleic anhydride and manitol and subsequent isomerisation of maleate fraction to fumarate. SFM resin was co-polymerized with alginate by acid catalysis to form SFM-alginate co-polymer (SFMA). This was then crosslinked with di(ethylene glycol) dimethacrylate (DEGDA) and the alginate fraction by Ca^{2+} to form the hydrogel scaffold, SFMA-DEGDA. Functional group analysis, hydrophilicity, water holding capacity, surface morphology and mechanical properties have been evaluated. The status of water was determined by DSC. Biological evaluations were carried out by MTT, direct contact and live /dead assay. The cell penetration was quantified for 1 month using reported methodology [1].

The contact angle measurements revealed the amphiphilic character of SFM-DEGDA hydrogel. The present hydrogel posseses better water holding capacity and swelling, which is essential for cell survival. The status of water in the hydrogel is freezing-free water which provides a suitable microniche for the cells to penetrate and to proliferate. ESEM analysis showed appreciable pore morphology for the cells to proliferate. The hydrogels were mechanically robust, able to withstand millions of stretch cycles and hemocompatible. The hydrogel extracts did not evoke any cytotoxicity to the L929 fibroblast cell or any change in cell morphology. Live dead assay revealed that these hydrogels were able to provide accommodation and maintain the healthy being of L929 cells grown on it. The cell infiltration was quantified to be around 60% even after 27 days of initial seeding (Fig-1). The present hydrogel SFM-DEGDA is a potent candidate for cardiac tissue engineering due to its compatibility, appreciable mechanical strength and amphiphilic nature that support long term cell growth and penetration.

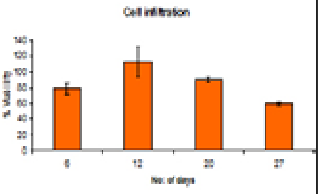


Figure-1. Quantification of cell infiltration showing the growth of L929 cells after 27 days.

References

[1]Finosh, G. T.; Jayabalan, M.; Vandana S.; Raghu, K. G. *Colloids Surf., B*, 107 (**2013)** 137.

Oral

Glycolic Acid Grafted Chitosan–Au–Fe_3O_4 Hybrid Nanoparticle Based Nanohybrid Scaffold for Drug Delivery and Tissue Engineering Applications

Sangeeta Kumari[a], Nayaku Chavan[a] and Raj Pal Singh[b*]
[a] *Division of Polymer Science and Engineering, National Chemical Laboratory,*
Dr. Homi Bhabha Road, Pune – 411 008, Maharashtra, India
[b,*] *Advanced Research Centre in Pharmaceutical Sciences & Applied Chemistry,*
Bharati Vidyapeeth University, Erandawane, Pune-411038. Maharashtra, India
Tel.: +91-20-25437237, Fax: +91-20-25437237
E-mail : rp.singh.ncl@gmail.com

Advances in nanotechnology play an important role in designing nanomaterials with specific functional properties that can address the shortcomings in the area of diagnostics and therapeutics. The hybrid nanostructures are desirable for many application like sustained drug delivery [1], biological and chemical sensing. A wide range of materials have been employed as drug carriers such as surfactant, dendrimers and natural or synthetic polymers [2]. Among these, polysaccharides have received increasing interest because of their outstanding physical and biological properties [3]. The research on biomedical applications of nanoparticles has seen an upsurge in recent years due to their unique capabilities in treatment of ailments. This work reports the synthesis of Au–Fe3O4 hybrid nanoparticles. The formation of these nanoparticles was confirmed by transmission electron microscopy (TEM) and physical property measurement system (PPMS). Next step of this paper reveals potential use of novel hybrid of chitosan-g-glycolic acid and Au–Fe3O4 hybrid nanoparticles in controlled drug delivery and tissue engineering applications. Grafting of glycolic acid and drug loading in porous scaffold was characterized by Fourier transform infrared spectroscopy.

The nanohybrid scaffolds (fig.1) were found to be stable regardless of pH of the medium and play a key role in cell adhesion, proliferation and migration. Au–Fe3O4 hybrid nanoparticles reinforcement was found to control the drug (cyclophosphamide) release rate in phosphate buffer saline solution (pH 7.4). Therefore, Au–Fe3O4 hybrid nanoparticles are viable additive for formulating sustained drug delivery systems based on glycolic acid grafted chitosan. The cell proliferation profile also shows that prepared nanohybrid is biocompatible providing suitable substrates for tissue engineering.

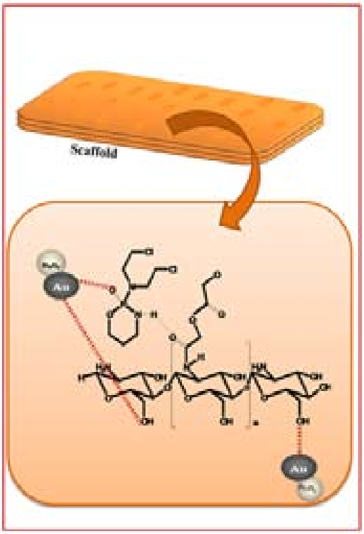


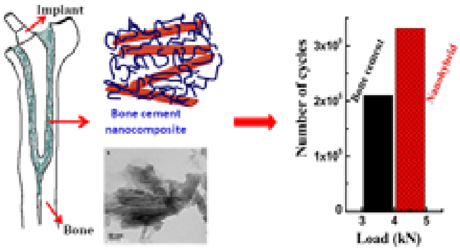
Figure 1. Grafting of glycolic acid on chitosan, formation of CS-g-GA and preparation of chitosan-g-glycolic and Au/Fe_3O_4 nanoparticle nanocomposite

References

[1] Cheng, H.; Kastrup, C.J.; Ramanathan, R.; Siegwart, D.J.; Ma, M.; Bogatyrev, S.R.; Xu, Q.; Whitehead, K.A.; Langer, R.; Anderson, D.G. *ACS Nano,* 4 **(2010)** 625.
[2] Duncan, R. *Nature Reviews Drug Discovery,* 2 **(2003)** 347.
[3] Liu, Z.; Jiao, Y.; Wang, Y.; Zhou, C.; Zhang, Z. *Advanced Drug Delivery Reviews,* 60 **(2008)** 1650.

Layered double hydroxide induced advancement in joint prosthesis using bone cement: The effect of metal substitution

Govinda Kapusetti[a], Nira Misra[a*], Pralay Maiti[b]
[a]School of Biomedical Engineering, Indian Institute of Technology
(Banaras Hindu University), Varanasi 221 005, India.
[b]School of Materials Science and Technology, Indian Institute of Technology
(Banaras Hindu University), Varanasi 221 005, India
* email i.d.: nira1953@yahoo.co.in



Poly (methylmethacrylate) based bone cement and its nanocomposites with layered double hydroxide (LDH) have been developed with greater mechanical strength and biocompatibility as grouting material for total joint arthroplasty. Bivalent magnesium has been replaced with trivalent aluminium with various mole ratios, keeping the layered pattern of the LDH intact, to cater the effect of varying substitution on the property enhancement of the nanocomposites. The intercalation of polymer inside the LDH layers makes them disordered and mechanically stiffer and tougher by more than 100%. The thermal stability of bone cement has increased by more than 30 °C in presence of 1wt% of nanoLDH, homogenously distributed in the bone cement matrix by creating inorganic thermal barrier out of LDH dispersion. The improvement in properties of the nanocomposites has been explained in terms of strong interaction between nanoLDH and polymer. The superior bioactivity and biocompatibility of the nanocomposites as compared to pure bone cement has been established through hemolysis assay, cell adhesion, MTT assay and cell proliferation using fluorescence imaging. The developed nanocomposites have been used as grouting material and significant improvements have been achieved in fatigue behaviour with gradual increment of Al substitution in Mg:Al mole ratio in nanoLDH, demonstrating real use of material in biomedical arena. In vivo experiment on rabbit clearly revealed the superior efficacy of bone cement nanocomposites over pure bone cement and blank.

References

[1] [29] Govinda, K.; Nira, M.; Vakil, S.; Kushwaha, R. K.; Pralay, M. *J. Biomed. Mat. Res. A,* 100 **(2012)** 3363.
[2] [21] Nira, M.; Govinda, K.; Shilpa, J.; Pralay, M. *J. Appl. Poly. Sci.,* 121 **(2011)** 1203.

Study of Polyelectrolyte Complex Formation of Gelatin with Sodium Carboxymethyl Cellulose and Sodium Alginate for Microencapsulation

N. Devi*, C. Deka and D.K.Kakati
Department of Chemistry, Gauhati University, Guwahati-781014, India
** E-mail: nimi262002@yahoo.co.in*

The microencapsulation of active ingredients and their delivery holds promise for improved therapeutics. Polymer hydrogel submicrometer-sized particles are finding widespread importance in the delivery of encapsulated toxic or fragile drugs [1]. Polyelectrolyte complex coacervation can be induced in systems containing cationic and anionic hydrophilic colloids for the microencapsulation of drugs. Gelatin, an amphoteric protein, which is positively charged below its isoeletric point and is expected to form polyelectrolyte complex coacervate with sodium alginate (SA) and sodium carboxymethyl cellulose (SCMC), which will have negative charges at lower pH [2].

Polyelectrolyte complex formation between gelatin with SA and SCMC was studied for microencapsulation. The efficiency of complex formation was followed by measuring viscosity, coacervate yield and turbidity of the test solutions. Maximum polyelectrolyte complexation for gelatin/SCMC was found to occur at pH=3.5 and SCMC/gelatin ratio of 1:2.33 in the mixture. For SA/gelatin, effective polyelectrolyte complexation was realized at pH= 3.7 and when the ratio of the two polymers was 1:3.5.

Microparticles containing a solid antitubercular drug, isoniazid were prepared by using the polyelectrolyte complexation of these two pairs of polymers. Microencapsulation of drug was carried out at the optimized ratio of the polymers and pH of the mixture. The encapsulation efficiencies of drug were dependent on the amount of crosslinker, drug loading and polymer concentration. Scanning electron micrographs showed the formation of agglomerated to free flowing spherical microparticles (Fig.1) depending on the amount of surfactant tween 80 and crosslinker (Fig.2). The size of microparticles tends to increase with the increase of the concentration of the polymer. For same amount of crosslinker used, drug release behaviour was governed by the differences in swelling of the microparicles in different pH media. Thermogravimetric analysis showed the improvement of thermal stability with crosslinking. Fourier Transform Infrared Spectroscopy study showed that there was no significant interaction between drug and gelatin/SA, gelatin/SCMC complex.

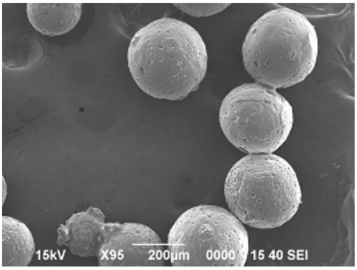


Figure 1. SEM image of spherical microparticles

Figure 2. Images of crosslinked microparticles

References:

[1] Becker, A.L.; Zelikin, A.N.; Johnston, A.P.R.; Caruso, F. *Langmuir*, 25 **(2009)** 14079.
[2] Shinde, U.A.; Nagarsenker, M.S. *Indian J Pharm Sci*, 71 **(2009)** 313.

Responsive Polymer Conjugated Magnetic Fluorescent Hybrid Nanoparticles For Targeted Drug Delivery

Banalata Sahoo, Panchanan Pramanik, Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur, W.B. 721302, India
**Corresponding author E.mail id:* dibakar@chem.iitkgp.ernet.in

Cancer specific targeted drug delivery has been emerged as excellent research area of current nanotechnology [1]. In this context, we prepared a dual responsive block polymer via RAFT polymerisation technique. Then this polymer was conjugated on magnetic iron oxide nanoparticles (Fe_3O_4) through covalent linkage to form magnetic core and responsive shell nanoparticles. Further, to achieve cancer specific tarfeting and fluorescent properties, cancer specifiec targeting ligand and fluorescent molecule were attached on magnetic nanocarrier. Finally Doxorubicin (Dox) as one of the model anticancer drug was loaded on these multifunctional nanoparticles via electrostatic interaction between block polymer chains with cationic group of drug molecules. The nanoparticles were characterized by XRD, TEM, SAED, FESEM, EDX, TGA, zeta potential, VSM measurements, FTIR, UV-Vis spectral analysis. From HRTEM analysis the size of magnetic nanocarrier was found to be 25-35 nm which is reasonble size for drug delivery purposes and the nanocarrier formed core-shell structure. From various biological studies, it is revealed that the targeting moiety attached and therapeutic loaded nanocarrier could achieve better cancer specific targeting properties. The drug was released in a sustained manner with response to stimuli. Moreover the polymer modified magnetic nanocarrier achieved better dispersion stability compared to pristine iron oxide magnetic nanoparticles and can be easily recovered with the help of simple permanent magnet. Again the drug loaded nanocarrier caused significant death to HeLa cancer cells in dose dependent manner as compared to its effect normal cells.

Figure 1. Drug loading picture showing initial Dox(left side) drug solution and decant Dox (right) after loading with polymer-Fe_3O_4 nanoparticles with magnetic separation.

References
[1] Pan, L.; He, Q.; Liu, J.; Chen, Y.; Ma, M.; Zhang L.; Shi, J. *J. Am. Chem. Soc.,* 134, **(2012)** 5722.

Evaluation of Antimicrobial Tissue Engineered poly (ε- caprolactone) Scaffolds for Vascular Constructs

Soumya Columbus[a], Lissy K Krishnan[b] and V Kalliyana Krishnan[a]*
Dental Products Laboratory[a], Thrombosis Research Unit[b], Biomedical Technology Wing
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Trivandrum, India.695012
Email: muralimanasi@gmail.com

Pathological conditions such as atherosclerosis and thrombosis that affect small diameter blood vessels adversely are one of major causes of mortality and morbidity all over the world [1]. Lack of availability of functional small diameter vascular grafts led to evolution of tissue engineered constructs intended to replace the diseased blood vessel by regeneration of vascular tissue with the aid of a biologically modified biodegradable scaffold [2]. Design strategies of the scaffold which mimics the natural blood vessel structure is expected to provide better opportunities to regenerate multilayered organization of vascular cells. The regulation of micro-architectural parameters such as pore size of scaffold may provide suitable homing sites similar to native extra-cellular matrix present in vascular tissue. Even though some of vascular tissue engineering approaches show emphasis on multilayered scaffolds, there exists a little consideration for optimum porosity characteristics for endothelial and smooth muscle cells [3,4]. Over and above the optimisation of the microstructure and mechanical properties of scaffold, the incorporation of antimicrobial agents like silver nanoparticles may be a promising strategy to prevent *in vitro* culture infections by micro-organisms [5].

In the present work, we have investigated the effect of morphological characteristics of electrospun polycaprolactone scaffolds intended for small diameter vascular graft applications upon mechanical properties and interaction with vascular cells. Poly(ethylene glycol) protected silver nanoparticle (SNPs) solution is prepared and characterized by TEM, XRD and particle size analysis. In order to impart antimicrobial activity, SNPs were incorporated into PCL solution and electrospun into tubular scaffold with two different layers. The pore size of the luminal and abluminal surface layers was regulated by varying fiber diameter using SEM (Figure 1) and Micro CT. The microstructure of both layers of scaffolds was optimized for appropriate endothelial and smooth muscle cell growth. The presence of SNPs was confirmed by EDS analysis and antimicrobial properties of the scaffolds were evaluated by Zone of Inhibition Assay. Contact angle measurements provided information on surface characteristics such as surface energy and distribution of polar/dispersion components. Mechanical properties evaluated using universal testing machine were found to be similar to natural blood vessel.

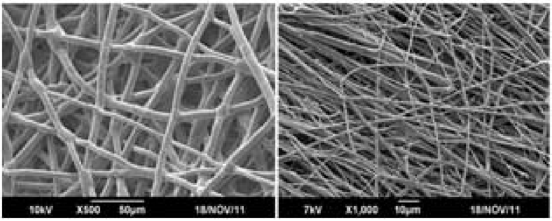


Figure 1: SEM image of electrospun PCL and PCL-SNP scaffolds

References

[1] Hoerstrup, S.P; Zund, G; Sodian, R; Schnell, A.M; Grunenfelder, J; Turina, M.I. *European Journal of Cardio-thoracic Surgery* 20 (**2001**) 164
[2] Ratcliffe, A. *Matrix biology* 19 (**2000**) 353
[3] Mathew, RW; Richard, B; Cay, K. *Biomaterials* 27 (**2006**) 3606
[4] Liang, Z; Jinanyc, Z; Qingping, L; Yingjic , W; Shengshou, H. *Biotechnology and bioeng*ineering 99 (**2008**) 1007
[5] Madhavan, RV; Rosemary, MJ; Nandkumar, MA; Krishnan, KV; Krishnan, LK. *Tissue engineering part A*. 17 (**2011**) 439

Converting palm oil into polymeric materials

Seng Neon Gan
University of Malaya, 50603 Kuala Lumpur, Malaysia

The environmental pollution issues have led to efforts in the polymer industry to reduce its dependence on petrochemicals which are non-sustainable. Plant oils offer many advantages in the production of polymeric materials, apart from being renewable resources. Their ready availability and relative low prices make them attractive. Diverse chemistry can be applied on them, leading to a great variety of polymers for many different applications. Malaysia is one of the world largest producers of palm oil. This paper presents our recent works of converting palm oil into specialized polymers, by three different approaches. Firstly, palm oil derivatives have been used as feedstock to produce bacterial polyhydroxyalkanoates (PHA), which are biopolymers, with potential medical applications. In the second approach, palm oil was converted into low molecular weight polyester polyols, which can then react with polyisocyanides to produce polyurethane adhesives and flexible foams. Lastly, through suitable chemical modifications, the palm oil is converted into macromers that are molecules having one or more polymerizable functional groups. These macromers could be used as additives in rubber compounding. Copolymerization with acrylic monomers has developed into new coating materials, UV-curable resin for as dental restorative resins to replace mercury amalgam, as well as making environmental friendly toner resin for the printing industry.

Fabrication and Characterization of Photocrosslinkable Poly (2-hydroxyethyl methacrylate) Based Hydrogels For Wound Dressing Applications

Rethikala P K and Kalliyana Krishnan.V*
Dental Products Laboratory, Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Trivandrum, India
muralimanasi@gmail.com

Hydrogels are three-dimensional networks of hydrophilic polymers which absorb and retain high water content within their matrix. Ability to absorb exudates while retaining high moisture content, non-adhesive character, excellent oxygen permeability and capacity to act as a barrier against microbial infections make them ideal for use as wound dressing materials[1]. Poly(2-hydroxyethyl methacrylate)(pHEMA), an excellent biocompatible hydrogel widely used in the biomaterials area as contact lens, drug delivery systems etc, suffers from poor mechanical properties[2,3]. In this work, we report the development of a pHEMA-poly(ε-caprolactone)–poly(ethylene glycol) (pHEMA-PCL–PEG) semi- interpenetrating polymer network hydrogel intended for wound dressing application. PCL is a biodegradable polymer approved by FDA for clinical applications and is expected to provide the optimum mechanical strength in association with PEG which provides a plasticising effect to the network.

Diphenyl (2,4,6 trimethyl benzoyl) phosphine oxide which dissociates at 410 nm was used as photoinitiator to polymerize a homogenous mixture of HEMA monomer, PCL (Mn 10000) and PEG 200. A light source of wavelength 380-510 nm was used to initiate the reaction at about 70-72°C. Hydrogel sheets thus obtained showed improved mechanical properties, vapour permeability and swelling characteristics compared to bare pHEMA hydrogels. Structural characterization of the IPN was carried out using FT-IR, ^{1}HNMR spectroscopy and XRD. Thermal properties of the hydrogel were studied using TGA and DSC. Contact angle studies provided data on nature of the hydrophilic-hydrophobic character of the polymer surface. *In vitro* cytotoxicity of the hydrogel was studied using L929 cell lines by direct contact method. Results indicate pHEMA-PCL –PEG IPN to be noncytotoxic (Fig 1). Test for haemolytic study showed the hydrogel to be hemocompatible. The polymer is expected to have good potential for wound and burn dressing applications.

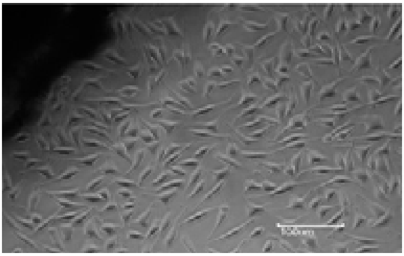


Figure 1. Morphology of L929 cells after incubating with hydrogel for 24h to 26 h at 37 ± 1^{0}C

References:
[1] Hye-Jin, Y.; Han-Do, K. *Journal Biomedical Materials Research Part B: Applied Biomaterials* 85(**2008)** 326
[2] Montheard, J. P.; Chatzopoulos, M.; Chappard, M. *Macromolecular Chemistry and Physics* 32 (**1992)** 1
[3] Blanco,M. D.; Trigo, R. M.; Teijon, C.; Gomez, C. *Biomaterials* 19 (**1998**) 861

Energy-Saving Dissolution of Wood Biomass in the Presence of Water

Mitsuru Abe[a,b], Yukinobu Fukaya[b], and Hiroyuki Ohno[a,b]*
[a]*Department of Biotechnology, Tokyo University of Agriculture and Technology,2-24-16, Koganei, Tokyo, Japan*
[b]*Functional Ionic Liquid Laboratories, 2-24-16, Koganei, Tokyo JAPAN*
**ohnoh@cc.tuat.ac.jp*

Introduction

Cellulosic biomass is a very abundant and renewable material and it does not compete with food. Biomass has therefore been considered to the fossil fuels substitute. However, an efficient energy converting process has not been constructed yet, because cellulose has strong intra- and inter-hydrogen bonding networks. Recently, ionic liquids are attracting attention as novel dissolving solvents for cellulose and cellulosic biomass [1]. We have already reported that some ionic liquids dissolved and extracted polysaccharides from cellulosic biomass at room temperature [2]. However, the cellulose-dissolving ability of these ionic liquids is considerably decreased under wet condition [3]. Since, plant biomass contains much water, drying processes are needed for ionic liquids and biomass, and it consume a great amount of energy. To overcome this problem, we searched for proper ions to treat cellulosic biomass with little energy. In this congress, we report a novel solvent, tetra-*n*-butylphosphonium hydroxide (TBPH), which contains certain amount of water and dissolves cellulose without heating. We will also report the energy-saving dissolution and extraction of polysaccharides from wood biomass [4].

Experimental Section

TBPH containing 60 wt% water and poplar powder (36-200 mesh) were provided by Hokko Chemical Industry Co., Ltd., and Forestry and Forest Products Research Institute, respectively. Cellulose or poplar powder was added to TBPH/water mixture and stirred without heating. After that, dissolved polysaccharides were precipitated by the addition of poor solvents to evaluate the extraction rate.

Results and Discussion

TBPH containing 40 wt% water dissolved 20 wt% cellulose (at the final concentration) within 5 minutes under gentle stirring at 25 °C. The TBPH contains 30-50 wt% showed the great ability to dissolve cellulose without derivatization or degradation, confirmed by both FT-IR measurement and a custom-made HPLC, which uses polar ionic liquid as an eluent. The hydroxide anion played an important role to dissolve cellulose through breaking the hydrogen bonding networks of cellulose.

Table 1. Correlation between water content of TBPH and extraction rate of polysaccharides after 1 hour stirring at 25 °C. The extraction rate calculated by the weight of added poplar, not contained polysaccharides.

Water Content (wt%)	Extraction Rate (wt%)
70	4.9
60	28
50	36
40	37
30	24

Natural wood powder was then treated with this hydroxide solution. As expected, this solvent extracted polysaccharides such as cellulose from wood powder without heating (Table 1). With 70 wt% water, TBPH extracted polysaccharides only 4.9 wt% of the added poplar, because TBPH solution cannot dissolve cellulose at this concentration. On the other hand, TBPH containing 40-50 wt% water successfully extracted 36-37 wt% of added poplar as the mixture of polysaccharides. We will also describe about the selective extraction and isolation of polysaccharides.

References

[1] Long, J. X.; Li, X. H.; Wang, L. F.; Zhang, N. *Sci. China-Chem.*, 55 (**2012**) 1500.
[2] Abe, M.; Fukaya, Y.; Ohno, H. *Green Chem.*, 12 (**2010**) 1274.
[3] Mazza, M.; Catana, D. A.; Garcia, C. V.; Cecutti, C. *Cellulose*, 16 (**2009**) 207.
[4] Abe, M.; Fukaya, Y.; Ohno, H. *Chem. Commun.*, 48 (**2012**) 1808.

Nylon11 Nanofibers Scaffold for Tissue Engineering Applications

M. Dhanalakshmi[a], A.K.Lele*[a], J. P. Jog[a], B.L.V.Prasad[b] Mugdha Gadgil[c]
a. Polymer science and engineering division, National chemical laboratory, pune-411008, India.
b. Physical & material chemistry division, National chemical laboratory, pune-411008, India.
c. Chemical engineering and Process development division, National chemical laboratory, pune-411008, India.
Corresponding author: Email address: ak.lele@ncl.res.in, phone number: 91-2025902199

Nylon11 nonwoven mats were prepared by electrospinning solutions in formic acid (Fig 1 a, b). The solution concentrations were varied from 5- 20wt/vol%. Increasing the concentration of Nylon11 increased the viscosity and conductivity of the solution, and this led to an increase in the average fiber size of the mat. The as-spun Nylon11 mats were hydrophobic. Surface modification of the mats by plasma treatment in presence of Hydrogen and Nitrogen gas increased the hydrophilicity of the mats due to the formation of amine groups on the surface. Further, gold nanoparticals (GNPs) were attached to the plasma treated electrospun mats (Fig 1 c, d). The GNPs were also were decorated with lysine. This surface modification increased the durability of surface hydrophilicity and provided better compatibility for cell adhesion and proliferation. Cell culture studies were done by inoculating the Nylon11 mats with HEK293 cells (Human embryonic kidney cells). SEM images showed that HEK293 cells adhered and spread on the surface modified Nylon11 electrospun mat. MTT assay showed that that the cell proliferation rate on surface modified Nylon11 electrospun mat increased by the 5th day.

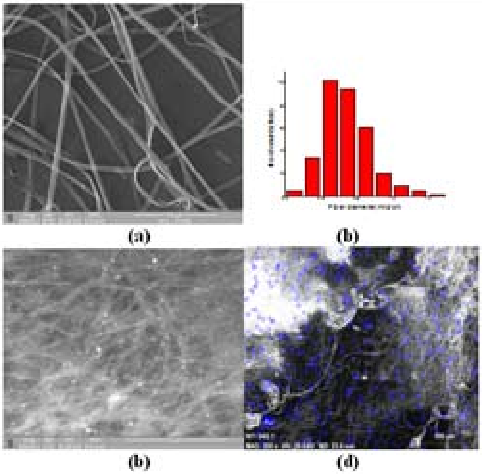


Figure 1. (a) SEM images of Nylon11 20wt/vol % electrospun mat (b) Fiber distribution study Nylon11 20wt/vol % electrospun mat (c)&(d) SEM images of surface modified Nylon11 20wt/vol % electrospun mat

References

[1] Zheng-Ming Huang.; Y.Z.Zhang; M.Kotaki.; S.Ramakrishna. Composites science and technology,63(2003) 2223-2253.
[2] S. Koombhongse.; W. Liu; D.H. Reneker. Journal of Polymer Science: Part B: Polymer Physics, 39(2001) 2598-2606.
[3] Kyungwha Oh.; Seong Hun Kim; Eun Ae Kim. Journal of Applied Polymer science, 81(2001) 684-694.

Biodegradable, Cytocompatible Polyesters With Tunable Physical Properties, Degradation Rate and Erosion Mechanism For Tissue Engineering Applications

Yashoda Chandorkar[a], Giridhar Madras[b], Bikramjit Basu[a,*]
[a] Laboratory for Biomaterials, *Materials Research Centre, Indian Institute of Science, Bangalore, INDIA*
[b] *Department of Chemical Engineering, Indian Institute of Science, Bangalore, INDIA*
**bikram@mrc.iisc.ernet.in*

Biodegradable polymers are of great importance in tissue engineering as the need for revision surgeries can be obviated by using these materials. The non-toxicity of the degradation products i.e. the monomers of such polymers also needs to be taken into account while designing their synthesis[1].

This work discusses the synthesis of a new family of biodegradable polyesters using sebacic acid, ricinoleic acid, citric acid and mannitol as monomers by a solvent free melt condensation process. The monomers were chosen by considering their functionalities and non toxicity. Ricinoleic acid acts as an analgesic and an anti-inflammatory agent, while mannitol and citric acid act as cross-linkers. Sebacic acid helps to increase the chain length.

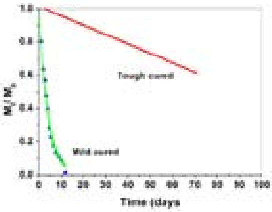


Figure 1: Polyesters showing variable degradation rates ranging from days to months depending on the curing time

A combination of FT-IR and NMR spectroscopy results revealed ester linkages and the incorporation of all the monomers in the as-synthesized polyesters. Depending on the relative ratios of the different monomers and the degree of curing, a range of elastic modulus (22 MPa -327 MPa), tensile strength (0.7-12.7 MPa) and degradation time (10 days to > 2 months) was obtained (Fig. 1).

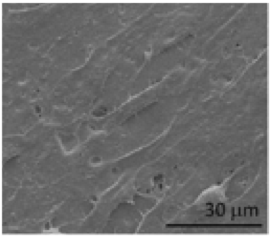


Figure 2: SEM image of C2C12 mouse myoblast cells proliferating on tough cured polyester after 3 days

The mild cured polyesters showed bulk erosion, while the tough cured polyesters showed surface erosion. The polymers show rubbery behaviour at physiological temperature (37 ^{0}C) and the contact angles measured showed that the polymers were hydrophilic Based on The cytocompatibility assessment of the cured polymers indicated good cell attachment and oriented growth of mouse myoblast cells (Fig. 2). To summarize, the results of this study indicate that the physical properties of the polymers can be tailored by varying the composition of the monomers and curing conditions. Hence, they exhibit potential for use as tissue engineering scaffolds and for localized drug delivery [2].

In my talk, I would like to elucidate the influence of monomer proportions and curing on mechanical strength and degradation properties as well as discuss a model we have proposed for curing.

References

[1] Shoichet, M.; *Macromolecules*, 43 (2) (**2009)** 581.
[2] Chandorkar, Y.; Madras, G.; Basu, B. *Journal of Materials Chemistry B*, 1(6) (**2013)** 865.

Self assembled PEG-PCL-PEG nanoparticles for Insulin delivery

Sanal Payyappilly[a], Santanu Dhara[b], Santanu Chattopadhyay[a]*
[a]*RubberTechnology Centre, Indian Institute of Technology,*
Kharagpur, India
[b]*School of Medical Science and Technology, Indian Institute of Technology, Kharagpur, India.*
*santanu@rtc.iitkgp.ernet.in

Amphiphilic nanoparticles were prepared using self assembled block copolymers for controlled release of Insulin under the physiological conditions. Biodegradable triblock copolymerof poly(ethylene glycol)-poly(ε-caprolactone)-poly(ethylene glycol) (PEG-PCL-PEG, PECE) was prepared by ring opening copolymerization and characterized using FTIR, ^{1}HNMR and GPC. PECE nanoparticles were prepared by nanoprecipitation mehtod. Prepared nanoparticles were analysed using HR TEM, DLS and DSC. Effect of concentration and block length on self assembly was studied. Polymers self assembled to nonoparticles were found to have size scale of 5 to 50 nm. The non-cytotoxicity of the nanoparticles were confirmed by the *in vitro* cytotoxicity test using HaCat cells. *In vitro* release of Insulin from the nanoparticles was investigated. Insulin retained its secondary structure after release as confirmed by CD spectrum.

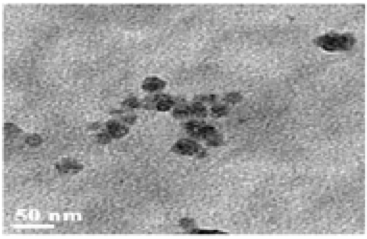


Figure 1. TEM image of PECE nanoparticle

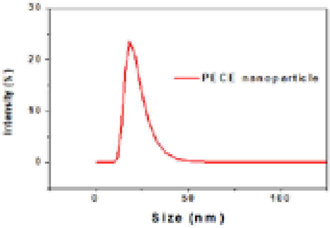


Figure 2. Distribution of the hydrodynamic radius (RH) of PECE nanoparticles.

References

[1] J. Panyam; V. Labhasetwar, *Advanced Drug Delivery Reviews*, 64 (**2012**) 61.
[2] S. G. Gaucher; M. H. Dufresne; V. P. Sant; N. Kang; D. Maysinger; J.-C. Leroux, *Journal of Controlled Release*, 109 (**2005**) 169.
[3] X. Wei; C. Gong; M. Gou; S. Fu; Q. Guo; S. Shi; F. Luo; G. Guo; L. Qiu; Z. Qian, *Int J Pharm*, 381(**2009**) 1.

Neem Oil: Renewable Source as a Substitute for Petroleum Based Feed Stock in Preparation of Polymeric Resins

Vikas V. Gite
Department of Polymer Chemistry, School of Chemical Sciences,
North Maharashtra University, Jalgaon, Maharashtra, India- 425 001
Email: vikasgite123@gmail.com

Preparation of polymers from renewable resources [1] has found great potential in a variety of industrial applications and can contribute to sustainable development in the future due to the environmental concerns, hike of prices and depleting of petroleum resources. Therefore exploration of renewable and non-conventional raw materials for preparation of polymers is one of the prime targets to researchers. Vegetable oils are the largest renewable source next to cellulose [2-3]. Neem Oil has traditionally been used in India for many applications viz. bio fertilizers [3], pharmaceutical [4] etc. Cultivation of neem trees do not required specific conditions. Hence neem treeare easily seen on barren lands, junglesand unused fertile lands in India. Although its availability is sufficient, it has not been focused as a potential source for production of polymeric feed stocks.

Recently we have shown that it can be used to prepare many polymeric resins which include diethanolamines [5], polyesteramides, polyetheramides, etc. The polymeric resins were used to prepare protective coatings for mild steel panels. Performance of coatings was tested for coating properties like glass, scratch resistance, bending, etc. Coatings were also tested for their thermal stability and other mechanical properties.Further the performance of coatings was also improved by formulating them as self-healing coatings.

References:-

[1] Coates G. W.; Hillmyer M. A.; Macromolecules, 42 (**2009**) 7987.
[2] Ronda, J. C.; Lligadas, G.; Galia, M.; Cadiz, V., Eur. J. Lipid Sci. Technol., 113 (**2011)** 46.
[3] Montero de Espinosa, L.; Meier, M. A. R., Eur. Polym. J., 47 (**2011**) 837.
[4] Bagle, A.V.; Jadhav, R.S.; Gite, V.V.; Hundiwale, D.G.; Mahulikar, P.P. Int. J. Polym biopolymer. Mat. 62 (**2013**) 421.
[5] Biswas, K.; Chattopadhyay, I.; Banerjee, R. K.; Bandyopadhyay, U. Curr. Sci. 82 (**2002**) 11Chaudhari, A.B.; Anand, A.; Rajput, S.D.; Kulkarni, R.D.; Gite, V.V. Prog. Org. Coat. (just accepted)

Poster

PB1

Electrochemical oxidation of glucose in ionic liquids using nitroxide radicals, gold nanoparticles, or Rh porphyrin as catalysts

Akira Konno [a, b], Mitsuru Abe [a, b], Hiroyuki Ohno [a, b]*
[a]Department of Biotechnology, Tokyo University of Agriculture and Technology
[b]Functional Ionic Liquid Laboratories (2-24-16 Naka-cho, Koganei, Tokyo, 184-8588, Japan.)
* ohnoh@cc.tuat.ac.jp

Energy production from inedible biomass is an important task for sustainable society. Cellulose is the most abundant organic polymer produced on Earth. Processing of cellulose in ionic liquids (ILs) should be one of the potential strategies to construct energy conversion system such as biofuel cell. Three steps are involved to product energy from biomass. The first step is the extraction and dissolution of polysaccharides from biomass. Some ILs have been proposed as good solvents for cellulose. We have reported that some polar ILs are useful to dissolve and extract cellulose from bran under mild condition [1, 2]. The second step is hydrolysis of polysaccharides into mono-, di-, or oligo-saccharides. The third step is conversion of chemical energy into electric energy. For efficient energy conversion of cellulose, we propose to carry out these steps in one pot with less energy. In this study, we have focused on the third step, i.e., oxidation of glucose in ILs.

We have used tetrabutylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) containing 40 wt% water [3] as well as 1-butyl-3-methylimidazolium propionate ($[C_4mim][C_2COO]$) and 1-ethyl-3-methylimidazolium methyl-phosphonate ($[C_2mim][(MeO)(H)PO_2]$) both containing 3 wt% water. All these dissolved cellulose at room temperature. Since 2-azaadamantane *N*-oxyl (AZADO) is known as an oxidation catalyst for primary and secondary alcohols in aqueous solutions, we used it for glucose oxidation catalyst. Gold nanoparticles (AuNPs) modified gold electrode was prepared as reported [4], and Rh porphyrin modified glassy carbon (GC) electrode was prepared as reported [5].

An oxidation current of glucose was obtained in $[C_4mim][C_2COO]$ (Figure 1 (i)) but no current was obtained in $[C_2mim][(MeO)(H)PO_2]$. An oxidation current of glucose was also obtained in $[P_{4,4,4,4}]OH$ (Figure 1 (ii), (iii)) but no current was found in $[C_4mim][C_2COO]$ nor $[C_2mim][(MeO)(H)PO_2]$. Presence of hydroxide anion might be necessary for glucose oxidation when AuNPs and Rh porphyrin were used. With the use of suitable IL and catalysts, both dissolution of cellulose and oxidation of glucose were concluded to be carried out. Especially when Rh porphyrin modified GCE was used, we achieved oxidation of glucose with relatively low overpotential.

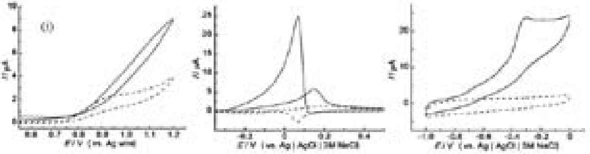


Figure 1. Cyclic voltammograms of (i) PFC electrode in $[C_4mim][C_2COO]$ containing 3 wt% water and 10 mM AZADO, (ii) AuNPs modified gold electrode in $[P_{4,4,4,4}]OH$ containing 40 wt% water, and (iii) Rh porphyrin modified GC electrode in $[P_{4,4,4,4}]OH$ containing 40 wt% water, respectively.
Scan rate was 1 mVs^{-1}.
Solid lines: in the presence of 100mM glucose (i, ii), or 500 mM glucose (iii), dotted lines: without glucose.

References

[1] Y. Fukaya, *et al.*, *Green Chem.*, 10 (**2008**) 44-46.
[2] M. Abe, *et al.*, *Green Chem.*, 12 (**2010**) 1274-1280
[3] M. Abe, *et al.*, *Chem. Commun.*, 48 (**2012**) 1808-1810.
[4] K. Murata, *et al.*, *Electroanalysis*, 22 (**2010**) 185-190.
[5] S. Yamazaki, *et al.*, *Chem. Commun.*, 46 (**2010**) 3607–3609.

PB2

Development and Characterization of Poly(2-hydroxymethyl methacrylate) Based Hydrogel for Controlled Drug Delivery

Akhtar Jahan Siddiqa*, Koel Chaudhury and Basudam Adhikari
[a]Materials Science Centre, IIT Kharagpur, WB-721302
[b]School of Medical Science and Technology, IIT Kharagpur, WB-721302
Email: 09ms9404@iitkgp.ac.in

Compared to conventional dosage forms, polymeric drug delivery system has many advantages, such as improved therapeutic effect, and reduced toxicity [1–2]. Hydrogels are 3D cross-linked hydrophilic polymers, from synthetic or natural origin, which have the ability to imbibe the fluid water [3]. Hydrogels used in the controlled release of drugs, made from polyhydroxyethylmetacrylate (pHEMA), polyvinyl alcohol (PVA), polyurethane (PU), polyethylene oxide (PEO) [4].

In the present work poly (2-hydroxyethyl methacrylate) was synthesized via bulk polymerization of 2-hydroxyethyl methacrylate (monomer) and then poly (2-hydroxyethyl methacrylate) was blended with polyvinyl alcohol solution, to obtained flexible and high strength membranes for controlled drug delivery. *In vitro* drug release studies were conducted with drug loaded hydrogel using Franz diffusion cell at 37 °C in incubator. PBS (phosphate buffer saline) solution was used as an acceptor for the release experiment, collected samples were analyzed spectrophotometrically at 236 nm. *In vitro* release, the initial burst was constant to 5 h due to dissolution of surface drug. From 6 to 72 h (Fig. 1) the drug diffusion slowly increased with increasing PVA dissolution as well as opening of pHEMA porous structure [5]. A clear macrophage separated structure and porosity was observed under optical microscopy and FESEM shows immiscible droplet morphology of blend in which drugs particle are uniformly dispersed in pHEMA (matrix) phase. A Fickian swelling of hydrogel system indicated the swelling controlled Fickian diffusion type of drug release.

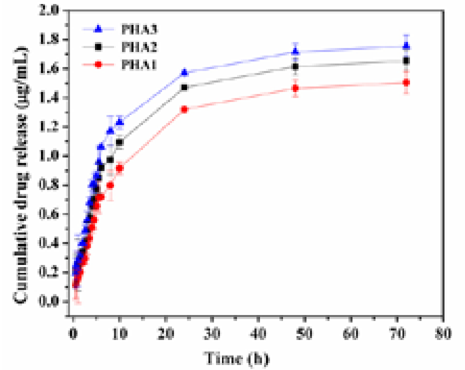


Fig. 1 *In vitro* release profile of drug from hydrogels in PBS (pH=7.4) at 37 °C

References:

[1] Chiba, M.; Hanes, J.; Langer, R.; Controlled protein delivery from biodegradable tyrosine-containing poly(anhydride-coimide) microspheres, *Biomaterials* 18 **(1997)** 893

[2] Tamada, J.; Langer, R.; The development of polyanhydrides for drug delivery applications, *J. Biomater. Sci., Polym. Ed.*, 3 **(1992)** 315

[3] N.A. Peppas, Hydrogels in Medicine and Pharmacy, **1987.** CRC Press, Boca Raton, FL,

[4] Lee, P.I.; Synthetic hydrogels for drug delivery: Preparation, characterization, and release kinetics, **1988** in: D. Hsieh (Ed.), Controlled Release Systems: Fabrication Technology, 2, CRC Press, Boca Raton, FL, p. 61

[5] Brazel, C. S.; Peppas, N. A., *Polymer* 40 **(1999)** 3383

PB3

Correlations of Cytocompatibility with Surface Energies and Tribological Performance of APTES Modified Multiwalled Carbon Nanotubes Reinforced UHMWPE /Al_2O_3 Nano-biocomposites

Anup Kumar Patel*(akpatel@iitk.ac.in) and Kantesh Balani*
*Biomaterials Processing and Characterization Laboratory, Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur 208016, India**

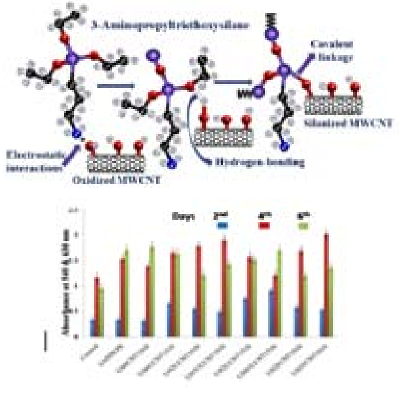


Figure1. Schematic illustration of (a) Model (b) L929 Cell viability assay on the UHMWPE/Al2O3/CNT composite

Ultrahigh molecular weight polyethylene (UHMWPE) is widely used biopolymer for articulating wearing surfaces of implant surfaces due to its excellent wear resistance and low coefficient of friction. But after implantation, generation of wear debris leads to aseptic loosening that limits the lifespan of implant and requires a revision of orthopedic surgery. In this study, to decrease the wear debris formation, carbon nanotubes [CNT] were modified by silane and synergistically reinforced with Al_2O_3 in UHMWPE matrix.

The composites were processed by compression molding method. The Phases, chemical and microstructure of the nanocomposites based on synergistic reinforced with Al_2O_3 and CNTs were studied by the methods of X-ray diffraction analysis, FT-IR spectroscopy, Differential Scanning Calorimetry, and Transmission and Scanning Electron Microscopy. The effects of the silane-modified CNTs on its reinforced composite were studied for their tribological, mechanical, thermal, and biological properties. The results showed that the elastic modulus and tensile strength of composites were improved by silane modification of the CNTs and higher than that of unmodified CNTs reinforced composites. The tensile strength of the silane-modified composite was higher than that of unmodified composites.

Tribological and thermal properties of the composites were also improved due to better interaction of the CNTs with UHMWPE polymer matrix. It was observed that due to reinforcements of functionalized CNTs and Al2O3 that were embedded in polymer matrix, leaching out of CNT was restricted and the tensile modulus and tribological performance of composites were enhanced by 59.56% & 29.41% respectively.

Keywords: Tribological properties, UHMWPE, Silanes, MWCNTs, artificial joints.

Email ID: akpatel@iitk.ac.in Fax No :(+91) (512) 257 7505

References

[1] Ji-Hoon Lee et.al.Polymer Engg. &ScienceVolume50, Issue7, (1433–1439), 2010
[2] Kantesh Balani *et al*.Acta Materialia 5692008)5984-5994

PB4

Electrospinning of 3D Nanofiber Matrices of Collagen Using a Novel Benign Solvent for Tissue engineering

Anuradha Elamparithi*, Dr. Alan M Punnoose, Dr. Sarah Kuruvilla
Cell and Tissue Engineering Lab, Sri Ramachandra University, India, Chennai- 600116.
** Corresponding author's email i.d. ; anuelam@gmail.com*

Collagen is a natural component of the extracellular matrix (ECM) and is abundant in many tissues, such as bone, skin, tendon, ligament and other connective tissues. At present, 29 distinct types of collagen have been characterized but only a few are used to produce biomaterials. Type I collagen is the most widely used in the field of tissue engineering.

Electrospinning is a technique, which uses a high electric field to produce ultra fine polymeric fibers with diameters ranging from nanometers to micrometers and a 3D architecture that mimics the native ECM. Currently nanofibers of Collagen have been electrospun using solvents such as 1,1,1,3,3,3- hexafluoropropan-2-ol (HFIP) and 2,2,2-trifluoroethanol (TFE), which are not only toxic but also expensive solvents. There is also evidence to indicate that using fluoroalcohols leads to a loss in the native integrity of collagen. Thus, the major challenge in producing electrospun collagen is to use an appropriate solvent system that does not denature or alter the biologically favorable properties of collagen.

We have successfully electrospun type I collagen using a novel benign binary solvent combination, which is not only environment friendly but also highly economical when compared to the fluoroalcohols *(patent filed: 640/CHE/2013)*. Briefly, the electrospun scaffolds were cross linked with (1-Ethyl-3- (3-dimethylaminopropyl) carbodiimide) (EDC) to maintain the stability of collagen nanofiber matrices. Scanning Electron Microscopy analysis revealed that the fiber diameter was in the nanometer range (200-800nm). The triple helical structure of collagen I was confirmed by transmission electron microscopy whereby the 67 nm banding typical of native collagen was observed in scaffolds stored in aqueous phosphate buffered saline. Biocompatibility of the nanofibrous scaffolds was confirmed using L6 skeletal myoblast cell lines and their proliferation on the 3D scaffolds was analyzed by 3-(4,5-dimethyl thiazol-2yl)-2,5-diphenyl tetrazolium bromide (MTT) assay and confocal microscopic analysis of muscle specific markers Desmin and Muscle Specific actin.

Our research provides evidence that the novel benign binary solvent maintains the molecular structural integrity of collagen in the electrospun matrices. The benign solvent combination provides a cost effective and non toxic alternative to the customary fluoroalocohol approach to electrospin collagen. Nanofibrous collagen matrices have a wide range of applications in 3D models *in vitro*, wound healing, dental applications and tissue engineering and this approach may potentially aid in making regenerative medicine more affordable to the common man.

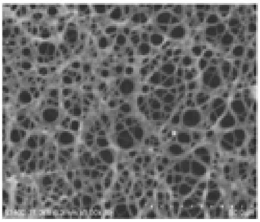


Figure 1. depicts the SEM image of three dimensional collagen fiber mat (magnification 1000x)

References

[1] M. D. Shoulders, R. T. Raines, Annu. Rev. Biochem. 2009, 78, 929..
[2] K. Gast, A. Siemer, D. Zirwer, G. Damaschun, Eur. Biophys. J. Biophy. 2001, 30, 273.
[3] J. A. Matthews, G. E. Wnek, D. G. Simpson, G. L. Bowlin, Biomacromolecules 2002, 3, 232.

PB5

Microencapsulation and release study of Neem Seed Oil as an insecticide with Melamine-Urea-Formaldehyde Polymer Shell

Avinash V. Bagle, Rahul K. Hedaoo, Vikas V. Gite, Dilip G. Hundiwale and Pramod P. Mahulikar
Department of Industrial Chemistry and Polymer Chemistry, School of Chemical Sciences,
North Maharashtra University, Jalgaon-425 001 INDIA

Microencapsulated pesticides are safer and convenient to handle and hence reduce environmental and mammalian toxicity. Therefore the prolong effect of encapsulated active ingredient (*a. i.*) is observed due to its regulated supply [1-6]. Melamine-Urea-Formaldehyde (MUF) polymer is used as shell material for the encapsulation of Neem seed oil, a well-known green insecticide. The process of microencapsulation was developed through *in-situ* polymerization using oil-in-water emulsion system [7]. Synthesized MUF microcapsules containing Neem seed oil were characterized by SEM analysis were considered for surface morphological studies as well particle size analysis for size distribution. The controlled release of neem seed oil was studied using UV-Visible absorption spectral response as probe. Neem seed oil, a green insecticide was successfully microencapsulated with Melamine-Urea-Formaldehyde (MUF) to fulfill the requirement of controlled release of Neem seed oil as an active ingredient (fig.1).

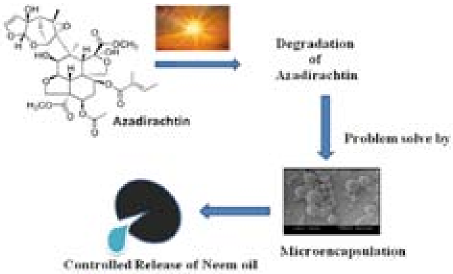


Figure 1. Overview for encapsulation

References:

[1] Jose, I.; Esmeralda, M.; Celia, M.; Juan, M. G. *Pest Management Science* 57 (**2001**) 688
[2] Manuel, F. N. *Journal Environmental Sciences and Health Part B* 42 **(2007)** 857
[3] Gunanand, C.; Jitendra, K.; Suresh, W.; Rajender, P.; Balraj, S. P. *Journal of Agricultural and Food Chemistry* 54 **(2006)** 4727
[4] Bagle, A.V.; Jadhav, R. S.; Gite, V. V.; Hundiwale, D. G.; Mahulikar, P. P. *International Journal of Polymeric Materials and Polymeric Biomaterials* 62 **(2013)** 421
[5] Abd Mohdy, H. L.; Hegazy, E. A.; Nesr, M.; Abd, E. M. *Journal of Polymer Research* 18 **(2011)** 1605
[6] Ali, P.; Bahareh, F.; Farzad, S. *Journal of Polymer Research* 16 **(2009)** 655
[7] Hedaoo, R. K.; Mahulikar, P. P.; Gite, V. V. *Polymer Plastic Technology and Engineering* 52 **(2013)** 243.

PB6

Benzyl ester of dehydrated castor oil fatty acid as plasticizer for PVC

Bhakti Mehta, Mukesh Kathalewar, Dr. Anagha Sabnis*
Department of Polymer & Surface Engineering, Institute of Chemical Technology,
Nathalal Parekh Marg, Matunga, Mumbai-400019, India.
** Dr. Anagha Sabnis: email: as.sabnis@ictmumbai.edu.in*

The polyvinyl chloride (PVC) industry plays an important role in today's total plastics industry. In most plastics producing countries, PVC is the leading plastic material[1]. The greater part of PVC is used as soft and plasticized PVC. PVC applications consume approximately 80% of the total production of plasticizers. Most of the common plasticizers are of aromatic esters of phthalic acid[3]. Since they are not chemically bonded to the polymer matrix, they can be released from materials while being used[2,6]. In majority of the countries phthalate plasticizer are banned because of its carcinogenic properties. The concern raised about toxicity led to a large demand of bio-based plasticizers which are non-toxic[4,5]. Hence, there is an increasing interest in replacing the phathalate plasticizers with esters that are produced from simple bio-based materials.

In this study, a modified natural plasticizer, was synthesized by esterification of dehydrated castor oil fatty acid (DCOFA) with benzyl alcohol in presence of catalyst (dibutyl tin di-laurate). The esterification reaction was carried out at 170-180 °C. The structure of the benzyl ester was confirmed by ^{1}H NMR, FTIR, acid value, hydroxyl value and SAP value. The modified plasticizer was blended with PVC and di-octyl phthalate in different proportions to make compressed sheets. The different properties of the sheets were evaluated by exudation and migration of plasticizers, hardness and yellowness index, mechanical testing (tensile and elongation etc.), X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Thermo-gravimetric analysis (TGA) and solvent resistance. The results obtained were compared with PVC-DOP blend.

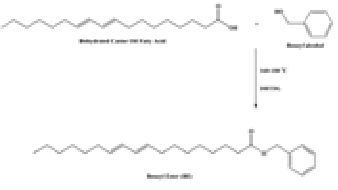


Figure 1: Schematic representation of synthesis of benzyl ester of DCOFA

References

[1] Rahman, M.; Brazel, C.S., *Progress in Polymer Science*, 29 **(2004)** 1223.
[2] Ekelund, M.; Azhdar, B.; Hedenqvist, M.; Gedde, U. *Polymer Degradation and Stability*, 93 (2008) 1704.
[3] Pielichowksi, K,.;.Swierz-Motysia, B. *Journal of Thermal Analysis and Calorimetry* 83 **(2006)** 207.
[4] Wilkison, C.F.; Lamb, J. *Regulatory Toxicology and Pharmacolgy,*30 **(1999)** 140.
[5] Tickner, J.A.; Schettler, T.; Guidotti, T.; McCally, M.; Rossi, M. *American Journal of Industrial Medicine*, 39 (**2001)** 100
[6] Adelia, F.F.M.; Mariana, A.S.; Mellisa, G.A.V.; Marisa, M.B. *Journal of Applied Polymer Science,* DOI: 10.1002/APP 37671.

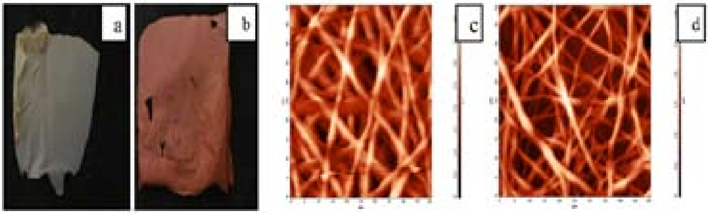
PB7

Fabrication of Electrospun Gelatin Nanofibers and Evaluation for Tuberculosis Drug Delivery

C. Selva Sukanya[a] and D. Ravi Shankaran[b]*
[a]*Department of Biomedical Engineering, PSG College of Technology,*
[b]*Nano-Bio Materials and Sensors Laboratory, PSG Institute of Advanced Studies,*
Coimbatore-641 004, INDIA
**drs@ias.psgtech.ac.in, dravishankaran@hotmail.com*

Gelatin is a biodegradable and biocompatible proteinaceous polymer utilised for various biomedical applications, primarily for drug delivery and tissue engineering. Nanofibers of gelatin have shown tremendous interest owing to the enhanced surface area required for biomedical applications. Electrospinning is one of the versatile methods for fabrication of nanofibers from various polymeric materials. The varying concentrations (10%, 12%, 15% and 20%) of gelatin in acetic acid were used and individually optimised. The electrospun fibers were characterised by optical microscope, atomic force microscope (AFM) and high resolution transmission electron microscope (HR-TEM). Gelatin nanofibers being water soluble, the mats were crosslinked with glutaraldehyde vapours make it hydrophobic to sustain degradation for a longer period of time [1].

Tuberculosis is a respiratory, communicable disease caused by Mycobacterium tuberculosis which can invade through various tissues and organs mainly lungs and bone. Higher quantities and frequent dosages are required to resist the growth of the TB microbes owing to its ability to survive unnoticeable to the immune system. In order to attain a reduction in the dosage frequency of the drugs, maintaining the same therapeutic index, the gelatin based biodegradable fibers were fabricated with embedded anti-tuberculosis combinatorial drugs, Rifampicin and Isoniazid. Owing to the fact that the fiber morphology determines the sustained release of the drugs, we have chosen Gelatin concentration of 15% w/v in this study. The drug embedded and pure gelatin fibers were further characterized by optical microscope and AFM. The release of drug from the crosslinked fibers was found to be slower and sustained compared to the naive fibers.



(a) & (c) Crosslinked pure gelatin fiber and AFM image
(b) & (d) Crosslinked drug embedded gelatin fiber and AFM image

Reference:

[1] Y.Z. Zhang, J. Venugopal, Z.-M. Huang, C.T. Lim, S. Ramakrishna, *Polymer,* Volume 27, Issue 8 **(2006),** 2911–2917

PB8

New Coordination Polymers for Protein Recognition

Rambabu Darsi, Abhimanew Dhir,* Chullikkattil P. Pradeep
School of Basic Sciences, Indian Institute of Technology, Mandi-175001,
Himachal Pradesh, India.
abhimanew@iitmandi.ac.in (*)

Co-ordination polymers are synthesized by organic linker which possesses donating groups (e.g. carboxylate) normally at both the ends with metal ion. They have wide variety of applications like gas storage, catalysis, adsorption, magnetism and sensors [1, 2]. However, their application in the field of biological sciences is still limited and need to be explored. Co-ordination polymers have a large surface area and may acquire hydrophobic and hydrophilic nature. Therefore, these surface properties of co-ordination polymers can be utilized for evaluating the recognition behavior toward different proteins. The protein adsorption on solid surfaces driven by different forces like van der Waals and hydrophobicity is a known phenomenon [3, 4].

Thus, with aim to develop new co-ordination polymers for protein recognition we designed, synthesized and characterized new fluorescent Cd(II) 3D coordination polymer $^{3}_{\infty}\{\mathrm{Cd\,(NDC)\,(QN)}\}$ utilizing 2,6 naphthalene dicarboxylate (NDC) and quinoline (QN) as ligands and cadmium as metal ion. Naphthalene and quinoline are utilized because of their fluorogenic nature. The Cd(II) ions are selected as they are good metal connector because of their high coordination affinity. The polymer has been fully characterized by single X-ray analysis. The recognition behavior of nano-dispersion of the synthesized polymer toward different proteins is in process. The details of the synthesis, characterization techniques and the recognition behavior analyzed will be presented in the symposium.

References

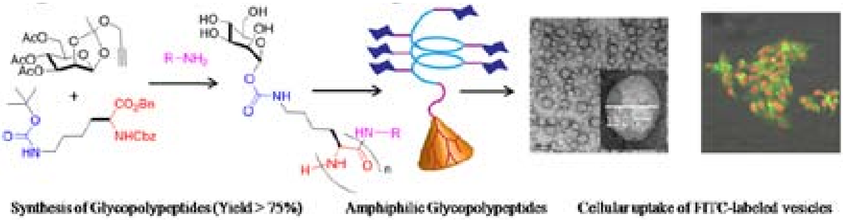
[1] Liu, Y.; Xuan, W.; Cui, Y.; *Adv. Mater.*, **2010**, 22, 4112.
[2] Natrajan, S.; Mandal, S.; *Angew. Chem. Int. Ed,* **2008**, 47, 4798.
[3] Tanford, C.; *The Hydrophobic Effect,* **1981** New York: Wiley.
[4] Porath, J.; *Pure Applied Chemistry*, **1979**, 51, 1549.

PB9

"Synthesis of Glycopolypeptides, Their Self-Assembly and It's Interaction with Lectins"

Debasis Pati, Soumen Das, Vinita Dhaware, Ashootosh Ambade and Sayam Sen Gupta*
Chemical Engineering Department, National Chemical Laboratory, Pune-411008.

Carbohydrates play a key role in a myriad of biological processes. In particular the saccharides that are conjugated to proteins, known as glycoproteins, are functionally very important in biology. In this regard glycopolymers, featuring synthetic macromolecules with pendant carbohydrate moieties, have found widespread biomedical applications. The glycopolypeptides (glycopolymers with pendant carbohydrates on a polypeptide backbone) mimic the molecular composition of proteoglycans and hence are expected to be biocompatible. During my work here at CSIR-NCL, we have developed a facile synthesis of high molecular weight water-soluble *O*-glycopolypeptide polymers by the ring-opening polymerization of their corresponding N-carboxyanhydride (NCA) in very high yield (overall yield > 70%) in three very high yielding steps[1]. The synthesized water-soluble glycopolypeptides were found to be α-helical in aqueous solution. We were also able to control the secondary conformation of the glycopolypeptides by polymerizing racemic amino acid glyco NCAs. The synthesized glycopoplypeptides were found to be polyvalent as was observed during binding studies with its corresponding lectin Con-A.[2] We then proceeded to develop these glycopolypeptides as vehicles for drug delivery in cancer cells. For 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 was synthesized as they could self-assemble into various nanostructures. We were the first to report synthetic glycopolypeptide-dendron conjugates that self-assembled into various nanostructures such as nanorods and micelles that displayed carbohydrates on their surface[3]. Our design of the highly anisotropic amphiphilic block copolymer architecture was based on a perfectly branched wedge-shaped hydrophobic dendron attached to a hydrophilic polypeptide chain with significant a-helical character displaying an ordered array of sugar residues. Finally, we have been able to synthesize amphiphilic glycopolypeptides from glycopolypeptides-polycaprolactone conjugates. The uniqueness of this amphiphilic polymer is that both the glycopolypeptide and caprolactone is expected to be biocompatible. We have shown that these nanostructures with multiple topologies such as vesicles, micelles and nanorods can be obtained upon self-assembly of these polymers with varying hydrophobicity/hydrophilicity. We have shown that vesicles made from glycopolypeptides having β-galactose in the side chain can enter specifically the liver cancer cell HepG2 by receptor mediated endocytosis using the over-expressed asialoglycoprotein receptor. We are currently evaluating these vesicles to deliver anti-cancer drugs into liver cancer cell[4].



Synthesis of Glycopolypeptides (Yield > 75%) Amphiphilic Glycopolypeptides Cellular uptake of FITC-labeled vesicles

Graphical Representation of glycopolypeptide self-assembled nano-structures for drug delivery

References:

[1] Pati, D. *et al. Polym. Chem.* **2011**, *2*, 805-811.
[2] Pati D. *et al. Biomacromolecules* **2012**, *13*, 1287-1295.
[3] Pati, D. *et al. J. Am. Chem. Soc.* **2012**, *134*, 7796-7802.
[4] Pati, D. *et al.* Manuscript under preparation.

PB10

Polyurethane-Graphene Nanohybrids for Biomedical Application

Dinesh Kumar Patel and Pralay Maiti
School of Materials Science and Technology, Indian Institute of Technology (B H U), Varanasi 221 005, India
Email:dineshbhud10@gmail.com

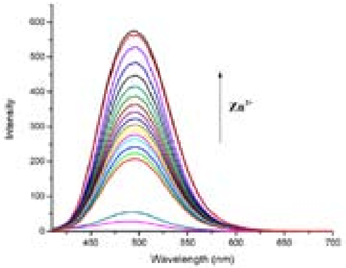
Polyurethanes have been synthesized using diol, diisocyanate and chain extender. Polyurethane/graphene nanohybrids were synthesized through in-situ polymerization technique. Nanohybrids of polyurethanes have been prepared using two dimensional graphene by dispersed it in diol followed by prepolymerization 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. Sustained drug release is obtained in nanohybrid leading to the use of the developed hybrid material for biomedical applications.

PB11

Pyridine appended pyrazoline based polymer fluorescent chemosensor for Zn(II) in aqueous solution

E. Hrishikesan and P. Kannan*
Department of Chemistry, Anna University, Chennai, India – 600 025.
Email: pakannan@annauniv.edu

Synthesis and polymerisation of pyrazoline derivative with pyridine ligand for metal detection . Structures of the synthesized compounds and polymer were confirmed using UV-Vis, FT-IR, ^{1}H-NMR, ^{13}C-NMR and ESI-Mass spectral data. Polymer was synthesized by simple addition polymersiation and its optical properties were studied by UV–Vis and fluorescence spectroscopies. The UV–Vis spectrum showed that the electronic transition bands of pyrazoline derivatives lied around at 320nm due to the $\pi \rightarrow \pi^*$ transition and emission around 500nm was observed. Upon addition of $Zn(ClO_4)_2.6H_2O$, the absorption maximum of the polymer **TPP** shifted to 355nm. However, no obvious spectral changes could be observed when other ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Ag^+, Al^{3+}, Mn^{2+}, and Cu^{2+}) were added, respectively. These results clearly suggested that the metal complexation of TPP show a great preference for Zinc (II) ion over other cations. The corresponding fluorescence spectra have been measured for the receptor's solution (10.0 mM) in the absence and presence of various metal ions. it can be seen that its intense emission peak at 460 nm upon addition of 100 equivalent of Zn^{2+} which may be ascribed to the suppression of PET effect in the pyrazoline moity.



References:
[1] Zhang. Z; Wang. F.; Wang. S.; Ge. F.; Zhao. B.; Miao. J.; *Org. Biomol. Chem.*, 10 (**2012**) 8640
[2] Ciupa. A.; Mahon. M. F.;. De Bank. P. A.; Caggiano. L.; *Org. Biomol. Chem.*10 (**2012**) 8753

PB12

Novel Castor Oil-Based Polyanhydrides for Biomedical Applications

Shruti Rattan[a], Janeni Natarajan[b], Giridhar Madras[c], Kaushik Chatterjee[a]
[a]Department of Materials Engineering
[b]Centre for Nano Science and Engineering
[c]Department of Chemical Engineering
Indian Institute of Science, Bangalore-560012 INDIA
** kchatterjee@materials.iisc.ernet.in*

We aim to develop novel biocompatible and biodegradable polymers that are derived from cheap and abundantly-available sources for use in drug delivery and tissue engineering applications. New castor oil-based biodegradable polyanhydrides were synthesized by catalyst-free and solvent-free melt-condensation reaction between prepolymers of Castor oil Maleate (COMApp) and Sebacic acid (SApp) with varying ratios (1:1, 1:2, 2:1, 4:1, and 1:4) (Fig 1).

The structures of the polymers were characterized by H^1-NMR and FT-IR which indicate the formation of the anhydride bond along the polymer backbone. The thermal properties of the polymers were analyzed using DSC and the crystalline nature of the polymers was confirmed by XRD. The molecular weight of the polymer was estimated by gel permeation chromatography (GPC). The contact angle measurements for the polymer with 1:1 ratio of the pre-polymers (67 °±2) show that the polymer surface is hydrophobic in nature. The mechanical properties of the polymer are being characterized using a dynamic mechanical analyser.

In vitro hydrolytic degradation was studied in PBS (pH= 7.4, 37 °C) by examining the weight loss, percentage anhydride loss and the surface morphology of the polymers. The effect of pH and volume of PBS on the degradation rate was also investigated. In vitro cell culture tests are currently underway to assess the cytotoxicity of the polymer. We are also studying the effect of changing the ratio of COMA and SA pre-polymers on the physical properties, degradation rates and biocompatibility.

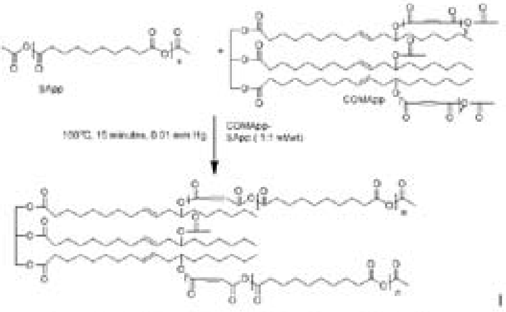


Figure 1: Reaction Schematic for synthesis for Castor Oil based polyanhydrides

Figure 1: Reaction Schematic for synthesis for Castor Oil based polyanhydrides

PB13

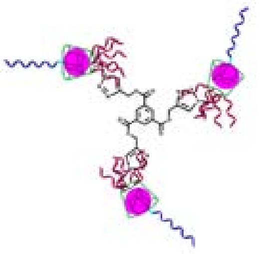
Trimerization of β–Cyclodextrin through Click Reaction and Synthesis of Its AB_6 type Mictoarm Star Polymer

Kanthikumar Tungala[a], P.Adhikary[b], S.Krishnamoorthi *

[a]*Research Scholar, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*

[b]*Young Scientist, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India.*

** Assistant Professor, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*



To improve the solubility of β–Cyclodextrin (β–CD), the investigation was done by its trimerization through click reaction, this could be very useful for drug solubility and encapsulation. Further, this trimer of β–CD was used to synthesize a new AB_6 type Mictoarm starpolymer based on star polymer of β–CD trimer - polyacrylamide (host) and Adamantane (AD) based polymeric guest.

For this purpose, the AD- polymeric guest was synthesized by reacting an AD-modified initiator through ATRP with methyl methacrylate (MMA). Then, this guest was treated with the star polymer based on β–CD trimer - polyacrylamide, which was prepared by the solution polymerization technique using $K_2S_2O_8$ as an initiator

References

[1] Huan, X.; Wang. D; Dong, R. Tu, C.; Zhu. B; Yan, D.; Zhu, X. *Macromolecules, 45,* (2012), 5941.
[2] Tang, B.; Liang, H.L.; Tong, L.L.; Li, P. *Bioorganic Medicinal Chemistry,* 14, (2006) 3947.

PB14

Synthesis of Polyglutamic Acid Dendrimer, Based on β-Cyclodextrin Core and Folic Acid Terminal

Krishna Kumar[a], P.Adhikary[b], S.Krishnamoorthi *
[a]*Research Scholar, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*
[b]*Young Scientist, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India.*
** Assistant Professor, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*

Dendrimers possess three distinct parts, each of which can be modulated: (i) a core, (ii) branching units and (iii) terminal branches. The synthesized dendrimers (β-CD-PGA-FA) possess a core of β-cyclodextrin[1], branching units were consecutively recapitulated by polglutamic acid (PGA) dendron by peptide linkage[2], and terminal branches attached by folic acid-NH_2 (FOL-NH_2) [3]. The dendrimer image is shown in fig. 1. A series of dendrimers were synthesized by varying the number of branching units. β-CD-PGA-FA comprises, hydrophobic cavity in central core, hydrophilic branching units of polyglutamic acid dendron, and terminal branches. The folic acid (FA) terminal may be useful as an anticancer drug receptor. The dendrimers were characterized by FT-IR, ^{1}HNMR and SEM.

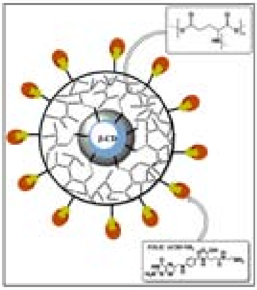


Figure 1 *- Dendrimer (β-CD-PGA-FA)*

References
[1] Li, J.; Sha, Y. *Molecules*, 13, (**2008**) 1111-1119.
[2] Choi, J. S.; Joo, D. K.; Kim, C. H.; Kim, K.; Park, J. S. *J. Am. Chem. Soc.*, 122, (**2000)** 474-480.
[3] Pan, J.; Feng, Si-S. Biomaterials, 29, (**2008**) 2663-2672.

PB15

Hemocompatible Hydroxyethyl Acrylate grafted Electrospun Poly (ethylene-vinyl alcohol) Fibers with Improved Hydrophilicity

Mayuri P.V. and Ramesh P.*
Polymer Processing Laboratary, Biomedical Technology wing
Sree Chitra Thirunal Institute for Medical Science and Technology, Thiruvananthapuram-695012
Kerala, INDIA
rameshsct@yahoo.com

Several approaches have been reported to improve the hydrophilicity of polymers such as coating, adsorption, plasma treatment, surface grafting polymerization etc[1]. Herein we adopt the method of surface grafting polymerisation in order to enhance the hydrophilicity of poly(ethylene-vinyl alcohol), a biostable polymer reported as a biomaterial with good biocompatibility and having functionalities for derivatization[2].

Hydrophilic monomer, 2-hydroxyethyl acrylate (HEA) was photografted, with the aid of photoinitiator benzophenone (BP), to the surface of poly(ethylene-vinyl alcohol) (EVAL) fibers [3], (fig.1) fabricated using the technique of electrospinning, a fascinating technique to generate polymeric fiboporous matrices, with controlled fiber diameters, either from polymer melts or from polymer solutions by the application of electric field[2].

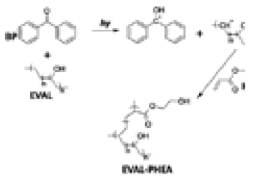


Figure 1. Mechanism of BP induced photografting of HEA to EVAL

Poly(ethylene-vinyl alcohol) was electrospun in i-propanol water mixture[2]. In order to facilitate a single step photografting, the monomer and initiator were fed into the polymer solution prior to electrospinning. The spun film were then UV treated to induce grafting. Homoplymer and unreacted components were washed off. The grafting was confirmed by the appearance and shifting of characteristic peaks in the FT-IR spectrum, shifting of the peak at 1725 cm^{-1} for the carbonyl stretch of homopolymer poly(2-hydroxyethyl acrylate) (PHEA) to 1735.6 cm^{-1} for the graft polymer. The peak at 1657.5 cm^{-1} in the electrospun initiator monomer loaded EVAL arising from a few vibrations including the carbonyl stretch of benzophenone initiator and the C=C stretch of monomer HEA, is disappearing after the grafting and subsequent washing, hence providing supporting evidence for grafting. Water contact angle of the polymers was decreased for grafted films indicating enhancement of hydrophilicity. Supporting evidences provided by improved wettability from the critical wetting surface tension values (CWST). The morphology of the grafted films were observed by scanning electron microscope. The static and dynamic mechanical properties were studied by universal testing machine and dynamic mechanical analyser respectively. All the grafted films were hemocompatible assessed by their haemolytic evaluation.

Acknowledgement : We acknowledge DST-INSPIRE, Govt. of India for providing the funding for the present study

References

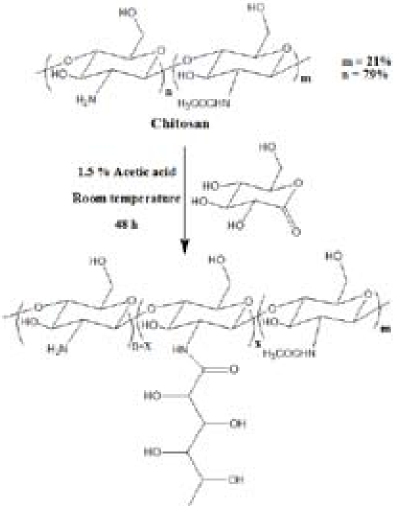
[1] Wang, Z.; Wan, L.; & Xu, Z. *Journal of Membrane Science,* 304 (**2007**) 8–23
[2] Kenawy, E.; Layman, J. M.; Watkins, J. R.; Bowlin, G. L.; Matthews, J. A.; Simpson, D. G. & Wnek, G. E. *Biomaterials*, 24 (**2003**) 907–913.
[3] Yang, C.; Cao, Y.; Sun, K.; Liu, J.; & Wang, H. *Applied Surface Science*, 257 (**2011**) 2978–2983.

PB16

Synthesis and Characterization of Galactosylated Chitosan

Niraj Kumar Vishwakarma[a], Tanu Gupta[a], Vijay Kumar Patel[a], Sumit Kumar Hira[b], Pradip Kumar Dutta[c], Partha Pratim Manna[b], and Biswajit Ray[a]*
[a] *Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi – 221005, India*
[b] *Department of Zoology, Faculty of Science, Banaras Hindu University, Varanasi – 221005, India*
[c] *Department of Chemistry, M N National Institute of Technology, Allahabad - 211004*
*Correspondence to: B. Ray (E-mail: biswajitray2003@yahoo.co.in)

Galactosylated chitosan has successfully been synthesized by simply reacting chitosan (79% deacetylated) with D-gluconolactone (1:1) molar in 1.5% (v/v) acetic acid solution at room temperature for 48 h. Resultant reaction mixture has been purified by dialysis against distilled water. Purified product has been characterized by FTIR, solid state NMR, TGA, and DSC. The product has also been explored as matrix for drug delivery.



References

[1] Duan, B.; Dong, C. H.; Yuan, X. Y.; Yao, K. D. *J. Biomater. Sci., Polym. Ed.*, 15 **(2004)** 797.
[2] Chung, T. W.; Yang, J.; Akaike, T.; Cho, K. Y.; Nah, J. W.; Kim, S.; Cho, C. S. *Biomaterials,* 23 **(2002)** 2827.
[3] Giacalone, G.; Bochot A.; Fattal, E.; Hillaireau, H. *Biomacromolecules*, DOI bm301832v.
[4] Jain N. K.; Jain S. K. *AAPS PharmSciTech,* 11 **(2010)** 686.

PB17

Functionalization of Bamboo and Sisal Fibres Cellulose in Ionic Liquids

N. L. Bhandari [1], W. Mormann [2], G. H. Michler [3], R. Adhikari [1]
[1] Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal
[2] Department of Macromolecular Chemistry, University of Siegen, Siegen, Germany
3 Institute for Physics, Martin Luther University Halle-Wittenberg, Halle/Saale, Germany
E mail: nlbhanadari@yahoo.com, nepalpolymer@yahoo.com

The aim of this work is to study the morphological changes after alkali treatment and functionalization of cellulosic materials present in crude bamboo and sisal flours using ionic liquid as solvents. The flours of bamboo (BF) and sisal (SF) were subjected to acetylation and silylation using acetic anhydride (AA) and hexamethyldisilazane (HMDS) as reagents. The changes in fibres structure and morphology were studied by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM), respectively. The results indicate that crude BF and SF are functionalized successfully which is confirmed by FTIR spectra and the solubility of the derivatives in different solvents. The microscopic structures of the cellulose microfiber bundles become more distinct after delignification

PB18

Thiolated Chitosan Immobilized/Methionine Modified Montmorillonite as a Drug Carrier for the Controlled Release of a β- Adrenergic Blocking Agent

* T. S. Anirudhan*, J. Parvathy , Sheeba Alexander
Department of Chemistry, University of Kerala, Kariavattom, Trivandrum-695 581, India
infrared_pj@yahoo.co.in

Polymeric materials have been used for wide range of applications in the modern medicine, as much of them are biocompatible with blood, tissues, cells, i.e., in the human body. The actual tendency is focussed on the development of materials that are assimilated by the organism producing minimum collateral effects. A polysaacharide Chitosan (CS), obtained by the alkaline deacetylation of chitin derived from the exoskeleton of marine crustaceans has emerged as a useful drug delivery matrix owing to its polycationic nature, biodegradability, biocompatibility and mucoadhesiveness. The chemical modification of CS by conjugating various functional groups allow the control of hydrophilicity and solubility at neutral and basic pH, thereby opening new oppurtunities to expand the application of this biopolymer. Thiolated CS (TCS) constitute an integral part of designated "thiomers", which show various promising properties such as mucoadheshion, efflux pump inhibition, *in situ* gelling capacity and controlled drug release. These novel polymers are capable of forming covalent bonds with the mucus forming constituents in contrast to unmodified CS.

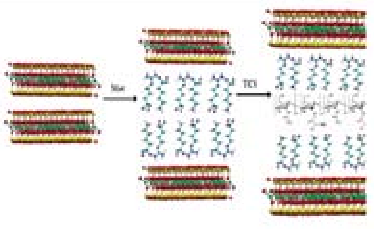


Figure 1. Preparation of TCS/Met-MMT

Montmorillonite (MMT), a potent detoxifier, which belongs to the structural family known as the 2:1 phyllosilicate, widely used for the preparation of drug carrier matrix, can provide mucoadhesive capability for the nanoparticle to cross the GI barrier. MMT could absorb dietary toxins, bacterial toxins associated with gastrointestinal disturbance, hydrogen ions in acidosis and metabolic toxins such as steroidal metabolites associated with pregnancy [1]. Pillaring of layered silicates widens their application possibilities, since the layers remain propped open even after removing the solvent that assures the swollen state of the unpillared layered silicate while it is present [2]. Among the various natural resources that can be easily obtained, amino acids are highly promising and are readily available from natural resources. The use of naturally occurring amino acids in these hybrids, forming organically modified clay increases the biocompatibility of such system and allows interactions with biological systems, which are advantageous for bioresorable sutures, screws or plates, tissue engineering scaffolds, and drug delivery systems [3].

In the present work, we prepared Thiolated Chitosan(TCS) immobilized – aminoacid, Methionine modified montmorillonite(Met-MMT) as a drug carrier vehicle for the controlled release of Timolol maleate, a β -adrenergic blocking agent which is effective against hypertension, arrhythmias, and angina pectoris, as well as for the secondary prevention of myocardial infarction . The different stages of the preparation of drug carrier vehicle were characterized using FT-IR, XRD, Thermal analysis techniques and the effects of pH on drug loading, swelling studies and controlled release were studied. The release profile depicts the controlled release of the drug in the basic medium than in the acidic medium.

References

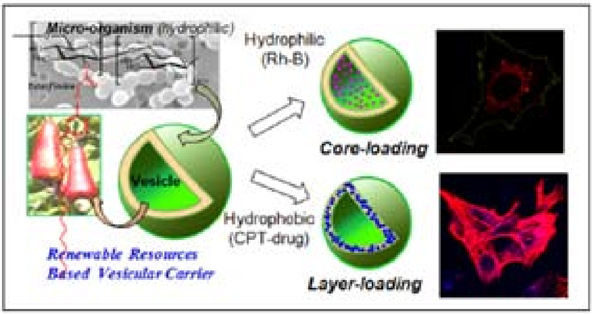
[1] Nanda, R.; Sasmal. A; Nayak, P.L. *Carbohydrate Polymers*, 83 (**2011**) 988.
[2] Turkdemir, M.H. ; Erdögdu. G ; Aydemir, T. *Journal of Analytical Chemistry*, 56 (**2001**) 1047.
[3] Marchal-Heussler, L.; Colling. N; Benoit, E. *Pharmaceutical Research*, 17 (**2000**) 1144.

PB19

Polysaccharide Vesicular Nano carrier for Encapsulation and Delivery of Anticancer Drugs

Pramod P.S.[1],Nagaraj Balasubramanian[2] and M. Jayakannan*[1]
[1]*Department of Chemistry and Department of Biology*
Indian Institute of Science Education & Research (IISER-Pune)
Dr.Homi Bhabha Road, Pune 411008, Maharashtra, INDIA

In the last two decades stimuli responsive polymeric vesicles (polymersome), have attracted rapidly growing interest based on their cell and virus mimicking dimension and potential application in the delivery of anticancer drugs to tumor tissues [1]. The present work is emphasized to design dextran vesicular carriers using renewable resources based on cardanol, pentadecylphenol (PDP) and commercially available stearic acid as hydrophobic tails.[2] The role of the hydrophobic segments on the molecular self-organization of dextran into vesicular assemblies or nanoparticles were investigated using saturated and partially unsaturated units. The vesicular structure of the amphiphiles was confirmed by TEM, SEM, 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. The protection of active lactone form of CPT in the vesicular structure was proved using HPLC technique. The *in vitro* drug release experiments conducted at pH 7.4 PBS at 37° C revealed that Rh-B and CPT got released in a controlled manner. The aliphatic ester linkage connecting the hydrophobic tail with dextran was found susceptible to cleave by esterase under physiological conditions for fast releasing of CPT or Rh-B. Confocal microscopic images confirmed that both Rh-B and CPT-loaded vesicles (better than CPT alone) were taken up by fibrobalsts, showing a perinuclear localization in cells. CPT loaded vesicles were found to be 2.5 fold more effective in killing fibroblasts compared to that of CPT alone in PBS. The responsiveness of this DEX-PDP system was further chemically tuned to exploit the acidic pH environment of tumor. Dextran and PDP linked via benzylic imine linkage were also self organized to form vesicular carrier and showed pH sensitive release of encapsulated molecules. The custom designed dextran vesicular nanocarrier provides new research opportunities for dual drug delivery into tumor cells.



References:

[1] Davis, M.E.*et al*; Nature Reviews Drug discovery. **2008**, 7,771.
[2] Pramod, P.S.; Takamura, K.; Chaphekar, S.; Balasubramanian, N.; Jayakannan, M.; *Biomacromolecules*, **2012**, *13,* 3627-3640.

PB20

Highly Sensitive Fluorescent Chemosensor for the Detection of Zn^{2+} using a Rhodamine B Spirolactam

R. Manjunath and P. Kannan*
Department of Chemistry, Anna University,
Chennai-600025 INDIA

A highly sensitive rhodamine based fluorescent chemosensor for Zn^{2+} was synthesized. The new fluorescent sensor an extreme selectivity for Zn^{2+} over other transition metal ions examined in the aqueous medium. The structures of synthesized compounds were confirmed by using ^{1}H-NMR, ^{13}C-NMR, IR, UV-Vis spectrometer and ESI-mass spectral data and its optical properties were studied by UV-Visible and fluorescence spectroscopy.

Chemosensing behavior of the synthesized polymer were tested with various metal ions such as Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Li^{+}, K^{+}, Mg^{2+}, Na^{+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Pb^{2+} in aqueous solution and also examined by absorption and fluorescence spectroscopy. From the absorbance the polymer shows the significant changes with Zn^{2+} ion having absorbance around 560nm. The UV-Visible characteristics of the non-complexed polymer showed absorption around 450nm due to the existence of the spiro ring in lactam form. Upon the interaction with Zn^{2+} ions an intense absorption band centered at 565nm (λ_{max}) appeared exclusively with Zn^{2+} ions due to the ring opening of rhodamine dye. Approximatly 20 fold enhancement in the fluorescence intensity around at 560nm was estimated.

References:

[1] G.H. Wu, D. X. Wang, D. Y. Wu, Y. Gao, Z. Q. Wang, J. Chem. Sci, 2009, 121, 543-548
[2] R. Tang, K. Lei, K. Chen, H. Zhao, J. Chen, J. Fluoresc, 2011, 21, 141-148
[3] J.Huang, Y.Xu, X.Qian, J. Org. Chem. 2009, 74, 2167-2170
[4] M.Suresh, A. Shrivastav, S. Mishra, E.Suresh, A.Das, Org. Lett., Vol. 10, No. 14, 2008

PB21

Microencapsulation and release study of Neem Seed Oil as an insecticide with Melamine-Urea-Formaldehyde Polymer Shell

Avinash V. Bagle, Rahul K. Hedaoo, Vikas V. Gite, Dilip G. Hundiwale and Pramod P. Mahulikar
Department of Industrial Chemistry and Polymer Chemistry, School of Chemical Sciences,
North Maharashtra University, Jalgaon-425 001 INDIA

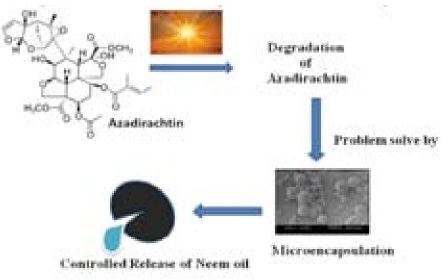


Figure 1. Overview for encapsulation

Microencapsulated pesticides are safer and convenient to handle and hence reduce environmental and mammalian toxicity. Therefore the prolong effect of encapsulated active ingredient (*a. i.*) is observed due to its regulated supply [1-6]. Melamine-Urea-Formaldehyde (MUF) polymer is used as shell material for the encapsulation of Neem seed oil, a well-known green insecticide. The process of microencapsulation was developed through *in-situ* polymerization using oil-in-water emulsion system [7]. Synthesized MUF microcapsules containing Neem seed oil were characterized by SEM analysis were considered for surface morphological studies as well particle size analysis for size distribution. The controlled release of neem seed oil was studied using UV-Visible absorption spectral response as probe. Neem seed oil, a green insecticide was successfully microencapsulated with Melamine-Urea-Formaldehyde (MUF) to fulfill the requirement of controlled release of Neem seed oil as an active ingredient (fig.1).

References:

[1] Jose, I.; Esmeralda, M.; Celia, M.; Juan, M. G. *Pest Management Science* 57 (**2001)** 688
[2] Manuel, F. N. *Journal Environmental Sciences and Health Part B* 42 **(2007)** 857
[3] Gunanand, C.; Jitendra, K.; Suresh, W.; Rajender, P.; Balraj, S. P. *Journal of Agricultural and Food Chemistry* 54 **(2006)** 4727
[4] Bagle, A.V.; Jadhav, R. S.; Gite, V. V.; Hundiwale, D. G.; Mahulikar, P. P. *International Journal of Polymeric Materials and Polymeric Biomaterials* 62 **(2013)** 421
[5] Abd Mohdy, H. L.; Hegazy, E. A.; Nesr, M.; Abd, E. M. *Journal of Polymer Research* 18 **(2011)** 1605
[6] Ali, P.; Bahareh, F.; Farzad, S. *Journal of Polymer Research* 16 **(2009)** 655
[7] Hedaoo, R. K.; Mahulikar, P. P.; Gite, V. V. *Polymer Plastic Technology and Engineering* 52 **(2013)** 243.

PB22

Smart Delivery of a Metallodrug to Tumors using Macromolecular Vehicles

Raja Mitra[a], Abhishek Ganguly[b], Sridevi V. Shinde[b], Duraippandi P.[a], K. Somasundaram[b]*, S. Ramakrishnan[a]* and A.G. Samuelson[a]*
[a]Department of Inorganic & Physical Chemistry, [b]Department of Microbiology & Cell Biology, Indian Institute of Science, Bangalore-560012, India
skumar@mcbl.iisc.ernet.in, raman@ipc.iisc.ernet.in, ashoka@ipc.iisc.ernet.in

Anticancer active metal complexes such as cisplatin are routinely used for treating cancer since 1983. However the side effects of cisplatin overwhelm its therapeutic potential to a great extent especially in the latter stages of treatment. The nonspecific cytotoxicity of cisplatin could be avoided if targeted delivery to cancer cells is achieved [1]. Several delivery vehicles for effective, site specific delivery of drugs are being sought after. Among them, macromolecules such as dendrimers and polymers have received pride of place due to several advantageous properties [2,3,4].

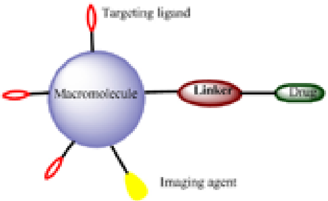


Fig 1: Schematic of a 'smart' macromolecular drug

We have functionalized PAMAM dendrimers with either folic acid or biotin for targeting and an imaging agent to test targeted drug delivery (Fig 1). A copper based drug [5] was also covalently attached to the functionalized G4 PAMAM dendrimer by a cleavable disulfide linker which enables the conjugates to release the drug in a controlled manner. Targeting efficacy of the dendrimer conjugates was checked against two glioma (brain tumor) cell lines. The ability of the conjugates and the copper complex to cross the blood brain barrier in mice was also estimated.

We have now extended this methodology to hyperbranched polymers (*hybramers*) decorated with propargyl groups in the periphery [6]. To make the *hybramers* more biocompatible, hydroplilic OH terminated TEG groups were attached to the hybramers through 'click' reactions. Subsequently a targeting group and a copper drug were attached to the *hybramer* using a 'click' reaction. Results from these studies will be presented.

References:

[1] Sawyers, C.; *Nature* **2004**, *432*, 294-297
[2] Dhar, S.; Gu, F.; Langer R.; Farokhzad O. C.; Lippard S. J.; *Proc. Natl. Acad. Sci. U S A.* **2008**, *105*, 17356–17361
[3] Baker, J. R. Jr.; *Nanotechnology for Hematology* **2009,** 708-719
[4] Aryal, S.; Hu, Che-M. J.; Zhang, L; *ACS Nano* **2010,** *4*, 251-258
[5] Palanimuthu, D.; Shinde, S. V.; Somasundaram, K.; Samuelson, A. G.; *J. Med. Chem.* **2013**, *56*, 722–734
[6] Ramkumar, S. G.; Amala Rose, K. A.; Ramakrishnan, S. *J. Polym. Sci. Chem. Ed.* **2010**, *48*, 3200.

PB23

Cervical cancer and its treatment; using a nanotransporter for anticancer drug delivery

Rajasegaran Elumalai[1], Shilpa Patil[2], Rajendra Kurapati[1], Paturu Kondaiah[2], Ashok M Raichur[1]*
[1]Biomaterials lab, Dept. of Materials Engineering, IISc, Bangalore
[2]Dept. of Molecular Reproduction, Development and Genetics, IISc, Bangalore.
Emai: amr@materials.iisc.ernet.in

The body is made up of trillions of living cells. Normal body cells grow, divide, and die in an orderly fashion but cancer cell growth is different from normal cells. Instead of dying, cancer cells continue to grow and form abnormal cells. Cancer begins when cells in a part of the body start to grow out of control. Cervical cancer is cancer that starts in the cervix (lower part of the uterus) by human papilloma virus. Worldwide, it is the third common type of cancer in women spread through sexual intercourse. In this study, we reported that using nanotransporter (biodegradable polyelectrolytes nanocapsules) for anticancer drug (doxorubicin) deliver into cervical cancer cells. The nanotransporters are polymeric nanocapsules were made by layer by layer deposition of two biodegradable polyelectrolytes called chitosan and dextran on silica nanoparticles. In post deposition, the nanoparticles were leached out by hydrofluoric acid to produce nanocapsules which were utilized for drug encapsulation studies. These nanotransporters are nontoxic, can dismantle by cellular enzymes in the biological systems.

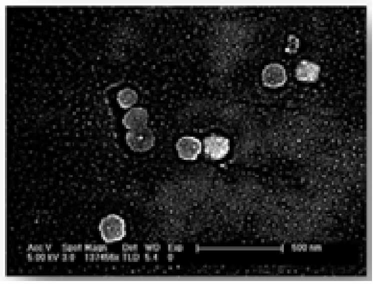


Fig 1. SEM characterization of nanotransporter (Polymeric hollow nanocapsules for drug delivery).

PB24

Graphene Oxide/Polymer Composite Layer-by-Layer Self-Assembled Multilayer Capsules: Multidrug Delivery and Light-Responsive Drug Release Applications

Rajendra Kurapati and Ashok M Raichur*
[1]Biomaterials lab, Dept. of Materials Engineering, IISc, Bangalore
[2]Dept. of Molecular Reproduction, Development and Genetics, IISc, Bangalore.
Emai: amr@materials.iisc.ernet.in

Graphene, a one-atom-thick two-dimensional (2D) layer of sp^2-bonded carbon, has received worldwide attention owing to its extraordinary physical and chemical properties. Recently, great efforts have been devoted to explore potential applications of graphene and its oxidized form, grapheme oxide (GO) in life science, especially in disease-related diagnostics, near-Infrared (NIR) phototherapy and imaging. By the combination of excellent properties of 2-dimensional GOin the layer-by-layer (LbL) self-assembly with other polyelectrolytes can generate a novel research area for biomedical applications. Here, we have developed novel composite graphene oxide (GO) and poly(allylamine hydrochloride) (PAH) multilayer capsules have been fabricated by LbLtechnique. The grapheme composite hollow capsules were found to possess unique permeability properties for various dyes and drugs compared to traditional LbL capsules. Especially, these hybrid capsules showed special "core–shell" loading property for encapsulation of dual drugs simultaneously into the core and shell of the capsules respectively.

In second part, a novel and simple route for near-infrared (NIR)-light controlled release od drugs from GO composite capsules has been demonstrated based on extraordinary optical properties of graphene oxide (GO) without addition of any external additives such as gold nanoparticles or carbon nanotubes in the shells of the capsules. Here, GO plays a dual role, serve as a structural component of the capsules as well as a strong NIR-light absorbing agent. Upon NIR-laser irradiation, the microcapsules were ruptured in a point-wise fashion due to local heatingphenomenon caused by irradiation of the GO by NIR-laser(1064 nm). Finally, we havesuccessfully demonstrated that GO composite capsules can be used to triggered to release the encapsulated real anticancer drug doxorubicin by the irradiation of 1064 nm pulsed laser.

References:

[1] **Rajendra Kurapati** and Ashok M Raichur, ***Chem. Commun.***,2012, *48* (48), 6013-6015.
[2] **Rajendra Kurapati** and Ashok M Raichur, ***Chem. Commun.***, 2013, 49, 734-736.

PB25

Effect of γ- and Electron Beam Irradiation on Polylactic Acid

N. Rajeswara Rao[a*], T. Venkatappa Rao[a], S.V.S. Ramana Reddy[a] and B. Sanjeeva Rao[b]
[a]*Department of Physics, National Institute of Technology, Warangal-506004, India.*
[b]*Department of Physics, Kakatiya Govt. Degree & PG College, Hanmakonda, Warangal, India.*
Email i.d: rajeshn9@gmail.com

Polylactic acid (PLA) is a biodegradable thermo-plastic material, and it is a replacement for many engineering plastics. Stability of PLA is reported to be enhanced by treating the polymer with γ-rays and electron beam (EB) [1]. By adding nucleating agents, complex formation taken place between PLLA and PDLA; causing an increase in melting point to 230°C [2]. Milicevic et al [3] have reported that gamma irradiation effects on PLA by differential scanning calorimeter (DSC) and scanning electron microscope (SEM) techniques. The glass transition temperature (T_g), melting point (T_m) and degree of crystalinity (X_c) were reported to decrease with increase of radiation dose.

In the present studies the authors attempt to study gamma as well as EB irradiation effects in PLA. PLA is in the form of granules used in the present study, which is of commercial origin. Electron spin resonance (ESR) spectra of irradiated PLA are recorded on Varian E line spectrometer operating at 9.1 GHz and 100 kHz modulation. γ -irradiation was carried out by ^{60}Co source with a dose rate of 0.15 Mrad/hr in air at room temperature. EB irradiation was carried out by electron beam accelerator which is ILU-6 type, pulse linear accelerator and can be operated up to energy 2 MeV and 20 kW power at BRIT, Mumbai delivering a dose rate of 0.5 Mrad/pass in air at room temperature.

The ESR spectrum observed for both the case was a doublet of quartet. The spectrum was assigned to radicals created by abstraction of methine group from the backbone having structure (I) & (II) [4]. The hyperfine coupling constants are 23 G and 10 G respectively.

PLA posses various X-ray diffraction (XRD) peaks at positions of 2θ= 16.45°, 18.47°, 29.04° and 31.04°. Differential scanning calorimeter (DSC) of PLA indicate two peaks at 61°C and 148°C, which were assigned to glass transition temperature (T_g) and melting point (T_m) of PLA respectively. On irradiation the T_g is lowered with the increase of irradiation dose; while T_m increase initially and later attain original value.

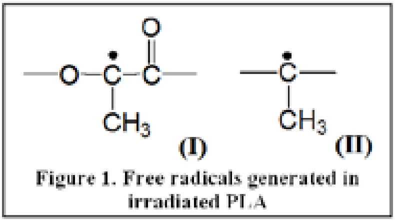


Figure 1. Free radicals generated in irradiated PLA

References

[1] Suhartini, M.; Mitomo, H.; Nagasawa, N.; Yoshii, F. J. App. Polym. Sci. 88 (2003) 2238.
[2] Tsuji, H.; Hyon, S.H.; Ikada, Y. Macromol. 24 (1991) 5651.
[3] Milicevic, D.; Trifunovic, S.; Galovic, S.; Suljovrujic, E. Rad. Phys. & Chem. 76 (2000) 1376.
[4] Babanalbandi, A.; Hill, D.J.T.; O'Donnell, J.H.; Pomery, P.J.; Whittaker, A. Polym. Degrad. & Stab. 50 (1995) 207.

PB26

In-vitro Degradation Behaviour of Electrospun Polycaprolactone/ Polyethyleneoxide Blends for Tissue Engineering Applications

K.R. Remya and P. Ramesh*
Polymer Processing Laboratory, Bio Medical Technology Wing
Sree Chitra Tirunal Institute for Medical Sciences & Technology
Thiruvananthapuram, Kerala-695012
rameshsct@yahoo.com

Degradation behavior of polymers is significant while designing scaffolds for tissue engineering applications [1]. Electrospun biodegradable polymeric nanofibers have become an attractive candidate for tissue engineering due to their biomimetic structure which physically resembles the native extracellular matrix (ECM) [2].

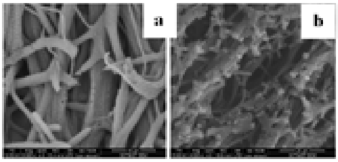


Figure 1. Morphology of PCL/PEO (50/50) blends after (a) 1 month (b) 3 month

In the present study, blends based on polycaporlactone (PCL), a slow degrading polymer and polyethyleneoxide (PEO) a water soluble polymer were fabricated by electrospinning technique. The effect of PEO content on the fibre morphology, surface hydrophilicity and static as well as dynamic mechanical was evaluated using scanning electron microscopy, goniometer, universal testing machine and dynamic mechanical analyzer .The stability of PEO in the blend system was further confirmed by differential scanning calorimeter and dynamic mechanical analyzer at different time period. *In-vitro* degradation of PCL/PEO blends was monitored by observing the changes in mass loss, fiber morphology and mechanical properties, for a period 6 months in phosphate-buffered saline (PBS, pH 7.4) at 37^{o}C.

Results revealed that the introduction of PEO changed the hydrophilic/hydrophobic balance and, influenced the degradation behaviour indicated by the fibre rupture as well as significant drop in mechanical properties. The potential of the fabricated scaffold to be used for biomedical applications was further evaluated by *in-vitro* cytotoxicity evaluation using direct contact and MTT assay.

References

[1] Spagnuolo, M.; Liu, L. ISRN Nanotechnology, (2012)
[2] Zander, N.E.; Polymers , 5 (2013)19

PB27

Urease Immobilized Polymer Hydrogel: Long-term Stability and Enhancement of Enzymatic Activity in Ambient Condition

S N Raju Kutcherlapati, Niranjan Yeole, Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad-500 046, India
Email: tjscuoh@gmail.com

Many enzymes display very poor stability and completely loss of enzymatic activity in ambient condition (room temperature) since the native protein structure undergoes into deactivated state. As a result enzymes uses in biomedical and biotechnological applications [1] are often limited to storage conditions; always ambient temperature is preferable for storage. Therefore, development of a simple and robust method for long term stability of enzymes in ambient condition is a challenging task and successful implementation will have immense effect on the widespread use of enzymes. Although several attempts have been made in the past, however, most often either methods are quite complex or enzymatic activity gradually decreases with storage time [2-3]. Recently, we have developed enzyme immobilized polymer hydrogel to address the above mentioned issues.

In the present work, the enzyme urease from Jack bean (*Canavalia ensiformis*) is used as a model and has been immobilized in poly(acrylamide-bis-acrylamide) hydrogel matrix, The amount of covalently attached urease in the polymer backbone is estimated by recording the absorbance of urease (at 280nm) in the immobilized hydrogel. The Berthelot reaction is used to study the urease-urea hydrolysis kinetics. The enzymatic activities of immobilized and free enzyme [42 days in immobilized state (UCG) and 19 days in free state] are calculated and compared by observing catalytic constant (K_2), Michaelis Menten constant (Km) and catalytic efficiency (ε) of urease with time at room temperature in 0.1M phosphate buffer saline (PBS) using 150mM sodium chloride. Enzymatic activity of immobilized urease is increasing where as in free state it is decreasing with time. This unexpected stability and activity further confirmed by the thermal and microscopy studies (fig 1 & 2). This enhanced activity can be explained probably by the larger total internal interface which is created after immobilization within hydrogel matrix.

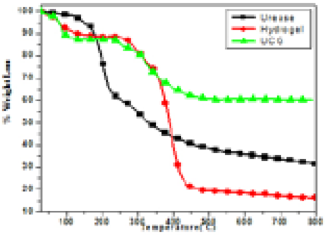


Figure 1. TGA curves of urease, hydrogel, urease coupled hydrogel

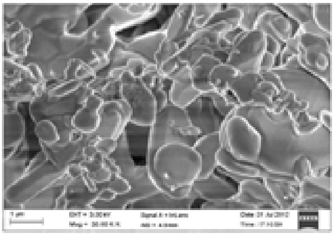


Figure 2. FESEM image of urease coupled hydrogel

Acknowledgement: We gratefully acknowledge financial support by CSIR, India.

References

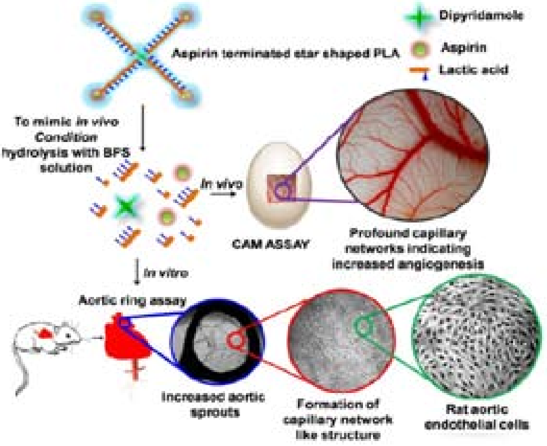
[1] Liang, J. F.; Li, Y. T.; Yang, V. C. *J. Pharm. Sci.,* 89 (**2000**) 979.
[2] Gurel, I. *Tr. J. of Chemistry,* 21 (**1997**) 387.
[3] Gabrovska, K.; Ivanov, J.; Vasileva, I.; Dimova, N.; Godjevargova. *Int. J. Biol. Macromol.*, 48 (**2011**) 620.
[4] Kutcherlapati, S. N. R.; Yeole, N.; Jana, T. (manuscript under preparation).

PB28

Bio-absorbable Star Shaped Polylactic Acid with the potential of angiogenesis

S Nagarajan[a,*], M S Kiran[b], and B S R Reddy[b]
a Materials Science and Technology Division, National Institute for Interdisciplinary Science & Technology (NIIST-CSIR), Thiruvanathapuram-695019, India.
b Industrial Chemistry Laboratory, Central Leather Research Institute, Chennai-600020, India.
E.mail: nagarajan.tech@gmail.com

To monitor the bio-absorbable polymer in the implants and to reduce the complexity, new hyperbranched star shaped polymers were developed with the synergetic combination of bio-absorbability and fluorescent characteristics. These hyperbranched polymers were synthesized using two different methods: (i) Arm first method (AFM)[1] and (ii) Core first method (CFM)[2]. This kind of advanced fluorescent specific bioabsorbable polymers are in high demand due to several advantages in replacing traditional materials for implants. Here, we have reported the molecular arrangement of the hyperbranched polymers with respect to the fluorescent behaviour and the feasibility of the material to analyze *in vitro* condition. The developed materials are potentially suitable for angiogenesis potentiality.



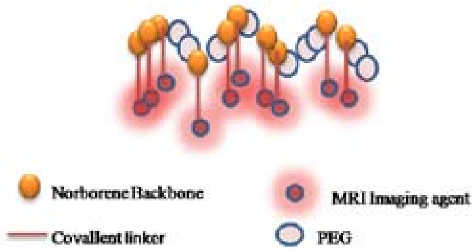
References:
[1] Nagarajan, S.; Reddy. BSR; Tsibouklis, J. European Polymer Journal, 48 (**2012**) 1357.
[2] Nagarajan S.; Reddy BSR; Patent-3888DEL2012.

PB29

Norbornene Based Magnetic Copolymers for Imaging Applications

Saikat Mukherjee, 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) is a powerful non-invasive diagnostic imaging modality that can provide high quality anatomic images and other physiologic data .Well-defined 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 nanocomposites are evaluated with DLS, TEM and AFM. The cobalt complex functionalization to the polymer is monitored by FTIR. 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 magnetic resonance imaging (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.;
[3] Gazeau, F.; Cabuil, V.; Lesieur, S. J. Am. Chem. Soc. 2005, 127, 10676–10685.

PB30

Glycolic Acid Grafted Chitosan–Au–Fe$_3$O$_4$ Hybrid Nanoparticle Based Nanohybrid Scaffold for Drug Delivery and Tissue Engineering Applications

Sangeeta Kumari[a], Nayaku Chavan[a] and Raj Pal Singh[b*]
[a] *Division of Polymer Science and Engineering, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411 008, Maharashtra, India*
[b,*] *Advanced Research Centre in Pharmaceutical Sciences & Applied Chemistry,*
Bharati Vidyapeeth University, Erandawane, Pune-411038. Maharashtra, India
Tel.: +91-20-25437237, Fax: +91-20-25437237
E-mail : rp.singh.ncl@gmail.com

Advances in nanotechnology play an important role in designing nanomaterials with specific functional properties that can address the shortcomings in the area of diagnostics and therapeutics. The hybrid nanostructures are desirable for many application like sustained drug delivery [1], biological and chemical sensing. A wide range of materials have been employed as drug carriers such as surfactant, dendrimers and natural or synthetic polymers [2]. Among these, polysaccharides have received increasing interest because of their outstanding physical and biological properties [3]. The research on biomedical applications of nanoparticles has seen an upsurge in recent years due to their unique capabilities in treatment of ailments. This work reports the synthesis of Au–Fe3O4 hybrid nanoparticles. The formation of these nanoparticles was confirmed by transmission electron microscopy (TEM) and physical property measurement system (PPMS). Next step of this paper reveals potential use of novel hybrid of chitosan-g-glycolic acid and Au–Fe3O4 hybrid nanoparticles in controlled drug delivery and tissue engineering applications. Grafting of glycolic acid and drug loading in porous scaffold was characterized by Fourier transform infrared spectroscopy.

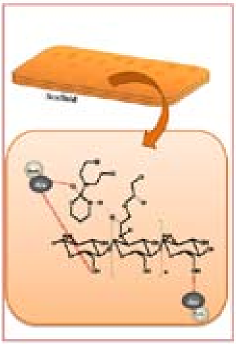


Figure 1. Grafting of glycolic acid on chitosan, formation of CS-g-GA and preparation of chitosan-g-glycolic and Au/ Fe3O4 nanoparticle nano-composite

The nanohybrid scaffolds (fig.1) were found to be stable regardless of pH of the medium and play a key role in cell adhesion, proliferation and migration. Au–Fe3O4 hybrid nanoparticles reinforcement was found to control the drug (cyclophosphamide) release rate in phosphate buffer saline solution (pH 7.4). Therefore, Au–Fe3O4 hybrid nanoparticles are viable additive for formulating sustained drug delivery systems based on glycolic acid grafted chitosan. The cell proliferation profile also shows that prepared nanohybrid is biocompatible providing suitable substrates for tissue engineering.

References

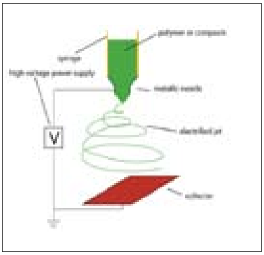
[1] Cheng, H.; Kastrup, C.J.; Ramanathan, R.; Siegwart, D.J.; Ma,
[2] M.; Bogatyrev, S.R.; Xu, Q.; Whitehead, K.A.; Langer, R.;
[3] Anderson, D.G. *ACS Nano,* 4 **(2010)** 625.
[4] Duncan, R. *Nature Reviews Drug Discovery,* 2 **(2003)** 347.
[5] Liu, Z.; Jiao, Y.; Wang, Y.; Zhou, C.; Zhang, Z. *Advanced*
[6] Drug Delivery Reviews, 60 **(2008)** 1650.

PB31

Synthesis of Bioresorbable Silica Nanofiber for Biomedical Precursor

Sanjeev K. Jat, Rama R. Bhattacharjee*
Nanotech Research Facility, PSG Institute of Advanced Studie, Coimbatore 641004, Tamilnadu, India.
** Rama R Bhattacharjee (Ph.D) ramaranjanb89@gmail.com.*

Pure silica gel is well known for their entraps and long preservation of biomolecules, non-thrombogenic, non-inflammatory, fully bio-absorbable, & evacuate through dissolution in body fluids featuring to make silica nanofibers as an excellent candidate of next generation drug carriers and as a materials for wound dressing. Recent years, more and more research attention has been paid to the development of producing Silica nanofibers due to its ordered structure, high surface area and ease of processing [1, 2]. Many effective approaches have been carried out in finding alternatives to the design of novel products through bioactive silica such as as implants used in tissue guiding or bone repairs. Moreover, bioactive silica nanofibers provide new functionalities with hybrid materials [3]. Recently, an approach with a new-type of sol–gel/organic hybrid composite material using gelatin or chitosan with tetramethoxysilane was reported [4].



Our intention will be there to synthesize the pure bioresorbable silica nanofiber for ideal drug delivery carrier or wound dressing materials through hydrolysis of Tetraethylorthosilicate (TEOS) using sol-gel process or using biopolymer Gelatin/Chitosan to form polymer/silica composite thru Electrospining [fig. 1] and then followed by biodegradation (or Calcination also) to remove organic compounds to get a pure silica Nanofiber mat. Divergent nanofiber with different bulk structures may be prepared by changing the composition and controlling the stage of spinnability. The gelatin solutions may homogeneously hybridize with various contents of a silica sol using simple magnetic stirring, which enable the construction of a Nanofiberous structure with a uniform distribution of the silica in the gelatin nanofibers [5]. The Nanofiberous gelatin–silica hybrid composite showed much better in vitro biodegradation stability and apatite-forming ability than the Nanofiberous pure gelatin scaffold [6]. A fine uniform pure silica nanofiber mat will appear after the calcination or biodegradation of polymer/silica composite. This silica composite may be use as bioresorbable negotiator for biomedical precursor.

The Silica Nanofiber can be designed to control the loaded drug release in the cells.

References

[1] Peter, X.; Choi. J. W.; *Tissue Engineering*, 7 (**2007**) 23.
[2] Wai, L.; Hu, N.; Zhang, Y. *Materials,* 3 (**2010**) 4066.
[3] Patel, A.C.; Li, S.; Yuan, J.M.; Wei, Y. *Nano Letter,* 6 (**2006**) 1042.
[4] Samitha, S.; Mukundan, P.; Kirishapillai, P.; Wairrer, K.G.K. *Materials Chemistry and Physics,* 103 (**2007**) 318.
[5] Coradin, T.; Bah, S.; Livage, J. *Colloids and Surfaces B: Biointerefaces,* 35 (**2004**) 53.
[6] Bosch, E.V. D.; Gielens, C. *International Journal of Biological Macromolecule*s, 32 (**2003**) 29.

PB32

Preparation and Characterization of Bio-Based Epoxy for Thermal Degradation Studies

D. Saranya and V. Selvaraj*
[1]Department of Chemistry, University College of Engineering-Villupuram, (A Constituent College of Anna University, Chennai), Kakuppam, Villupuram-605 103, Tamil Nadu, India

An intercross linked network of oil based biodegradable linoleic ester modified epoxy nanocomposite is developed by reacting linoleic ester with epichlorohydrin by using benzyltrimethylammonium as catalyst. The resulting compound produces an oxirane ring. The synthesized epoxy is characterized by NMR Spectroscopy and FT-IR. The varying percentages (5,10,15) of diglycidyl ether of bisphenol-A(DGEBA) epoxy resinis incorporated into the linoleic ester modified epoxy. The resultant epoxy mixture is cured with diaminodiphenylmethane (DDM)as well as Diamino diphenyl sulphone (DDS)as curing agent.Thermal propertiesare analyzed by DSC and TGA.Rate of degradation is tuned by varying the curing condition. The cured sample exhibits good thermal stability excellent chemical and water absorption resistance. The morphological studies by SEM technique further confirmed phase homogeneity network of cured system.

References:

[1] Petra Lenz, Marc Hans ,Hendrik Luttikhedde,A novel biopolymer-based coating additive performance the natural way 05 (2012)
[2] Witold Brostow · Nathaniel M. GlassCure progress in epoxy systems: dependence on temperature and time, Mat Res Innovat (2003) 7:125–132
[3] Yun Zheng,1,2 Kim Chonung,1,2 Genlin Wang,1,2 Ping Wei,1,2 Pingkai Jiang1,2Journal of Applied Polymer Science, Vol. 111, 917–927 (2009)
[4] Jiahua Zhu, Suying Wei, Jongeun Ryu,§ Luyi Sun,| Zhiping Luo,⊥ and Zhanhu Guo*, Applied materials & interfaces Vol .7 .2100–2107 (2010)

PB33

Controlled RAFT Synthesis of Biocompatible Fluorescent Cationic Chiral Tryptophan Containing Polymers with Smart pH-responsiveness

Saswati Ghosh Roy and Priyadasi De*
Polymer Research Centre, Department of Chemical Sciences
Indian Institute of Science Education Research, Kolkata
Mohanpur-741242, Nadia, West Bengal, INDIA
** E-mail id : p_de@iiserkol.ac.in*

In recent years, among the different types of polymeric delivery devices, stimuli responsive polymers, specially, pH responsive amino acid based synthetic polymers have drawn considerable attention in biomedical and pharmaceutical applications due to their biomimetic structure and properties [1]. Herein, we reported controlled reversible addition-fragmentation chain transfer (RAFT) polymerization of methacrylate monomers having a chiral tryptophan moiety (L- and D-) in the side chain, Boc-tryptophan methacryloyloxyethyl ester (Boc-L/D-Trp-HEMA), with well-defined molecular weight and low polydispersity index of the resulting homopolymers and further confirmed to have retained end-group functionality by using these polymers as macro-chain transfer agents (macro-CTAs) to prepare well-defined block copolymers with methyl methacrylate (MMA). The presence of chiral and fluorescent tryptophan moieties in the side-chain of homo- and block-copolymers rendered chiroptical and fluorescence behaviour in them, which was studied through polarimetric measurements and fluorescence spectroscopy, respectively. Successive Boc group deprotection from the polymers produced pH responsive and cationic primary amine moieties at the side chain, which were respectively confirmed by UV-visible spectroscopy and dynamic light scattering (DLS). The *in vitro* cytotoxicity study using a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide reduction (MTT) assay established the cellular viability of HeLa cells in the presence of the poly(L-Trp-HEMA) homopolymer (Figure 1) [2]. The excellent biocompatibility of these fluorescent pH responsive cationic polymers can make them suitable candidates for siRNA delivery.

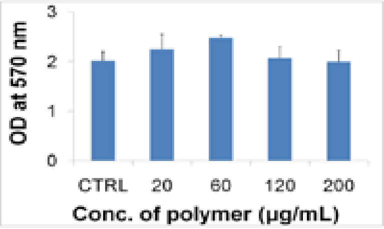


Figure 1. Cytotoxicity of P(L-Tryp-HEMA) in HeLa cells

References:

[1] Kumar, S.; Roy, S. G.; De, P. *Polym. Chem.*3 (**2012**) 1239–1248
[2] Roy, S. G.; Acharya, R.; Chatterji, U.; De, P. *Polym. Chem.* 4 (**2013**) 1141-1152

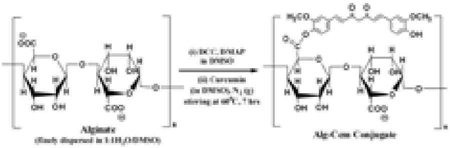
PB34

Synthesis and Characterization of Alginate-Curcumin Conjugate

Soma Dey and K. Sreenivasan*
Laboratory for Polymer Analysis, BMT Wing
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Trivandrum – 695012, INDIA
** E-mail: sreeni@sctimst.ac.in*

The concept of covalently bound polymer-drug conjugates, proposed by Ringsdorf [1], is widely accepted for better and safer delivery of diverse hydrophobic drugs with improved aqueous solubility, controlled delivery of drugs in optimum dosages, enhanced therapeutic efficacy and reduced side effects. Curcumin, the polyphenolic compound found in Indian spice turmeric (*curcuma longa*), is well studied as a potential drug for various diseases including cancer [2]. One of the serious limitations associated with curcumin is its extremely low water solubility and consequently poor bioavailability. To redress this problem several approaches have been proposed like encapsulation of curcumin in liposomes and micelles, formation of polymer-curcumin conjugates *etc*. [3, 4].

Herein we report the synthesis and characterization of Alginate-curcumin (Alg-Ccm) conjugate. Alginate, the natural polysaccharide copolymer was chosen to develop the drug conjugate for its several advantages such as biodegradability, high biocompatibility, non-toxicity, non-immunogenicity and the scope of chemical modification. In Alg-Ccm, curcumin was directly covalently conjugated to the C-6 carboxylate functionality of alginate via an ester linkage using DCC chemistry (Scheme 1). The formation of Alg-Ccm was confirmed by FT-IR spectroscopy. Alg-Ccm consisting of both hydrophobic (curcumin) and hydrophilic (alginate) moieties, self-assembled in aqueous solution forming nanosized micelles with an average hydrodynamic diameter of 459 ± 0.32 nm and their spherical morphology was visualized by TEM. The conjugate micelles showed potential stability in aqueous solution with a net zeta potential (ζ) of - 45.4 mV (at pH 7.4). The critical micelle concentration (CMC) of Alg-Ccm conjugate was determined by both fluorescence and UV-Vis spectroscopic techniques employing "1-Pyrenecarboxaldehyde" as the probe molecule and both the methods produced identical CMC values (0.25 mg/mL and 0.21 mg/mL respectively). Alg-Ccm can itself function as a potential drug conjugate and at the same time can be useful as delivery vehicles for other hydrophobic drugs.



Scheme1. Schematic presentation of the synthetic strategy of Alg-Ccm Conjugate

References:
[1] Ringsdorf, H. *J. Polym. Sci., Polym. Symp.*, 51 (**1975**) 153.
[2] Aggarwal, B. B.; Sung, B. *Trends Pharmacol. Sci.*, 30 (**2009**) 94.
[3] [Manju, S.; Sreenivasan, K. *J. Colloid Interface Sci.*, 368 (**2012**) 151.
[4] Anitha, A.; Deepagan, V. G.; Divya, R. V. V.; Menon, D.; Nair, S. V.; Jayakumar, R. *Carbohydr. Polym.*, 84 (**2011**) 1164.

PB35

Synthesis of Silk Fibroin-Glycopolypeptide Conjugates for Biomedical Application

Soumen Das [a], Debasis Pati [a], Neha Tiwari [a], Anuya Nisal [b], and Sayam Sen Gupta* [a]
[a] Chemical Engineering Division, [b] Polymer Science and Engineering Division, National Chemical Laboratory (CSIR), Pune – 411 008, India,
*Corresponding Author. E-mail: ss.sengupta@ncl.res.in

Silk fibroin (SF), a natural fibrous protein created by the *Bombyx mori* silk worm, forms the silk fibre that has been extensively used in textile industry. Silk fibroin is a high molecular weight biopolymer that is characterized by repeat hydrophobic and hydrophilic peptide sequences. The hydrophobic domains, consisting mainly of Gly-Ala-Gly-Ala-Gly-Ser repeats, constitute a large part of the silk proteins and leads to the formation of both inter and intramolecular β-sheet structures that are responsible for the insolubility, high mechanical strength and thermal stability of silk fibers. On other side, Glycopolymers, synthetic polymers 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 biomolecular recognition events such as extracellular recognition, adhesion, cell growth regulation, cancer cell metastasis, and inflammation. We reasoned that if synthetic glycopolypeptides (GP) can be covalently attached to silk fibroin, the new hybrid material will have both the mechanical properties of native SF and the molecular recognition property of the carbohydrates in the glycopolypeptide.

In this study, we have conjugated synthetic glycopolypeptides (GP) that were synthesized by controlled ring opening polymerization of *α-manno*-lys NCA's onto silk fibroin (SF) by using Cu (I) catalyzed click reaction. These hybrid materials (SF-GP) have both the mechanical properties of native silk fibroin and the molecular recognition property of the carbohydrates in the glycopolypeptide. By controlling the amount of glycopolypeptide grafted onto silk fibroin, we have made three SF-GP conjugates that differ in their ability to assemble into films. SF-GP conjugates having a very high content of GP formed completely water soluble brush like polymer which displayed very high affinity towards the lectin Con-A. Films cast from SF-GP conjugates using lower amounts of grafted GP were more stable in water and the stability can be modulated by varying the amount of GP grafted. The water insoluble film SF-GP_{25} was also found to bind to fluorescently labelled Con-A as was seen by confocal microscopy. Such SF-GP hybrid films may be useful as mimics of extracellular matrices for tissue engineering.

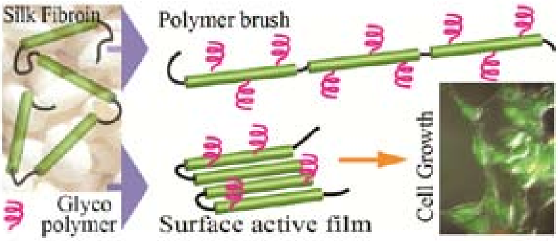


Figure 1. Schematic representation for the formation of water soluble brush like polymer or water insoluble film by varying the amount of glycopolypeptide grafted onto silk fibroin.

References

[1] Das, S.; Pati, D.; Tiwari, N.; Nisal, A.; Gupta, S. S. *Biomacromolecules*, 13 (**2012)** 3695–3702.

PB36

β-Cyclodextrin Embedded Polyacrylic Acid Hydrogels as Sustained Drug Delivery Carriers

Subhraseema Das and U. Subuddhi*
Department of Chemistry, National Institute of Technology,
Rourkela-769008, ODISHA, INDIA

Stimuli-responsive hydrogels have garnered considerable interest for biomedical and biotechnological applications because of their good tissue compatibility. Acrylic Acid (AAc) is one of the extensively studied polymers in the field of pH-responsive hydrogels. However pure polyacrylic acid (PAAc) hydrogels lack mechanical strength. An interpenetrating polymer network (IPN) is generally utilized to impart tougher mechanical properties to a conventional hydrogel. Polyvinyl Alcohol (PVA) is widely used for hydrogel production because of its low toxicity, high degree of swelling in water, biocompatibility and ability to be easily crosslinked by chemical agents like multifunctional aldehydes or acids and by physical method like freeze-thawing [1, 2]. Loading of hydrophobic drugs into hydrogel matrix by itself is a difficult task. Moreover, the high water content of hydrogels causes rapid release of drugs from the gel matrix.

In order to overcome these shortcomings, growing interest has focused on incorporation of particulate systems (microspheres, liposomes, microemulsions, micelles, microgel *etc.*) into the hydrogel matrix to form composite or "plum pudding" hydrogel networks [3, 4]. In this context, our approach is to incorporate beta cyclodextrin (CD) moieties in the PVA/PAAc hydrogel matrix. pH-sensitive IPN hydrogels composed of PAAc and PVA were prepared and 1:1 complex of dexamethasone with CD was incorporated. The hydrogels were characterized by FTIR, DSC, SEM and XRD. Swelling behaviour and drug release studies have been carried to understand the mechanism of swelling and drug releasing properties. The release profile of dexamethasone loaded hydrogels showed negligible drug release over a period of 2h in simulated gastric fluid (SGF) and its transfer to intestinal fluid (SIF) showed consistent release of drug. Cyclodextrin incorporated hydrogels exhibited prolonged drug release compared to normal hydrogels.

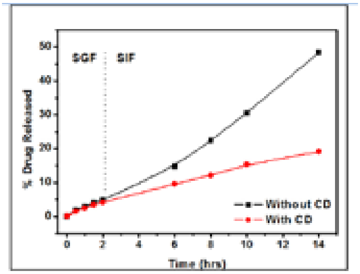


Figure 1. Drug Release Profile in SGF ad SIF

References

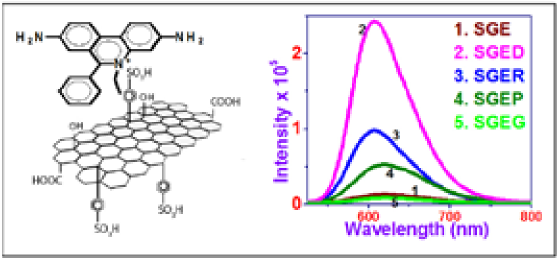
[1] J. Yun, J. S. Im, A. Oh, D. Jin et al., *Mat. Sci. Eng. B*, 176 (**2011)** 276.
[2] M. Hamidi, A. Azadi, P. Raifei, *Adv. Drug Deliv. Rev.,* 60 (**2008**) 1638.
[3] A. Salvati, O. Soederman, I. Lynch, *J. Phy. Chem. B*, 111 (**2007**) 7367.
[4] D. Gulsen, C. C. Li, A. Chauhan, *Curr. Eye Res.,* 30 (**2005**) 1071.

PB37

Sulfonated Graphene Template as a Platform for Preferential Sensing of DNA

Sudipta Nandi, Parimal Routh, Rama K. Layek and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata- 700 032, India
* For correspondence: A.K.Nandi, email psuakn@iacs.res.in

Recently, graphene oxide (GO) has attracted persistent interest to the scientific community due to its high specific surface area, excellent water solubility and the intrinsic fluorescence property in the visible and NIR range [1] extending its potential application in biological field such as drug delivery, live cell imaging [1], biosensors [2]. GO can be considered to be a weak acid cation exchange resin because of the ionizable carboxylic acid groups [3], and this excellent property of GO may be used to preferentially sense DNA using the dye ethidium bromide (EtBr) by fluorescence spectroscopy. A better approach of it is to use sulfonated graphene (SG) as it possesses better water solubility [4] than GO due to the presence of charged SO_3^- units which prevent the graphitic sheets from aggregation in solution. In our experiment, SG is used as an adsorbing platform for the water soluble EtBr (a cationic dye), that act as a fluorescent probe due to its excellent fluorescence property which get enhanced after binding with nucleic acids. It is generally agreed that strong fluorescence enhancement accompanies intercalation [5] of the dye into the helix of the nucleic acids but there is also evidence for additional nonintercalative, less fluorescence-enhanced sites which are presumed to involve electrostatic binding [6].



Here, SG is used as EtBr binding platform, to preferentially sense DNA among the other biomolecules like RNA, bovine serum albumin (BSA) and glucose using fluorescence spectroscopy. EtBr has lost its intrinsic fluorescence property after binding with SG. DNA can "turn on" the quenched fluorescence of SG-EtBr hybrid to a greater extent compared to the RNA, BSA and glucose. UV-vis absorption spectra and CD spectra also support the higher ability of DNA to release adsorbed EtBr from SG surface in comparison to RNA. An analysis of Raman spectral data indicates that the interaction of EtBr in its adsorbed state on SG template is greater with DNA than that with RNA.

References

[1] Sun, X.; Liu, Z.; Welsher, K.; Robinson, J. T.; Goodwin, A.; Zaric, S.; Dai, H. *Nano research,* 1 **(2008)** 203.
[2] Liu, Y.; Dong, X.; Chen, P. *Chem. Soc. Rev.,* 41 **(2012)** 2283.
[3] Balapanuru, J.; Yang, J. –X.; Xiao, S.; Bao, Q.; Jahan, M.; Polavarapu, L.; Wei, J.; Xu, Q. –H.; Loh, K. P. *Angew. Chem.*
[4] Int. Ed., 49 **(2010)** 6549.
[5] Si, Y.; Samulski, E. T. *Nano Lett.,* 8 **(2008)** 1679.
[6] Waring, M. J. *J. Mol. Biol.,* 13 **(1965)** 269.
[7] Pritchard, N. J.; Blake, A.; Peacocke, A. R. *Nature,* 212 **(1966)** 1360.

PB38

Synthesis of Biodegradable Polymeric Peroxides *via* Oxidative Copolymerization of 2-(Acetoacetoxy)ethyl Methacrylate and Molecular Oxygen

Sunirmal Pal and Priyadarsi De*
Polymer Research Centre, Department of Chemical Sciences
Indian Institute of Science Education and Research, Kolkata, PO: BCKV Campus Main Office, Mohanpur - 741252, Nadia, West Bengal, India
* E-mail id : p_de@iiserkol.ac.in

Polymerization of vinyl monomers in the presence of high oxygen pressure gives polyperoxides, which are alternating copolymers of vinyl monomers and main chain weak peroxy (-O-O-) linkages. Polymerization of 2-(acetoacetoxy)ethyl methacrylate and molecular oxygen under high pressure at 50 °C in the presence of AIBN as radical initiator gives poly[2-(acetoacetoxy)ethyl methacrylate] peroxide (PAEMAP). Elemental analysis, mass spectral fragmentation analysis, FTIR and NMR spectroscopy have been used to verify the alternating copolymer structure with peroxy bonds in the copolymer backbone. Thermal degradation studies of the PAEMAP by using differential scanning calorimetry reveal that PAEMAP degrades highly exothermically (Figure 1). The thermal degradation of PAEMAP is also investigated by thermogravimetric analysis. The mechanism of the primary exothermic degradation has been supported by thermochemical calculations. Biodegradation using horseradish peroxidase enzyme and *in vitro* biocompatibility to HeLa cells have been studied for PAEMAP. These results indicate that incorporation of -O-O- links in the backbone favours enzymatic degradation of PAEMAP [1-4].

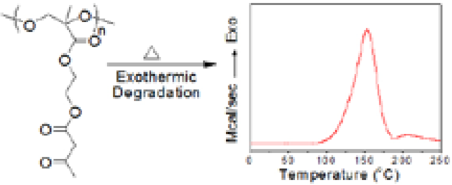


Figure 1. Exothermic degradation of PAEMAP

References:
[1] Pal, S.; Das, A.; Maiti, S.; De, P. *Polym. Chem.* 3 **(2012)** 182
[2] Pal, S.; Das, A.; Maiti, S.; De, P. *J. Biomat. Sci., Polym. Ed.* 23 **(2012)** 2105
[3] Pal, S.; Ghorai, P. K.; De, P. *Polym. Bull.* 69 **(2012)** 149
[4] Pal, S.; De, P. *Chem. Commun.* 48 **(2012)** 4229

PB39

Selective and Sensitive Detection of Dopamine by Doped Polypyrrole/chitosan stabilized Ag Nanoparticles Modified Electrode

Suparna Saha and Priyabrata Sarkar*
Department of Polymer Science and Technology, University of Calcutta, 92 APC Road,
Kolkata 700009, India
Email: sarkarpriya@gmail.com
Ph: +913324852975

Dopamine (3, 4-dihydroxyphenyl ethylamine, DA) is one of the most important neurotransmitters in the mammalian central nervous system [1]. Electrochemical techniques show more promising compared to other techniques for the analysis of neurotransmitters in general since there are possibilities of direct measurement of the analytes. A new approach was applied to detect dopamine by electrochemical sensor based on a composite containing chitosan stabilized silver nanoparticles and doped ultrathin polypyrrole film to explore its synergism between conducting polymer matrix and silver nanoparticle. Silver/chitosan nanocomposites were prepared by using basic chitosan suspension as a stabilizer and as a reductant in the absence of other chemicals [2]. These were characterized by TEM, XRD, UV-vis and FTIR, EDAX. Surface morphology of doped PPy was confirmed by SEM, shown in Fig 1.

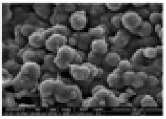


Figure 1. Surface morphology of doped PPY

Favorable electrostatic interaction between the negatively charged modified electrode and cationic species of DA [3] mainly contribute to the response of DA with no virtual interferences from ascorbic acid, uric acid, epinephrine, L-Dopa, glucose etc. The sensor displayed a linear range from $1x10^{-9}$M to $1.2x10^{-7}$M in 0.05M phosphate buffer solution (pH 7.0) with a correlation coefficient of 0.98 (Fig 2) and the detection limit estimated was 0.5 nM. It could be seen that the sensor could achieve highest sensitivity and lowest time of detection (9s). The practical analytical utility of the method was illustrated by quantitative determination of dopamine in commercially available human blood serum without any pretreatment.

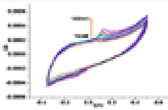


Figure 2. CVs for different conc. of DA at 40mVs-1 scan rate

The modified electrode showed excellent sensitivity, good selectivity, and reusability and antifouling properties in neutral pH**.** A mechanism for the oxidation of DA on the modified electrode has also been proposed.

References

[1] Wightman, R.M.; May L.J.; Michael, A. C. *Anal. Chem*. 60 (**1988**) 769A.
[2] Huang, H.Z.; Yuan, Q.; Yang, X.R.; *Colloids Surf. B* 39 *(***2004**) 31.
[3] Okajima, P R.; Ohsaka, T.; Bioelectrochem 59 **(2003**) 11.

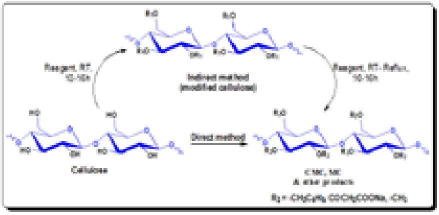
PB40

Development of Synthetic Strategy for Chemical Modification of Cellulose into Value Added Products

Surendra Singh Bisht[a]* and Madhushri H.[b] *
[a]*Chemistry of Forest Product Division, Indian Council of Forestry and Education- Institute of Wood Science and Technology, Bangalore, INDIA*
[b]*Department of Chemical Engineering, Dayananda Sagar College of Engineering, Bangalore, INDIA*
**Email- ssbisht@icfre.org*

Chemical modification of polymers is one of the methods used to synthesize new polymeric compounds and it is the most active fields of research in polymer sciences for the past 30 years. It is introduce functional or reactive groups into polymers, to alter polymer surfaces and to provide wide applications of polymer.

In this study, the aim was to investigate and explore the versatility of cellulose for the synthesis of cellulose-based materials like carboxymethyl cellulose (CMC), methyl cellulose (MC) etc. and to introduce new synthetic methods for cellulose modification with respect to high degree of substitution (DS). The synthesized products were characterized by Fourier Transform infrared spectroscopy (FTIR), ^{1}H- and ^{13}C-NMR spectroscopy. These products hold an impressive potential for fundamental knowledge as well as for large-scale production in a wide range of applications such as pharmaceutics, cosmetics, food, oil drilling, paper, paints, and textiles.



References
[1] [1] Barai, B.K.; Singhal, R.S.; Kulkarni, P.K. *Carbohydrate Polymers*, 32 (**1997**), 229.
[2] [2] Fahmy, T.Y.A.; Mobark, F.; *Carbohydrate Polymers*, 72 (**2008**), 751.
[3] [3] Eyholzer, Ch.; F. Lopez-Suevos, Tingaut, P.; Zimmermann, T.; Oksman, K. *Cellulose*, 17 (**2010**), 4, 793.

PB41

Albumin based Drug Delivery Carriers Fabricated via Layer-by-layer Approach

V. Mohanta, S. Patil*
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India
** satish@sscu.iisc.ernet.in*

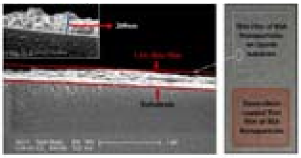


Figure 1. Layer-by-layer assembled thin film of BSA nanoparticles

The ability to fabricate thin films out of variety of substances (polymers, proteins, dendrimers, enzymes, nucleic acids, micelles) by layer-by-layer (LbL) approach finds tremendous applications in biomedical field as in drug delivery and improving biocompatibility of biomedical implants [1-3]. In our study, we have incorporated Bovine Serum Albumin (BSA) nanoparticles into multilayer thin films making use of this LbL technique. The protein nature of BSA ensures the biocompatibility and biodegradability of the drug carrier. BSA nanoparticles (~100 nm) prepared by desolvation method [4] show a high negative zeta potential in aqueous medium (-55 mV) and form a stable dispersion in water without agglomeration and hence, is successfully assembled on a substrate via electrostatic interaction with a positively charged polyelectrolyte (chitosan in acidic medium). Anti-cancer drug doxorubicin is loaded in the films and its release behaviour is studied [5].

Moreover, BSA transports many of the bioactive hydrophobic molecules in the circulatory system and this property can be exploited to solubilize water-insoluble therapeutics[6]. We have non-covalently conjugated a hydrophobic molecule, pyrene (as model drug) and a water-insoluble drug, Curcumin with BSA and the same has been assembled into thin film via LbL approach. Further, using porous calcium carbonate microparticle as template, a multi-agent drug carrier is accomplished by pre-encapsulating protein in the porous calcium carbonate microparticle and assembling the BSA conjugates of pyrene and Cucumin on the surface of template. Microcapsules with aqueous interior have been subsequently prepared by dissolving the template.

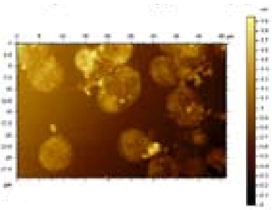


Figure 2 . Layer-by-layer assembled microcapsules of BSA-pyrene conjugate.

References

[1] Decher, G. *Science* 277 (**1997**) 1232.
[2] Tang, Z.; Wang, Y.; Podsiadlo, P.; Kotov, N. A. *Adv. Mater.* 18 (**2006)** 3203.
[3] Zelikin, A. N. *ACS Nano* 4 (**2010)** 2494.
[4] Weber, C.; Coester, C.; Kreuter, J.; Langer, K. *Int. J. Pharm*. 194 (**2000)** 91.
[5] Mohanta, V.; Madras, G.; Patil, S. *J. Phys. Chem. C* 116 (**2012)** 5333.
[6] Kratz, F. *J. Controlled Release* 132 (**2008)** 171.

PB42

7 Arm Star polymers Based on Cyclodextrin and N-Isopropylacrylamide via RAFT-Polymerization

Venkanna Azmeera[a], P.Adhikary[b], S.Krishnamoorthi *
[a]*Research Scholar, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*
[b]*Young Scientist, Lab No.16A, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India.*
** Assistant Professor, Department of Chemistry, Banaras Hindu University, Varanasi-221005, Uttar Pradesh, India*

A novel 7 arm star polymer of β-Cyclodextrin–poly N-isopropylacrylamide (β-CD-PNIPAM) was synthesized through reversible addition fragmentation chain transfer (RAFT) polymerization. β-cyclodextrin core (7-Br-β-CD) was synthesized by the esterification reaction of β-CD and 2-bromopropionyl bromide. Further alkynyl-terminated xanthate core macroinitiator (7 arm β-CD-xanthate) was synthesized by the reaction of 7-Br-β-CD with Potassium O- propynyl xanthate. The 7 arm star polymer of β-CD-PNIPAM (Figure.1) was prepared by treating NIPAM with 7 arm β-CD-xanthate through RAFT polymerization.

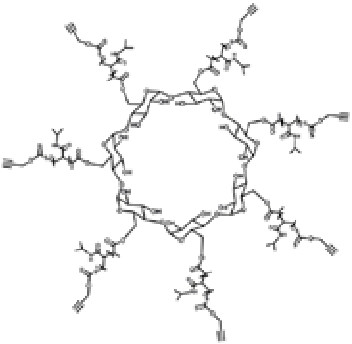


Figure.1

References

[1] Weizhong Yuan, Hui Zou, Wen Guo, An Wang and Jie Ren. *J. Mater. Chem*., (2012), 22, 24783.
[2] Huijuan Zhang, Qiang Yan, Yan Kang, Lilin Zhou, Hang Zhou, Jinying Yuan, Sizhu Wu. *Polymer*. (2012), 53, 3719.

PB43

Visible light cure dental restorative composites based on calcium containing inorganic-organic hybrid resins; effect of calcium content on physio - mechanical properties

Vibha C and Lizymol P.P. *
Dental Products Laboratory, Biomedical Technology Wing,
Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Thiruvananthapuram 695012.
Email: lizymol@rediffmail.com

Replacement of damaged tooth is necessary for good aesthetics and proper function. Polymeric composites are usually used as tooth coloured restorative materials. Commercially available composites are based on combinations of Bis GMA/UDMA/TEGDMA as resin medium. The polymerization shrinkage [1] associated with these composites creates contraction stresses in the resin composite restoration, internal stress and deformation in the surrounding tooth structure resulting in poor marginal adaptation, postoperative pain, and recurrent carries [2]. One way to resolve these limitations is to switch the resin matrix to a novel monomer like inorganic-organic hybrid resin [3, 4]. Objective of the present work is to synthesize inorganic-organic hybrid resins containing calcium, magnesium, zinc and their combinations and to investigate the effect of calcium content on physio-mechanical properties of visible light cure composites prepared from these resins.

These inorganic–organic hybrid resins with polymerisable methacrylate group were synthesized by sol-gel process [4] using γ-Trimethoxy silyl propyl methacrylate. The synthesized resins were characterized using FT IR spectroscopy and confirm the presence of polymerisable methacrylate groups. Visible light cure composites were prepared with inorganic-organic hybrid resin as the resin matrix, silanated quartz and pyrogenic silica as the filler and (-) Diphenyl(2,4,6-trimethyl benzoyl) phosphine oxide (TPO) as the photoinitiator and evaluated in terms of diametral tensile strength (DTS), flexural strength (FS), Vickers hardness (HVN), depth of cure and shrinkage. Previous studies showed that incorporation of calcium, magnesium or zinc as inorganic contents in these resin matrix exhibited better hardness and lower shrinkage compared to BisGMA [5]. Present study showed that light cure composites prepared from hybrid resins having combination of calcium, magnesium and zinc exhibit better properties compared to composites prepared using calcium/magnesium/zinc containing resin (fig 1). Better mechanical properties and low shrinkage obtained for the new material will make it an ideal substitute for the existing restorative materials.

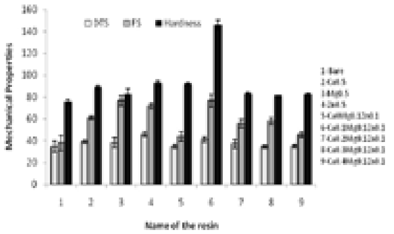


Figure 1. Effect of inorganic content on mechanical properties of visible light cure composites.

References

[1] Helvatjoglu-Antoniades, M; Kalinderis, K; Pedulu, L; Papadogiannis, Y. *Journal of Oral Rehabilitation,* 31 **(2004)** 1068.
[2] Jeon, M. Y; Yoo, S. H; Kim, J. H; Kim, C. K; Cho, B. H. *Biomacromolecules,* 8 **(2007)** 2571.
[3] Karl-Heinz Haas. *Advanced Engineering Materials*, 2 **(2000)** 572
[4] Lizymol P. P. *Journal of Applied Polymer Science*, 116 **(2010)** 509.
[5] Vibha, C; Lizymol, P P. Proceedings 24 th Kerala Science Congress, Rubber Research Institute of India, Kottayam, **(2012)** 538.

PB44

Biomaterials with Biopolymers and Date Seed Powder: Properties and Oil Migration

Vikas Mittal[a,*], Nadejda Matsko[b]
[a]*Chemical Engineering Department, The Petroleum Institute, Abu Dhabi, UAE*
[b]*Graz Centre for Electron Microscopy, Graz, Austria*
**Vikas Mittal, vmittal@pi.ac.ae*

The microstructure of bio-polyester and poly(lactic acid) composites with date seed powder filler was characterized using rheology as well as microscopy. The poly(lactic acid) composites with filler fraction higher than 20% exhibited significant phase immiscibility, whereas corresponding polyester composites were relatively miscible. The poly(lactic acid) composites also exhibited increase in the elastic response over the viscous response as a function of filler fraction, whereas the polyester composites retained the viscous dominance irrespective of the date seed powder content. The TEM and light microscopy characterization revealed presence of voids in the composites which were present around the filler particles as well as dispersed in the polymer matrix. The AFM analysis of the pure polymers also revealed the absence of these features thus confirming that these phenomena resulted from the incorporation of the filler in the polymers. Such features were opined to be resulting from the escape of date seed oil produced at high temperature during composite processing. The composites with 10% date seed powder content had lower extent of such voids and the morphology remained relatively unchanged with time. In the composites with 30% date seed powder (DSP) content, in the seasoned sample, a soft and sticky phase resulting from the surface migration of date seed oil was also observed. The extent of the soft phase was higher in poly(lactic acid) composites probably due to the higher compounding temperature used to generate poly(lactic acid) composites. The generation of this soft phase was also a slow process as 24 h were not enough to generate this phase. The migration of the oil to the surface was also confirmed by the IR and X-ray diffraction studies. The controlled component migration can lead to potential generation of commercially important self-lubricating composite materials.

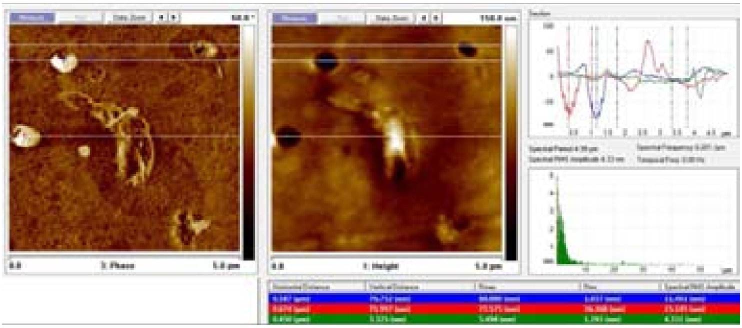


Figure 1. AFM height variation analysis of the polyester composite with 30% date seed powder Content.

PB45

Synthesis and Self-assembly of Amphiphilic Homoglycopolypeptide

Vinita Dhaware,[a] Ashif. Y. Shaikh,[b] Mrityunjoy Kar,[a] Srinivas Hotha*,[b] and Sayam Sen Gupta*[a]
[a]Chemical Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008
[b]Department of Chemistry, Indian Institute of Science Education & Research, Pune – 411008, India
* Corresponding authors: Sayam Sen Gupta ss.sengupta@ncl.res.in
Shrinivas Hotha s.hotha@iiserpune.ac.in

Glycoproteins play major role in the biological processes like cell signal transmission, fertilization, cell-cell recognition, inflammation and protein folding among others. [1] Glycopolypeptides are the synthetic mimics of the natural glycoproteins and hence are expected to be biocompatible. Since glycopolypeptides are typically polyvalent,this enhances their affinity and selectivity for carbohydrate binding proteins like lectins by many folds. Also, the ability of these glycopolypeptides to self-assemble in well defined secondary structure (e.g. helix) allows the ordered display of the carbohydrate moieties on the surface. Such polyvalent interactions can be used for drug delivery applications. For glycopolyeptides to be used as drug delivery vehicles, these have to be assembled into supramolecular nanostructures such as polymerosomes. Amphiphilic block copolymers containing glycopolpeptides as one of their blocks have been used to form nanostructures by us and others.[2]

If such amphiphilicity could be engineered on a smaller length scale (i.e., on a monomer scale) would be very interesting because this would allow great tunability in the supramolecular assemblies. We synthesized amphiphilic homoglycopolypeptides having amphiphilicity in each monomer unit and studied its self-assembly in water. The synthesis of amphiphilic homoglycopolypeptide was carried out by a combination of NCA polymerization and click chemistry to yield a well-defined polypeptide having an amphiphilic carbohydrate on its side chain. The amphiphilicity of the carbohydrate was achieved by incorporation of an alkyl chain at the C-6 position of the carbohydrate thus also rendering the homoglycopolypeptide amphiphilic. The homoglycopolypeptide formed multi-micellar aggregates in water (fig.1) above a critical concentration of 0.9 µM due to phase separation. This multi-micellar aggregates encapsulate both hydrophilic as well as hydrophobic dye as was confirmed by confocal microscopy. Next, amphiphilic random polypeptides containing 10 and 20% α-D-mannose in addition to glucose containing a hydrophobic alkyl chain at its 6 position was also synthesized. These polymers were also found to assemble into spherical nanostructures. The spherical assemblies of amphiphilic random glycopolypeptides containing 10 and 20% mannose were found to be surface bioactive and were found to interact with the lectin Con-A.

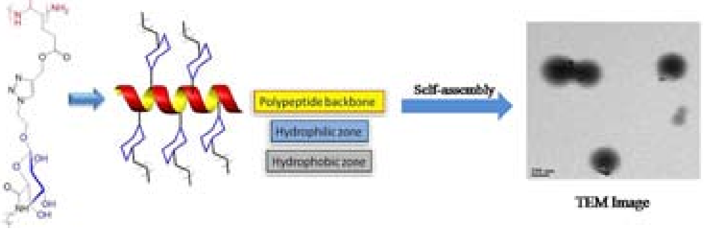


Figure 1: Design of amphiphilic homopolypeptide and its self-assembly in water

References

[1] Bertozzi, C. R.; Kiessling; Laura, L., *Science*, 291, (**2001**), 2357.
[2] Pati, D.; Kalva, N.; Das, S.; Kumaraswamy, G.; Sen Gupta, S.; Ambade, A. V., *J. Am. Chem. Soc*, 134, (**2012**), 7796.

Blends and nanocomposites

Invited

Temperature and Electrical Memory of Nanocomposites

Fabienne Grillard, Célia Mercader, Pierre Miaudet, Cécile Zakri, Philippe Poulin*
Centre de Recherche Paul Pascal – CNRS, University of Bordeaux, 115 Avenue Schweitzer, 33600 Pessac, France
** poulin@crpp-bordeaux.cnrs.fr*

Conventional Shape Memory Polymers (SMPs) are deformed at high temperature (T_d) and then cooled down under fixed strain to freeze the deformed polymer chains, thus storing mechanical energy. Upon reheating, typically in the vicinity of the glass transition temperature (T_g), the polymer chains become mobile and the material relaxes by reverting towards its original shape. Polymers can display large strain and recovery rates. However, these large deformations are often associated to a low stress of a few MPa typically. Consequently the combination of stress and strain results in a low gravimetric energy density. Several features including temperatures of transitions, mechanical stress generated during heating, shape fixity and strain recovery ratio strongly depend on the chemical composition of the polymer. But the shape memory behavior depends also on the programming process. This dependency has remained until recently rather qualitative. In particular it was known that the stress generated by a shape memory polymer is greater when the polymers are manipulated in the vicinity of the glass transition temperature. More quantitative dependences and greater generation of stress well above the glass transition have been recently reported in polymer nanocomposites made of polymers loaded with carbon nanotubes (CNTs) [1, 2]. It has also been observed that the stress generated when the polymer is heated up at fixed strain exhibits a maximum at a temperature close to T_d. This dependence reflects an accurate "temperature memory" of the polymer. This feature allows smarter SMPs to be developed because the shape memory properties are not anymore only imposed by the composition of the polymer but can also be precisely controlled by the programming process [1-5]. This concept opens opportunities towards memorization of complex programming processes such as deformation stages at different temperatures or on different time scales during heating or cooling. This could lead to unprecedented behaviors coupling complex dimensional changes, temporal dependency and generation of large mechanical stress. We will discuss in this presentation recent findings in the field and focus on particular features of CNT-polymer nanocomposites. Such materials are electrically conductive and can be stimulated by Joule's heating. This allows changes of shape to be triggered without any external heating source. In addition, their electrical conductivity has been observed to strongly vary during the programming processes and shape recovery behavior. The conductivity has even been found to exhibit an accurate temperature memory, in analogy with the mechanical properties. We will finally discuss dynamical effects and try to identify consequences of the time-temperature superposition principle of the glass transition in the shape memory behavior of glass forming polymers.

References

[1] Miaudet, P. *et al.*, *Shape and temperature memory of nanocomposites with broadened glass transition.* Science **318** (5854), 1294 (2007).
[2] Viry, L. *et al.*, *Nanotube fibers for electromechanical and shape memory actuators.* Journal of Materials Chemistry **20**, 3487 (2010).
[3] Xie, T., *Tunable polymer multi-shape memory effect.* Nature **464,** 267 (2010).
[4] Sun, L.; Huang, W. M., *Mechanisms of the multi-shape memory effect and temperature memory effect in shape memory polymers.* Soft Matter **6,** 4403 (2010).
[5] Kratz, K. *et al.*, *Temperature-Memory Polymer Networks with Crystallizable Controlling Units.* Advanced Materials **23,** 4058 (2011).

Pros and Cons of Development of Thermoplastic Vulcanizate (TPV) via Various Routes

Kinsuk Naskar
Rubber Technology Centre, I.I.T Kharagpur, West Bengal-721302
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. 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 vulcanisates (TPVs) 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. TPVs based on blends of polypropylene (PP) and ethylene propylene diene terpolymer rubber (EPDM) are most significant from a commercial point of view, where the rubber phase is generally cross-linked either by activated phenol formaldehyde resins or by peroxides. The disadvantages of resins and peroxides create a demand for other alternatives.

In this investigation TPVs based on PP/EPDM are developed by a novel avenue, namely *electron beam induced reactive processing.* A 1.5 MeV electron accelerator was directly coupled to an internal mixer in order to induce chemical reactions by energy input via high energy electrons under dynamic conditions of melt mixing of PP and EPDM. The influence of absorbed dose (25 kGy to 100 kGy) as well as electron energy (1.5 MeV and 0.6 MeV) and electron treatment time (15 s to 60 s) have been studied. Drastic increase of mechanical properties of the TPVs indicates in situ compatibilisation of PP and EPDM as well as cross-linking in the EPDM phase upon electron induced reactive processing. Dynamic mechanical analyses showed a decrease in value of glass transition temperature peak of EPDM in tangent delta curve with increasing dose. This also indicates higher degree of cross-linking in EPDM phase, which is further supported by a gel content that is higher than the EPDM content itself in the blend. Morphology of the TPVs is also investigated in details to show how rubber particle size from micro to nano-level can control the mechanical properties of the TPVs.

Reference

[1] Rajesh Babu, R.; Naskar, K. Adv Polym Sci 239: (2011) 219

Polymer composites for biomedical applications

Pralay Maiti
School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University),
Varanasi 221 005; (pmaiti.mst@itbhu.ac.in)

Nanostructure, key to property alteration, has widely been diverse by using two- dimensional nanoparticle in different stages of polymerization. Molecular level self-assembly starting from nano-scale 2-D molecular sheet to optically observable micro-scale crystallite has been unraveled step wise for thermoplastic elastomer like polyurethanes. The nature of self-assembly can be tuned by judicious choice of polymerization procedure in presence of organically modified nanoclay. The effect of modulated nanostructure and self-assembly has been explored for the unusual property enhancement including thermal, mechanical, barrier, controlled drug delivery and biological (genotoxicity) properties. Both the stiffness and toughness increase in nanohybrid without any trade-off. The unique splintering phenomenon and its variation under a dynamic frequency were investigated using a fixed concentration of nanoparticle by changing the route of synthesizing nanohybrids. For understanding the controlled cellular responses of the implant, cell adhesion, hemocompatibility and detailed genotoxicity studies reveal the total biological recognition of the developed nano-bio-hybrids. Bone cement based nanohybrids have been developed for faster bone healing with superior mechanical responses.

Fracture Kinetics of Polyamide Based Blends and Nanocomposites

Bhabani K. Satapathy
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi-110016
Email: bhabaniks@gmail.com

Understanding the inputs from real-time synchronization of crack propagation behavior of polymer based blends and nanocomposites may be crucial in developing new material concepts. In this regard polyamide/polyolefin blends and their filled nanocomposites as model systems have been critically evaluated following post-yield fracture mechanics (PYFM) principles by using double edge notch tension (DENT) specimens. The kinetics of crack propagation and strain field evolution characteristics have been systematically analyzed. The correspondence of strain in the inner fracture process zone to crack-initiation resistance and in outer plastic deformation zone to crack-propagation resistance could be experimentally established by real time deformation analysis. Furthermore, it could be deduced that toughening in unfilled blends may be determined by shear yielding whereas the same in nanocomposites may primarily be attributed to microstructure controlled delayed yielding phenomenon. Fracture surface morphology investigations have successfully indicated the possible failure mechanisms.

Polymer Nanocomposites : An Advanced Material for Functional Fibers

Mangala Joshi
Department of Textile Technology
Indian Institute of Technology,
Hauz Khas, New Delhi 110016, India
Tele: 91-11-26596623, fax 91-11-26581103
mangala@textile.iitd.ac.in

Polymer nanocomposites have recently gained a great deal of attention because of the much superior properties and show promising applications in developing advanced textile materials such as- Nanocomposite fibers, nanofibers and other nanomaterial incorporated coated textiles for applications in medical, defense, aerospace and other technical textile applications.

Polymers nanocomposites offer tremendous potential when produced in fiber form and offer properties that leapfrog those of currently known commodity synthetic fibres. Nanocomposite fibres that contain nanoscale embedded rigid particles as reinforcements show improved high temperature mechanical property, thermal stability, useful optical, electrical, barrier or other functionality such as improved dyeability, flame retardance, antimicrobial property etc. The work on spinning of nanocomposites started about nine years ago and several research groups across the world are exploring the synthesis, fiber processing, structure- property characterization and correlation and molecular modeling of these unique new composites fibers. Polymeric nanocomposite fibres have been mostly spun through three basic methods of fiber spinning -Melt spinning, Solution spinning and Electrospinning. Although, most of the research reports on polymeric nanocomposites are in form of films or molded specimens there are fewer reports on their spinning into Nanocomposite fiber form.

This paper discusses the recent developments in this area and presents some of the highlights of the research and development activity that we have undertaken at Textile Department, IIT Delhi, in this area.

References

[1] ***M. Joshi*** *and A. Bhattacharyya, Nanotechnology: A New Route to High Performance and Functional Textiles,* ***Textile Progress*** *43 (3) (2011), 155-233.*

[2] A. Bhattacharyya & ***M. Joshi****, Development of Polyurethane based Conducting Nanocomposite Fibers via Twin Screw Extrusion,* ***Fibers and Polymers****, 12 (6), 2011, 734-740*

[3] ***M. Joshi*** *and V. Viswanathan, High Performance Filaments from compatibilised PP/clay nanocomposites, Journal of Applied Polymer Science, 102(3) (2006) 2164-2174.*

[4] Sachin Kumar, B S Butola and ***M Joshi****, Preparation of hybrid Polypropylene/POSS nanocomposite monofilaments by radiation induced grafting,* ***Fibers and Polymers*** *11(8), 1137-1145, 2010*

[5] M Joshi, D Biswas, A Sarvanan and R Mukhopadhyay, Nylon 6/ Nanoclay filaments and their cords, **Journal of Applied Polymer Science**, 125,E224-E234,2012.

Synthesis and Morphological Study of Branched PE-PCL Immobilized Biocompatible Superparamagnetic Nanocomposite

S. Panja and S. Chattopadhyay*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur-721302, India
Corresponding author email: santanuchat71@yahoo.com

Biodegradable polymer immobilized superparamagnetic nanoparticles (MNPs) have many potential application including magnetic targeted drug delivery[1] and magnetic resonance imaging (MRI)[2]. MNP has an inherent tendency to form agglomerates due to its high surface energy and magnetic nature. Agglomeration of MNP leads to deterioration of the attributes for biomedical applications. Because of this major bottleneck, magnetic nanoparticles can be removed by macrophages or the reticuloendothelial system before it can reach at the targeted site [3]. To resolve this problem a number of superparamagnetic as well as biocompatible nanocomposite were prepared by immobilization of pentaerythritol poly(ε-caprolactone) (PE-PCL) onto the surface of two different sizes MNPs. Between two different sizes of MNPs one of them having size scale nearing 5nm (5nm-MNP) and other having an average size scale of 15nm (15nm-MNP) in diameter. The immobilization of PE-PCL onto the surface of MNPs was done trough urethane (-NHCO-) linkage by using 4 4'-methylenediphenyl diisocyanate (MDI). The morphological study of different nanocomposites was done by HRTEM analysis. Interestingly, particles having smaller size scales are found to be dispersed more uniformly compared to the particles having larger size range which show a gross agglomeration tendency. The variation of the value of saturation magnetization (Ms) for different sizes of MNP and their corresponding composites were studied by SQUID magnetometer measurement. A higher value of Ms was shown by 15nm-MNP compare to 5nm-MNP. The thermal stability of all nanocomposites was studied by TGA analysis. The effect of percentage of MNP content on cell viability i.e. biocompatibility was also studied by MTT assay.

Reference

[1] Zhang, J. L.; Srivastava R. S.; Misra, R. D. K. *Langmuir,* 23 (**2007)** 6342.
[2] Na, H. B.; Song, I. C.; Hyeon, T. *Adv. Mater,* 21 (**2009)** 2133.
[3] Yuan, Q.; Venkatasubramanian, R.; Hein, S.; Misra, R.D.K. *Acta Biomaterialia,* 4 (**2008)** 1024.

Oral

Role of pristine graphene tactoids and their hybrid fillers in reinforcing acrylonitrile butadiene rubber matrix.

Tony V. Varghese[a], H. Ajith Kumar[b], S. Anitha[b], S. Ratheesh[b], R.S. Rajeev[c]*,
[a]School of Nanoscience and Technology, National Institute of Technology, Calicut, India
[b]Propellant Engineering Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, India
[c]Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, India
rs_rajeev@vssc.gov.in

When Andre Geim and Konstantin Novoselov [1] proved that two dimensional one atom thick graphene is stable with exceptional properties, it generated widespread interest among polymer scientists. Graphene has been incorporated into thermoplastics, thermosets and a few elastomers mainly after suitable surface modification of the former [2-4]. In the present study, pristine graphene tactoids without any surface modification were mixed with acrylonitrile butadiene rubber (NBR) by melt mixing method to study their effect in the various properties of the rubber. The properties of the graphene incorporated rubber compositions were compared with composites containing carbon black alone and 1:1 mixture of graphene and carbon black. The studies showed that graphene significantly contribute to the cure characteristics of NBR. Incorporation of minute amount of graphene caused increase in cure characteristics such as rheometer torque (fig.1). Though similar loading of carbon black gave higher rheometer torque, this was at the expense of scorch safety.

The role of pristine graphene in reinforcing the NBR matrix is evident the analysis of mechanical properties (fig.2). Tensile strength was increased more than 190% when 5 phr graphene was added to the matrix whereas to achieve the same strength, 5 times more of carbon black was needed. Though graphene was found to increase the compression set of the rubber, the compositions containing 1:1 mixture of the fillers displayed compression set values in between those containing graphene or carbon black alone. Viscoelastic characteristics of the rubber were also found optimum for such compositions. Creep compliance of the rubber showed significant reduction in presence of graphene. The platelet structure of graphene helped in reducing the helium leak rate of the composites which is advantageous where gas barrier properties are required. The studies show that by tuning the compounding techniques, very small concentration of graphene can reinforce NBR matrix without subjecting the former to any kind of surface modification.

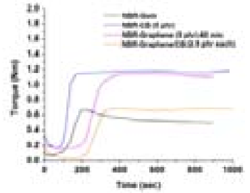


Figure 1. Comparison of rheograms of NBR-graphene, NBR-carbon black and NBR-graphene-carbon black compositions

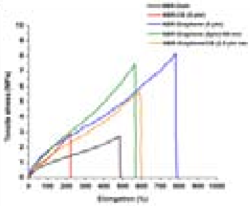


Figure 2. Comparison of stress-strain curves of selected NBR-graphene, NBR-carbon black and NBR-graphene/carbon black compositions with NBR-gum

References

[1] Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. *Science* 306 **(2004)** 666.
[2] [2] Kuilla, T.; Bhadrab, S.; Yaoa, D.; Kim, N.H.; Bose, S.; Lee, J.H. *Prog. Polym. Sci*. 35 **(2010)** 1350
[3] [3] Mu, Q.; Feng, S. *Thermochim Acta* 462 **(2007)** 70
[4] [4] Bai, X.; Wan, C.; Zhang, Y.; Zhai, Y. *Carbon* 49 **(2011)** 1608

Nanostructured Epoxy Resin/Styrenic Block Copolymer Blends and Nanocomposites

R. Adhikari[1], R Pandit[1], A. Berkessel[2], R. Lach[3], W. Grellmann[3], G. H. Michler[4]
[1]*Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal*
[2]*Department of Organic Chemistry, Cologne University, Cologne, Germany*
[3]*Centre of Engineering, Martin Luther University Halle-Wittenberg, Halle/Saale, Germany*
[4]*Department of Physics, Martin Luther University Halle-Wittenberg, Halle/Saale, Germany*
E-mail: nepalpolymer@yahoo.com

The blends of a star shaped polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymer with epoxy resin (diglycidyl ether of bisphenol-A; DGEBA) in presence of methylene dianiline (MDA) as a hardener were investigated. The SBS samples were epoxidized by using meta-chloroperoxybenzoic acid (MCPBA). It was found that the interplay between macro- and microphase separation in those blends occurs depending upon the degree of epoxidation of the block copolymer. The techniques used were Fourier transform infrared (FTIR) spectroscopy and electron microscopy (TEM as well as SEM) for the morphological characterization and microindentation tests for the determination of mechanical properties.

The presence of nanostructured morphology was attested by the optical transparency of the blends as well as of the composites with nanofiller. Consequently, the mechanical properties of the blends could be adjusted by controlling the degree of epoxidation and amount of the block copolymer used to prepare the blends. A brittle to ductile transition was observed in the copolymer modified epoxy resin.

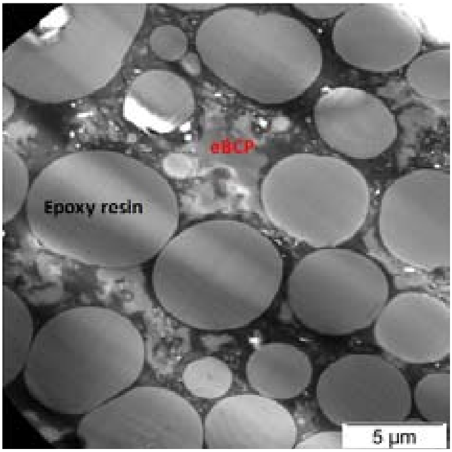


Figure 1: Phase separated structure of epoxy/ block copolymer (70/30) blend with 25% epoxidation of the butadiene units

References

[1] Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Science 306 **(2004)** 666.
[2] Kuilla, T.; Bhadrab, S.; Yaoa, D.; Kim, N.H.; Bose, S.; Lee, J.H. Prog. Polym. Sci. 35 **(2010)** 1350
[3] Mu, Q.; Feng, S. Thermochim Acta 462 **(2007)** 70
[4] Bai, X.; Wan, C.; Zhang, Y.; Zhai, Y. Carbon 49 **(2011)** 1608

Temperature and Pressure Dependence of the Viscosity of Miscible Polymer Blends

Ruth Cardinaels[a], Lucas A. Polito[a], Jürgen Pionteck[b] and Paula Moldenaers[a]*
[a]*Soft Matter, Rheology and Technology, Department of Chemical Engineering, KU Leuven, Willem de Croylaan 46, BE-3001 Heverlee, Belgium*
[b]*Department of Polymer Reactions and Blends, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straβe 6, D-01069 Dresden, Germany*
**Paula.Moldenaers@cit.kuleuven.be*

Figure 1. Pressure chamber attached under the capillary rheometer

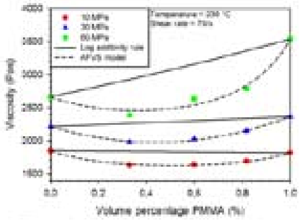


Figure 2. Viscosity versus concentration

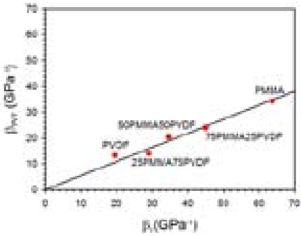


Figure 3. Pressure coefficient from PVT data versus pressure coefficient from rheology

The viscosity of molten polymers depends on the processing conditions such as temperature, pressure and shear rate. To design polymer processing equipment, the dependency of the viscosity on the processing parameters should be known. For simple polymeric systems, consisting of one component, these relations are well established. However, polymers are frequently blended to generate materials with enhanced properties. Due to their low entropy of mixing, most polymers are immiscible. Nevertheless, some miscible polymer pairs have found commercial applications. Due to possible interactions between the blend components, predicting the blend viscosity based on that of the components is non-trivial. In addition, the effects of temperature and in particular pressure on the viscosity of polymer blends have not received much attention until now. In this work, the temperature and pressure dependence of the viscosity of miscible polymer blends is systematically studied. Thereto, miscible PMMA/PVDF blends of different compositions have been prepared by melt extrusion. The melt viscosity at different temperatures and pressures is measured by means of a capillary rheometer equipped with a pressure chamber (Figure 1). With this device, exit pressures up to 70 MPa have been applied. For the temperatures and pressures under investigation the viscosity of the blends shows a negative deviation from the log additivity rule. The viscosity as a function of composition can be described with the altered free volume state (AFVS) model [1] (Figure 2). Based on the temperature and pressure dependent viscosities, temperature and pressure coefficients of viscosity are determined. These coefficients are defined by the following equations: in which ε is the temperature coefficient of viscosity and β the pressure coefficient of viscosity. Three different analysis methods [2], leading to coefficients at constant shear rate or constant shear stress, are employed. An interesting and relevant result is that both the temperature and pressure coefficients show a linear dependency on the blend concentration. Finally, the temperature and pressure coefficients of viscosity are also calculated by using the free volumes obtained from PVT measurements. This way, good estimates of the pressure coefficients can be obtained without performing tedious viscosity measurements at elevated pressure (Figure 3).

References

[1] Sood, R.; Kulkarni, M.G.; Dutta, A.; Mashelkar; R.A. *Polym. Eng. Sci.*, 28 **(1988)** 20.
[2] Cardinaels, R.; Van Puyvelde, P.; Moldenaers, P. *Rheol. Acta*, 46 (**2007)** 495.

Graphene oxide – Polystyrene Pickering Emulsions: Colloidal Nanocomposites for Self-Assembly.

Kattimuttathu I.Suresh*, K.Chithambaram, N.Rajendar and M.V.Reddy
Polymers and Functional Materials Division,
CSIR- Indian Institute of Chemical Technology,
Tarnaka, Hyderabad - 500007, A. P. (state), India.
E mail: kisuresh@iict.res.in

The fabrication of colloidal spheres into two- and three-dimensional ordered structures is one of the most exciting fields in material research since it provides a relatively simple, cost efficient strategy for fabricating nanostructured films in important potential applications, such as photonic crystals, biosensors, smart coatings, etc.., due to the structural color of the crystal films[1]. Pickering emulsion polymerization is a versatile and well defined approach for the design and production of well defined nanostructured colloids [2]. Precise control of the final structure and morphology of the resulting nanocomposites would pave the way for developing high performance nanocomposites and nanostructures. Graphene oxide (GO) is a widely studied precursor of graphene and has been the center of attention during the past few years for the production of graphene based materials [3,4]. Huang et al recently uncovered the high surface activity of GO, named it the functional surfactant [4b]. This novel characteristic of GO opens a venue for the development of a broad range of graphene based nanostructures. Recently, the self assembly behavior of GO at the liquid–liquid interface with MMA to facilitate a uniform distribution of graphene in the polymer, using an organic soluble initiator has been reported [4b].

Figure 1. Schematic of the preparation procedure used for graphene oxide – polystyrene (PS) pickering emulsions

However, the preparation of GO-pickering emulsions is not straight forward and several parameters like pH, size of the GO platelets, presence of additional surfactant etc.. need to be optimized for stable nanosized emulsions [5]. In this work we report the preparation of stable graphene oxide – polystyrene Pickering emulsions through seeded emulsion polymerization and the characteristics of the opaline crystal structures formed on drying these dispersions. The effect of parameters such as graphene oxide content on the size, morphology, optical properties as well as structural color has been studied. The self assembly behavior of the nanocomposite particles has been studied with FE-SEM and atomic force microscopy. The SEM images confirm the spherical size of the particles and its close packing into *fcc* structures upon film formation.

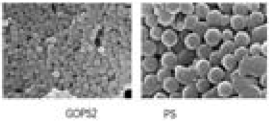


Figure 2. SEM images showing the uniform size distribution of the pickering emulsion particles prepared with GO surfactant.

References

[1] Ge, J.; Yin, Y.; *Angew. Chem. Int. Ed.*, *50,* **(2011)**, 1492.
[2] Boker, A.; He, J.; Emrick, T.; Russell, T. P.; *Soft Matter*, *3*, (**2007)** 1231.
[3] Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K.S. ; Govindaraj, A.; *Angew. Chem. Int. Ed.*, *48*, **(2009)**, 7752.
[4] Moazzami, M. G.; Sharif, F.; *Soft Matter* 7, **(2011)**, 3432; b) Kim, J. Kote, L.J. Kim, F. Yuan, W.; Shull, K.R. and Huang, J.; *J.Am.Chem. Soc. 132*, (**2010**), 8180.
[5] Song,Y.; Yang,J;.Liu and Zhao, H. *Langmuir*, *27*, **(2011)**, 1186.

Isothermal Crystallization Behavior of PP and PP-*g*- GMA Copolymer at High Undercooling

Shashidhara G. M.*, S. H. Kameshawari Devi and S. Preethi
Department Polymer Science and Technology, Sri Jayachamarajendra College of Engineering,
Mysore- 570006 INDIA
email: gm.shashi@yahoo.in

The temperature dependence of the effect of nucleating agent on crystallization becomes important since it helps to determine the processing conditions and controls the properties of molded products [1, 2, 3].

The study involves synthesis of polypropylene grafted with glycidyl methacrylate (PP-*g*-GMA) using three different initiators, benzyl peroxide, dicumyl peroxide and tertiary butyl cumyl peroxide (TBCP). Among the peroxides used, dicumyl peroxide resulted in considerable reduction of molecular weight of the resulting graft copolymer is shown in Fig1 [4]. The melting/crystallization behavior and isothermal crystallization kinetics of PP homopolymer and PP-*g*-GMA copolymers were studied with differential scanning calorimetry (DSC) at high undercooling (44–60°C).

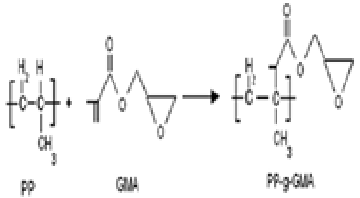


Figure.1 Chemical Reaction involved in the synthesis of PP-g-GMA copolymer

The results showed that the degree of crystallinity and overall crystallization rate of copolymers is greater than that of virgin PP. Among the three initiators used, TBCP exhibited lowest half crystallization time. The isothermal crystallization kinetics of the PP and copolymers was described with the Avrami equation and Sestak Berggren (SB) equation. The Avrami exponent n of the PP and copolymers were found to be in the range 1.03 to 1.41 at high undercooling conditions employed in this study. The agreement between the values of n calculated from SB kinetics and Avrami equation is satisfactory with few exceptions. The crystallization rate of PP-*g*-GMA copolymer was found to be more sensitive to temperature. The isothermally crystallized samples showed a single melting peak for PP while a double peak at lower temperature was recorded for PP-*g*-GMA copolymer samples. The equilibrium melting point was deduced according to Hoffman Weeks theory. The decrease of recorded for the PP modified with GMA suggests that the thermodynamic stability of the PP crystals is influenced by the chemical interactions.

References

[1] X. Xu, J. Qiao, J. Yin, Y. Gao, X. Zhang, Y. Ding,Y. Liu, Z. Xin, J. Gao, F. Huang, and Z. Song, J. Appl.
[2] Polym. Sci. 63 **(1997)** 1565.
[3] J. Li, C. Zhou, G. Wang, Y. Tao, Q. Liu and Y. Li, Polym Test, 21 **(2002)** 583.
[4] H. Lu, J.Qiao, and Y.Yang, Polym. Int. 51 **(2002)** 1304.
[5] M. Pracella, M. Minhaz Ul Haque, and V. Alvarez, Polymers, 2, **(2010)** 554.

Effect of multiwall carbon nanotubes on the segmental motions and phase separation behavior of near critical PS/PVME blends

Priti Xavier, Goutam Prasanna Kar, Suryasarathi Bose*
Department of Materials Engineering, Indian Institute of Science,
Bangalore-560012 INDIA

The effect of preferentially adsorbed polymer chains onto multiwall carbon nanotubes (MWNTs) on the concentration fluctuation, interfacial driven elasticity, phase morphology and the local segmental dynamics of the chains for near critical compositions of PS/PVME [polystyrene/ poly(vinyl methyl ether)] blends was systematically investigated using shear rheology, polarizing optical microscopy (POM), atomic force microscopy (AFM) and dielectric spectroscopy. PS/ PVME blends show viscoelastic phase separation[1] caused due to the dynamic asymmetry of the polymers, ie the large difference in their T_g. The onset of phase separation was characterized by an increase in the storage modulus due to the concentration fluctuation.[2] It was observed that PVME evolved as an interconnected network during the early stages of phase separation and coarsened into matrix droplet morphology in the late stages. The preferential adsorption of PVME onto MWNTs induced miscibility in the blends and moreover, retained the interconnected network of PVME for longer time scales as supported by rheology and POM respectively. Both the binodal and the spinodal temperatures up shifted by ca.11-12 ^{o}C in the blends in presence of MWNTs. Dielectric spectroscopic studies illustrate the effect of MWNTs on the dynamic heterogeneity and the local segmental motion of the blend, which can be attributed to the selective interaction of MWNTs with PVME.

References

[1] H. Tanaka, *Advanced Materials* **2009**, *21*, 1872.
[2] A. Gharachorlou, F. Goharpey, *Macromolecules* **2008**, *41*, 3276.

Thermally Stable Antistatic Material from Polyimide - Carbon Nanotubes Nanocomposites

Lalatendu Nayak, Dipak Khastgir, and Tapan Kumar Chaki*
Rubber Technology Centre,
Indian Institute of Technology, Kharagpur 721302, India
*Corresponding author: Tapan K. Chaki; e-mail: tapanchaki2009@gmail.com

The development of new technology and its use in different adverse environments like aerospace, high vacuum and radiation have given a great focus on high performance polymers having high thermal stability along with good chemical and corrosion resistance. Among the high performance polymers, aromatic polyimides (PIs) have received considerable scientific and technological attention due to their outstanding characteristics such as excellent thermal and radiation stability, high glass transition temperature, good flammability and exceptional tensile strength [1]. Because of their outstanding thermal and mechanical properties, they have been widely used in the manufacture of integrated circuits, thermally stable films, adhesives, coating and components in spacecraft and electromotors. However, PIs have some limitations such as their insulating nature. 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 PIs.

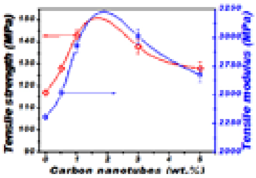


Fig. 1. Variation of tensile strength and modulus of PI/MWCNT nanocomposites with MWCNT loading

In recent times, carbon nanotubes (CNTs) have been widely used as effective fillers to enhance the electrical conductivity of PIs without deterioration of other properties. By the incorporation of this filler into PI matrix, one can produce highly conductive thin film at low filler loading and reach a level of electrical conductivity, which will be high enough for electromagnetic interference shielding and also for the prevention of electrostatic discharge. For economic reasons and to retain the intrinsic properties of the PI, very low percolation threshold of CNTs is required. The low percolation threshold depends on the preferential distribution of CNTs inside the polymer matrix. The agglomerating nature of CNTs and their weak interaction with polymers are the obstacles for low percolation threshold.

In order to reduce the agglomerating nature and achieve the electrical percolation threshold at very low filler concentration, in this investigation PI nanocomposite filled with different concentration of air oxidized multi walled carbon nanotubes (MWCNT) have been prepared by in-situ polymerization technique. The state of dispersion and interconnected conducting networks formation of MWCNT inside the PI matrix, mechanical, electrical, and dielectric properties of the nanocomposites have been investigated. The tensile strength and modulus of nanocomposite are increased by 22% and 27% respectively as compared to the pure PI matrix at 1 wt% MWCNT (Fig. 1). The DC conductivity of nanocomposite obeys the power law of percolation theory providing very low percolation threshold at 1 wt% MWCNT in PI nanocomposites (Fig. 2). EMI SE of the nanocomposites has also been investigated in X- band microwave range.

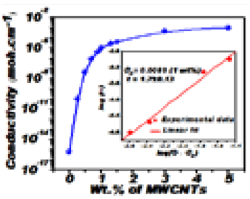


Fig. 2. DC conductivity of PI/MWCNTs nanocomposites

References:
[1] Singh B. P., Deepankar Singh, R. B. Mathur ,T. L. Dhami, Nanoscale Res Lett 3 (**2008**) 444
[2] Luonga N D., Ulla Hippia, Juuso T. Korhonenb, Antti J., Polymer 52 (**2011**) 5237e5242

Fluorescent Graphene oxide-Polymer Hybrids as Efficient Sensing Materials

Aniruddha Kundu, Rama K. Layek and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata- 700032, INDIA

Graphene oxide (GO) in acidic medium (pH 4) emits bluish green light but in neutral and alkaline medium the emission is negligible. The pH dependent fluorescence property of GO has been first observed by Chen et al [1]. Based on this phenomenon we have developed a facile route to prepare fluorescent GO-hybrid using biocompatible, non-toxic polymers namely, methyl cellulose (MC) and poly (vinyl alcohol) by non-covalent approach. The hybrids are designed as GO-MC and GO-PVA respectively. Supramolecular interaction (hydrogen bond) between GO and polymer has been found to be the main factor for enhancement of fluorescent property. Since, the H-bond interaction reduces the non-radiative electron-hole recombination induced by the different oxygen containing functional groups of GO [2]. This type of interaction has been proved by DSC, FT-IR and Raman spectroscopic investigation. The GO-MC hybrid has been used to detect nitro-explosives [3]. This hybrid system acts as a good sensor for the detection of nitro-aromatics by instantaneous photoluminescence quenching with a detectable limit of 2 ppm (Figure 1).

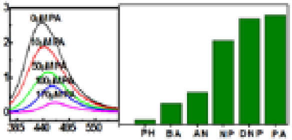


Figure 1

The GO-PVA hybrid shows fibrillar morphology as evidenced from fluorescence microscopic image and FESEM image (Figure 2), which in turn support supramolecular organization between GO and PVA by H-bonding [4]. This fluorescent GO-PVA hybrid has been used as a fascinating tool for selective sensing of Au^{3+} ion in aqueous media with a detectable limit of ~ 275 ppb. The selective sensing of Au^{3+} ion (Figure 2) is attributed to the higher reduction potential value of it, which facilitate the excitonic transfer from GO-PVA hybrid to Au^{3+} ion and hence causes selective PL-quenching.

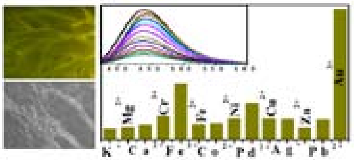


Figure 2

References

[1] Chen, J. L; Yan, X. P. *Chem. Commun.*, 29 (**2011**) 3135.
[2] Mei, Q.; Zhang , K.; Guan, G.; Liu, B.; Wang, S.; Zhang, Z. *Chem. Commun.*, 46 (**2010**) 7319.
[3] Kundu, A.; Layek, R. K.; Nandi, A. K. *J. Mater. Chem.*, 22 (**2012**) 8139.
[4] Kundu, A.; Layek, R. K.; Kuila, A. ; Nandi, A. K. *ACS Appl. Mater. Interfaces*, 4 (**2012**) 5576.

Thermal Properties of Poly(Hydroxylalkanotes)s and Stabilization of the Morphologies of the Reactive Blends of Poly(Hydroxylalkanotes)s and Epoxidized Natural Rubber

Chin Han Chan*[a], Hans-Werner Kammer[a], Yoga Sugama Salim[a,b], Seng Neon Gan[b], Kumar Sudesh[c]
[a]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia
[b]Department of Chemistry, Universiti Malaya, 50603 Kuala Lumpur, Malaysia
[c]School of Biological Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia
Email: cchan@salam.uitm.edu.my

Poly(hydroxyalkanoate)s (PHAs) are the microbial polyesters produced from fermentation. They are of the interest of scientists and environmentalists due to their wide-ranged combinations of monomers, biodegradability and biocompatibility properties. We discuss thermal properties (isothermal crystallization and the corresponding melting behaviour) of the homopolymer, poly(hydroxybutyrate) (PHB), the copolymers, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) with 12 mol% of hydroxyvalerate content as well as the poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHHx) with 3, 8 and 12 mol% of hydroxyhexanoate content. Immiscible blends of PHBV and PHB blended with epoxidized natural rubber (ENR) with 50 mol% of epoxide content are discussed in the subsequent section. The crystallinities of PHB and PHBV stay approximately constant in the blends. At temperature above the melting points of PHB and PHBV, thermal decomposition of the materials via random scission process takes place leading to shorter chains with terminal carboxyl groups. These terminal carboxyl groups may trigger chemical reactions with the reactive sites in ENR. This melt reaction may serve as *in-situ* compatiblization for these immiscible polymer blends. Isothermal melt reaction of PHB and PHBV with ENR were detected at temperatures ranging from 184 to 199 and 220 to 234 °C, respectively. The rate of reaction increases with the increasing isothermal melt reaction temperature (T_a). Merging of the separate glass transition temperatures (T_g) (corresponding to those of the neat constituents) into one T_g may reflect increasing adjustment of the two constituents after melt reaction. The rates of crystallization of PHB and PHBV impede significantly after melt reaction for all blend compositions.

Effect of Multiwall Carbon Nanotube (MWNT) Functionalization on Poly (ε-caprolactone)/MWNT Composites

Sachin Kumar, Priti Xavier, Suryasarathi Bose, Kaushik Chatterjee*
Department of Materials Engineering, Indian Institute of Science, Bangalore-560012
* author to whom all the correspondence should be addressed
Email: kchatterjee@materials.iisc.ernet.in (KC); Tel: +91-80-22933408

Poly (ε-caprolactone) (PCL) is a semi-crystalline, hydrophobic polymer used for biomedical applications. However, it cannot be used for load-bearing application due to poor mechanical properties. We are studying the effect of incorporating multiwall carbon nanotubes (MWNTs) in PCL matrix. Specifically, we are studying how surface functional groups of MWNTs can affect interactions with the polymer matrix and in turn influence the properties of the polymer.

We prepared nanocomposites by melt-mixing of PCL with different types of MWNTs: pristine (p-MWNT), ~NH_2 functionalized (a-MWNT), and ~COOH functionalized (c-MWNT). The state of dispersion of MWNTs in the nanocomposites was assessed by melt-rheology, differential scanning calorimeter (DSC) and scanning electron microscopy (SEM). SEM images indicated that all three types of MWNTs were well dispersed in PCL. Interestingly, the rheological percolation in PCL was observed between 0.25-0.5 wt% in the case of a-MWNTs whereas, it was > 0.5 wt% for both c-MWNTs and p-MWNTs. This observation indicates possible interactions, during melt mixing, between the ester carbonyl groups in PCL and the ~NH_2 functional moieties in a-MWNTs. Tensile strength of the polymer was enhanced by the incorporation of MWNTs and further increased by favorable chemical interactions in the case of a-MWNTs. DSC analysis revealed heterogeneous nucleation of PCL in presence of MWNTs. X-ray diffraction studies of the composites indicated that addition of MWNT did not changed the crystal structure of PCL. Contact angle measurement of the composites showed that addition of MWNT increased wettability of PCL with highest wettability seen in the case of hydrophilic c-MWNT. Thus, these studies indicate MWNTs can be dispersed in PCL and the functional groups on the surface of MWNTs can influence the interactions with PCL.

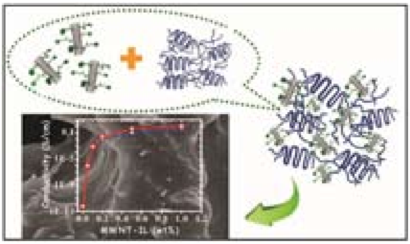
Poster

BL1

Enhancement of Mechanical and Conductivity Properties of Poly(vinylidene fluoride) Nanocomposite films by the Integration of Ionic Liquid Functionalized Multiwalled Carbon Nanotube

Amit Mandal and Arun K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata - 700 032, India.

Polymer nanocomposites have drawn considerable research interest because of their dramatic enhancement in physical, thermal, mechanical and electroactive properties [1,2]. Poly(vinylidene fluoride) (PVDF) and its copolymer have been widely studied because of their largest piezo and pyro-electric response also having five different crystalline polymorphs (α, β, γ, δ and ε) [3]. Carbon nanotubes (CNTs) are ideal nanofillers for fabrication of multifunctional materials for it's excellent electrical, thermal and mechanical properties [4,5]. The homogeneous dispersion, alignment of the nanofillers and interfacial stress transfer in polymer matrix are main criteria for these reinforcement properties in polymer nanocomposites [6]. The dispersion of CNTs in polymer matrix is difficult but it has been improved by chemical modification [7]. Ionic liquids (IL) have strong interactions with PVDF which afford new way to fabricate CNTs in PVDF films [8]. The covalent integration of CNTs with ionic moiety improves the mechanical and conducting properties due to strong interfacial interaction and easier charge transport.



Here, we functionalized the multi-walled carbon nanotubes (MWNTs) with a ionic liquid (MWNT-IL), 1-methylimidazolium bromide, which act as a compatibilizer for the homogeneous dispersion of MWNTs in PVDF matrix. The MWNT-IL incorporated into PVDF matrix by the solution and melt blending method to prepare the PVDF/MWNT-IL nanocomposite films. It was found that MWNT-IL are homogeneously dispersed in the PVDF matrix. The glass transition temperature (T_g) gradually increases and the storage modulus (G') of the composites increases significantly showing a maximum increase of 101.3% for 0.5 wt % MWNT-IL. The Young's modulus increases with MWNT-IL concentration and using Halpin-Tsai equation suggests that at low concentration they orientated parallely to the film surface but at higher concentration it is randomly oriented. The elongation at break in the solvent cast samples shows a maximum but in melt-blended samples it decreases continuously with increasing MWNT-IL concentration. The nancomposite films exhibit a very low conductivity percolation threshold at 0.05 wt% and follow three dimensional conducting networks. It shows higher conductivity (~1S/cm for 1% MWNT-IL) than other MWNT/PVDF composites system which attributed to the anchored ionic liquid from the MWNT surface.

References:

[1] Vaia, R. A.; Krishnamoorti, R. **2001**. *Polymer Nanocomposites*: *Synthesis, Characterization, and Modeling*, ed. R. Krishnamoorti, R. A. Vaia, p1. American Chemical Society, Washington: DC
[2] Moniruzzaman, M.; Winey, K. I. *Macromolecules* 39 (**2006**) 5194
[3] Lovinger, A. J. *Science* 220 (**1983**) 1115
[4] Ajayan, P. M. *Chem. Rev.* 99 (**1999**) 1787
[5] Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* 106 (**2006)** 1105
[6] Coleman, J. N.; Khan, U.; Gun'ko, Y. K. *Adv. Mater.* 18 (**2006**) 689
[7] Baskaran, D.; Mays, J. W.; Bratcher, M. S. *Angew. Chem. Int. Ed.*, 43 (**2004**) 2138
[8] Shang, S. M.; Zeng, W.; Tao, X. M. *J. Mater. Chem.* 21 (**2011)** 7274

BL2

Poly(ε-caprolactone)/ Titanate Nanocomposites for Bone Tissue Engineering

Amrit Bagchi and Kaushik Chatterjee*
Department of Materials Engineering, Indian Institute of Science, Bangalore
** kchatterjee@materials.iisc.ernet.in*

There is a need to develop scaffolds for bone tissue regeneration that closely mimic the tissue architecture inside the body. A scaffold for bone tissue engineering should exhibit good mechanical and chemical properties in order to support cell functions such as proliferation and differentiation to facilitate tissue generation.

Previously it has been shown that incorporation of titania nanoparticles improves mechanical properties of polymer matrices with improved cell growth. However, titania particles lack biochemical activity to stimulate bone cells such as that seen with hydroxyapatite. In this study, we have developed poly(ε-caprolactone) (PCL)-based nanocomposites of various titanates (Ca, Sr, Ba) that incorporate ions known to stimulate osteogenesis. Composites were prepared by dispersing nano-titanates in PCL solution. Mechanical tests indicate that the elastic modulus and yield stress increased of for all the nanocomposites in contrast to neat PCL. The increase exhibited the following trend: $CaTiO_3 > TiO_2 > SrTiO_3 > BaTiO_3 >$ Neat PCL. SEM of the cryo-fractured surfaces indicate that this increase in mechanical properties correlates with the efficiency of particle dispersion. Denser particles such as $BaTiO_3$ and $SrTiO_3$ tend to aggregate more than less dense $CaTiO_3$ and TiO_2. XRD and DSC data corroborate the results of the mechanical tests.

Nanofibrous tissue scaffolds of the composites have been prepared by electrospinning (Fig. 1). In vitro cell studies are currently underway to evaluate osteoblast response to the different composites.

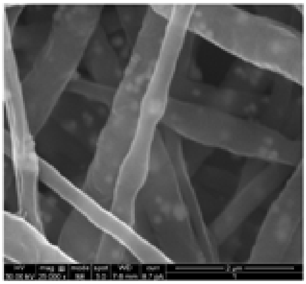


Figure 1: SEM micrograph of nanofibers of PCL-10wt%$SrTiO_3$

BL3

Non-covalent Modification of the Multiwall Carbon Nanotubes by Polyaromatic Molecule to Prepare Conducting Composites

Amrita V. Poyekar[abc], Arup R. Bhattacharyya[ab]*, Ajay S. Panwar[ab], George P. Simon[ac]
[a] IITB-Monash Research Academy,
Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
[b] Department of Metallurgical Engineering and Materials Science,
Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
[c] Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia
** Arup R. Bhattacharyya: e-mail: arupranjan@iitb.ac.in*

Polyamide6 (PA6) and acrylonitrile butadiene styrene copolymer (ABS) blends with multiwall carbon nanotubes (MWNTs) were prepared using melt-mixing by adopting simultaneous mixing protocol. In order to overcome the aggregated state of MWNTs due to significant cohesive energies [], a non-covalent approach was exploited for the surface modification of the MWNTs with a polyaromatic pyrene based molecule: 1-pyrenecarboxaldehyde (PyCHO). The state of dispersion and the localization of the MWNTs in the polymer blends as well as the phase morphology were investigated via solution experiments, scanning electron microscopic (SEM) and transmission electron microscopic analysis (TEM), AC electrical conductivity measurements and through the crystallization studies. The electrical conductivity measurements showed a significant enhancement in the electrical conductivity values in the presence of PyCHO modified MWNTs 1:1 (wt/wt) as compared to values exhibited by the blends with untreated MWNTs [Figure 1]. The blends with PyCHO modified MWNTs showed blend composition independent variation in the electrical conductivity values, as opposed to the blends with unmodified MWNTs in which a blend composition dependence of electrical conductivity was observed [].

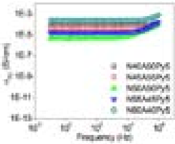


Figure 1. AC electrical conductivity with frequency for PA6/ABS blends with PyCHO modified MWNTs, (1:1) wt/wt

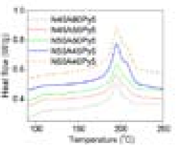


Figure 2. Crystallization exotherms of PA6/ABS blends with PyCHO modified MWNTs

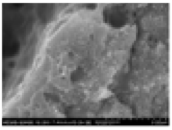


Figure 3. SEM micrograph of 60/40 (wt/wt) PA6/ABS blend with 5 wt% PyCHO modified MWNTs (ABS phase removed using THF)

The crystallization studies showed the presence of double crystallization peaks of PA6 [Figure 2] in the presence of PyCHO treated MWNTs. With increasing concentration of PA6, the height of the crystallization peak at higher temperature has increased, indicating an enhanced crystallization of PA6 chains in the vicinity of the MWNTs surface as in the case of the blend with higher PA6 concentration []. The effective surface coverage of the MWNTs surface by the PyCHO molecules is found to be the most likely reason for the decreased available surface area of the MWNTs. SEM and TEM analysis showed improved dispersion of the MWNTs in the blend due to facilitation of the debundling of the MWNTs via π-π interaction between the MWNTs surface and the PyCHO molecules [] [Figure 3].

References:

[1] Parsegian A. V., "Van der Waals Forces: A handbook for biologists, Chemists, Engineers, and Physicists" Cambridge University Press, New York, 2006.
[2] Poyekar A. V.; Bhattacharyya,A. R.; Simon G. P.; Panwar A. S.; Khare R. A.; Dhar S.; Mishra J. K., Manuscript in preparation
[3] Brosse A.C.; Girault S.T.; Piccione P. M.; Leibler L. Polymer 49 (2008) 4680.
[4] Yan Y.; Cui J.; Pötschke P.; Voit B. Carbon 48 (2010) 2603.

BL4

Polybenzimidazole–Metal Organic Framework Composites as Membrane Material for Gas Separation

Anand Bhaskar, Rahul Banerjee and Ulhas K. Kharul*
Polymer Science and Engineering Division, National Chemical Laboratory, Pune – 411008, India.
uk.kharul@ncl.res.in

Polymers as membrane materials for gas separation have been widely investigated. Their easy, reproducible and economical transformation into high surface area modules is advantageous over other type of membrane materials based on inorganic/metals. It is reflected in their current dominance in commercial membrane gas separations. Further advancement in this field is limited by trade off in gas permeation properties of polymers (i.e. increase in permeability leads to lowering in selectivity or *vice versa*) [1, 2]. Thus there is a need for new material development for improving membrane performance. To achieve this goal, one of the alternatives being pursued is to make composite membranes with porous materials such as zeolites [3], aluminophosphates [4], metal organic frameworks, (MOFs) [5] etc. This way, the advantages of polymer processability are amalgamated with gas uptake specificity and thermal stability of inorganic materials.

Metal organic frameworks are organo-inorganic hybrid porous materials with great structural and compositional diversity [6]. They seems to be good choice for composite membrane preparation due to their hybrid nature, as it can help in obtaining better compatibility with polymers.

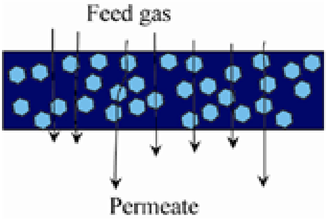


Figure 1. Schematic of gas flux through composite membrane.

Aromatic polybenzimidazoles (PBIs) have rigid molecular structure, excellent thermo-chemical stability and retention of its mechanical properties at high temperature [7]. They are good candidates for gas separation in harsh chemical environment. They have low gas permeability due to close chain packing (originating from strong interchain H-bonding). They are ideal polymers for composite membrane preparation as filler MOFs can have better adherence due to strong H- bonding interactions and can improve gas permeability due to their high porosity. In this study, we used PBI-BuI (PBI based on *5-tert*-butylisophthalic acid and *3,3'*-diaminobenzidine) and its *N*-substituted derivatives as parent polymers. CuBCT (copper benzenetricarboxilate) and ZIF-8 (zinc 2-methylimidazolate) were chosen as two representative MOFs (having high surface area and high selective CO_2 sorption) to make PBI-MOF composites. CuBTC and ZIF-8 shown different behavior in governing gas permeation properties of resulting composite membranes.

References

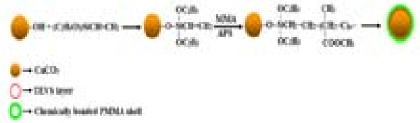
[1] L. M. Robeson, *Journal of membrane science*, 62 **(1991),** 165-185.
[2] L. M. Robeson, *Journal of membrane science*, 320 **(2008),** 390-400.
[3] T. S. Chung, L. Y. Jiang, Yi Li, Santi Kulprathipanja, *Progress In Polymer Science*, 32 **(2007),** 483–507.
[4] H. B. Tanh Jeazet, Claudia Staudt, and Christoph Janiak, *Dalton transactions*, 41 **(2012),** 14003-14027.
[5] Stephen J. Miller, Alexander Kuperman, De Q. VU, *US 2005/0139065* **(2005)**.
[6] David J. Tranchemontagne, Jose´ L. Mendoza-Corte´ s, Michael O'Keeffe and O. M. Yaghi, Chem. Soc. Rev., 38 **(2009)**, 1257–1283.
[7] H. Vogel, C.S. Marvel, Journal of polymer science, 50 (1961), 511.

BL5

Core-Shell Nano-Calcium Carbonate ($CaCO_3$)/Poly(Methyl Methacrylate) [PMMA]/ Polypropylene [PP] Nanocomposite

Aniruddha Chatterjee* and Satyendra Mishra
Department of Polymer Technology,University Institute of Chemical Technology, North Maharashtra University, Jalgaon-425001, Maharashtra, India

Calcium carbonate (nano-$CaCO_3$)/poly(methyl methacrylate) (PMMA) core-shell nanoparticles in the range of 10-100 nm were successfully synthesized by atomized microemulsion method. The polymer chains were grafted onto the surface of nano-$CaCO_3$ through triethoxyvinyl silane (TEVS) as a coupling agent. Encapsulation of nano-$CaCO_3$ by PMMA was confirmed by using transmission electron microscope (TEM). Fourier transform infrared (FTIR) spectroscopy and X-Ray Diffraction (XRD) curves revealed the existence of a strong interaction at the interface of nano-$CaCO_3$ particle and PMMA, which implies that the polymer chains were successfully grafted onto the surface of nano-$CaCO_3$ particle through the link of the coupling agent [1]. Rheological, thermal, mechanical and morphological properties of core-shell [$CaCO_3$/PMMA]/PP with different wt% loading were investigated in this paper. All composites were prepared individually by incorporating nano-$CaCO_3$/PMMA hybrid nanoparticles with 0.10-1 wt% loading on Brabender Plastograph [2]. It was shown from the experimental results that rheological, thermal, mechanical and morphological properties were improved as hybrid nano-$CaCO_3$/PS particles reinforced in PP matrix. The interaction between nano-$CaCO_3$ particles and PP matrix was significantly improved when the nano-CaCO3 nanoparticles were grafted with PMMA. SEM (scanning electron microscope) and AFM (atomic force microscope) images showed a perfect dispersion of the nano-$CaCO_3$ particles in PP matrix [3].



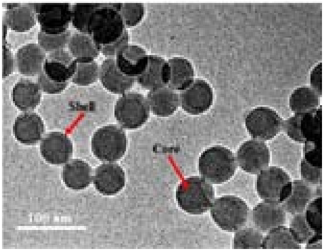


Figure 2. TEM Micrograph of nano-CaCO3/PMMA core-shell nanoparticles (CSNP)

References:

[1] Mishra, S.; Chatterjee, A.; Singh, R. P. *Polymer for Advanced Technology*, 22 (**2011**) 2571
[2] Chatterjee, A.; Mishra, S. *Particuology* (Accepted, **2012**).
[3] Chatterjee, A.; Mishra, S. *Macromolecular Research*, (Published Online, **2013**)

BL6

Epoxy Resin Formulations for Structural Composites

Anoop Anand*, Rahul Harshe, Prachi Panse, Makarand Joshi
Composites Research Center, Research and Development Establishment (Engineers)
DRDO-Ministry of Defense, Pune-411015, India
**aanand@rde.drdo.in*

The field of military services strive to design their equipment to such a standard wherein the entire paraphernalia perform the best during an inevitable combat scenario. Earlier when the domain of materials was dominated by metals and alloys, the major setbacks faced by the defence were mostly, but not limited to, low strength to weight ratio and inadequate corrosion resistance. These problems were rectified with the entry of composites into the arena of manufacturing and they are consumed currently in almost every sector of modern warfare systems ranging from deployable bridges to complex structures of fighter crafts.

Pioneering advancements in the field of composites are recently dominated by the development of hybrid composites that are conceived by the amalgamation of two or more reinforcements in a single matrix. With due regard to the emerging nanotechnology, class of hybrid composite materials has enriched its stand today; attempts have been made to hybridize load bearing composites with nanoparticles. Some prominent research has been carried out in this field and positive results have been obtained with respect to thermal and mechanical properties [1].

In the present study, Resin Film Infusion has been used for realising advanced composites with near-zero void fractions [2]. The process involves sandwiching of reinforcement fabric and polymer resin films and curing by vacuum bagging. The matrix materials are proprietary epoxy formulations that are developed in house from commercially available di glycedyl ether of Bisphenol-A based epoxy resins. The recipe has an optimal ratio of epoxies to tune the tackiness and rheological properties matching for its local flow during composite fabrication under vacuum at elevated temperatures. A cure hardener - accelerator combination ensured a straightforward curing and excellent thermal and mechanical properties. A solvent based ultrasound assisted dispersion process has also been used to disperse low loading fractions of nanofillers in the resin matrix. A complete thermal and mechanical characterisation of the resin formulations and their hybrid composites are reported.

References

[1] Anand, A.; Harshe, R; Joshi, M. *Journal of Composite Materials*, DOI: 10.1177/002199831245987312 (**2012**).
[2] Anand, A.; Harshe, R; Joshi, M. *Journal of Applied Polymer Science*, DOI: 10.1002/app.38855 (**2012**).

BL7

Effect of Modified Graphite Nanoplatelets on the Physical and Mechanical Properties of Styrene Butadiene Rubber/Polybutadiene Rubber (SBR/BR) Blends

Asish Malas, Mrinal Kanti Kundu and Chapal Kumar Das*
Materials Science Centre, IIT Kharagpur, Kharagpur-721302, West Bengal, India.
** Email i.d: chapal12@yahoo.co.in*

Recently, development of high performance tire, which shows good wet grip, wear resistance and lower rolling resistance at the same time, is the on-going direction of the tire industries. The purpose of the present research work is that expanded graphite (EG) and isocyanate modified graphite nanoplatelets filled SBR/BR blend takes the place of natural rubber (NR) in some application areas. SBR/BR blends are well-known in the rubber industry because of their applications in tread rubber compounds in tires. Expanded graphite (EG) is known as a low density carbon material, and it shows a list of individual properties: developed specific surface area (› 100 m^2.g-1), stability to aggressive influences, and moderate thermal conductivity [1]. Figure 1 shows the SEM images of the prepared EG. Figure 2 shows the structure of SBR and BR.

EG and isocyanate modified graphite nanoplatelets have been used as reinforcing nanofillers in the present investigation. EG was prepared from the graphite intercalation compounds (GICs) [2]. Isocyanate modified graphite nanoplatelets were prepared by treating oxidized EG with 2, 4-Toluene di-isocyanate (2, 4-TDI). The present study investigated the effect of isocyanate modified graphite nanoplatelets on the physical, mechanical and thermo-mechanical properties of SBR / BR blends in the presence of carbon black (CB). Graphite sheets were modified to enhance its dispersion in the rubber matrix, which resulting in an improvement in the overall physical and mechanical properties of the rubber blend. Compounds based on 50:50 of BR and SBR with ~3 wt. % nanofillers in the presence of CB were fabricated by melt intercalation. The morphology of the filled rubber blends was investigated by wide angle X-ray diffraction (WAXD) and high resolution transmission electron microscopic (HR-TEM) analysis. Intercalated and delaminated structure of the nanofiller loaded rubber blends was observed. Scanning electron microscopic (SEM) analysis of the tensile fractured surface of the rubber blends showed more rough and tortuous pathway of the fractured surface compared to the fractured surface of the only CB loaded rubber composites. Filled rubber compounds exhibit increase in the ΔS (torque difference) value and reduced scorch and cure time compared to their respective control. Dynamic mechanical thermal analysis (DMTA) of the filled rubber compounds showed an increase in the storage modulus compared to control. Isocyanate modified graphite nanoplatelets containing SBR/BR compound in the presence of CB showed an increase in the mechanical, dynamic mechanical, hardness, abrasion resistance and thermal properties compared to the alone CB filled SBR/BR blend.

Figure 1: SEM image of EG.

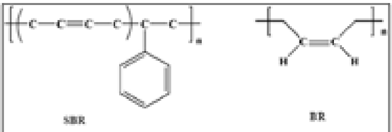


Figure 2: Structure of SBR and Polybutadiene Rubber (BR).

References

[1] Chung, DDL. J Mater Sci, 22 **(1987)** 4190.
[2] Gu, W; Zhang, W; Li, X; Zhu, H; Wei, J; Li, Z. J Mater Chem, 19 **(2009)** 3367.

BL8

Effect of silver nanoparticles on the phase separation and segmental chain dynamics of near critical PS/PVME blends

Avanish Bharati[1], Priti Xavier[2], Giridhar Madras[1], Suryasarathi Bose[2*]
[1]Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India
[2]Department of Materials Engineering, Indian Institute of Science, Bangalore-560012, India
Email: sbose@materials.iisc.ernet.in (SB)

The effect of silver nanoparticles (nAg) on the concentration fluctuation, interfacial driven elasticity, evolution of morphology and the local segmental dynamics of the chains for near critical compositions of PS/PVME [polystyrene/poly(vinyl methyl ether)] blends was systematically investigated using shear rheology, polarizing optical microscopy (POM), atomic force microscopy (AFM) and dielectric spectroscopy. It was observed that PVME evolved as an interconnected network in the early stages of phase separation which coarsened into matrix droplet morphology in the late stages. The nAg particles induced miscibility in the blends and retained the interconnected network of PVME for longer time scales as supported by rheology and POM respectively. These phenomenal changes were observed to be a function of concentration of nAg particles. Thermodynamics that drive phase separation in blends also led to migration of nAg particles to the PVME phase as supported by AFM. A bimodal distribution of the dielectric relaxation processes in the blends was observed due to dynamic heterogeneity and the local segmental dynamics of the chain segments was greatly influenced by the presence of nAg particles. The latter effect was attributed to the selective interaction of nAg with PVME. An increase in the relaxation time and activation energy in the presence of nAg particles (0.5 wt%) in the PS/PVME blends further supported the role of nAg particles in delaying the phase separation processes and augmenting the miscibility gap.

Keywords: phase separation; blends; silver nanoparticles; rheology, dielectric spectroscopy

BL9

Cobalt ferrite and Conducting polymer laminated SWCNTs for high Performance Microwave Absorbing Applications

Avinandan Mandal*, Chapal Kumar Das
Materials Science Centre-Indian Institute of technology, Kharagpur- 721302, West Bengal, India
** E-mail ID: avinandanmandal@gmail.com*

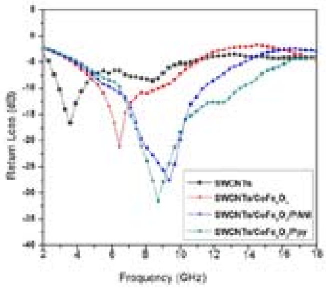


Figure 1. absorbing properties of the composite materials

The use of electromagnetic waves in the gigahertz range in wireless communication tools, local area networks, other communication equipments etc. are increasing day by day. In recent years, electromagnetic interference is a major headache mainly in civil and military applications due to increasing usage of electromagnetic wave devices [1-2]. To overcome this problem, magnetic, dielectric and also conducting materials are used as electromagnetic wave or microwave absorbers with high loss energy. The excellent microwave absorber should have certain criteria such as absorb strong microwave radiation over a wide range of frequency; preferably should be thin and lightweight. Magnetic materials such as ferrites, magnetite, hematite etc are effectively used for microwave absorption. Low densities, electrical conductivity, thermal and chemical stability of SWCNTs are attributed to the dielectric loss of target materials. Composites, prepared by two or more materials with definite combination show enhanced properties that are not found in the individual component.

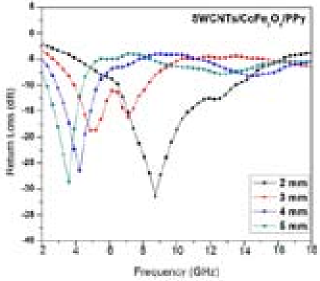


Figure 2. absorbing properties of SW-CNTs/CoFe2O4/PPy composites with different thicknesses

In this study, $CoFe_2O_4$ coated SWCNTs have been successfully prepared by in situ high temperature hydrolysis method [3]. After that, conducting polymer (PANI/PPy) laminated SWCNTs@$CoFe_2O_4$ have been synthesized via oxidative polymerization method. Composite samples were prepared by uniformly mixing the powders in paraffin matrix and then pressing the mixture into a cylindrical shaped mold (φ_{outer}= 7.00 mm and φ_{inner}= 3.04 mm). The electromagnetic parameters of the composites were measured in the 2-18GHz range by employing Agilent vector network analyzer (PNA E8364B). Figure 1 shows the absorbing properties of the composite materials. SWCNTs/CoFe2O4/PPy composite achieved a reflection loss below−10dB (90% absorption) at 6.5–13.5 GHz, and the minimum value is −31.52 dB at 8.72 GHz. Figure 2 shows the absorbing properties of SWCNTs/CoFe2O4/PPy composites with different thicknesses. From Figure 2, it was seen that with increasing sample thickness, the slopes of return loss of the developed nanocomposites shifted toward lower frequency region. The composite materials exhibited microwave absorbing properties mainly due to dielectric loss [4].

References:

[1] Feng, Y.B.; Qiu T.; Shen, C.Y. *J. Magn. Magn. Mater*. 318 **(2007)** 8
[2] Xu, P.; Han, X.; Jiang, J.; Wang, X.; Li, X.; Wen, A. *J. Phys. Chem. C*. 111**(2007)** 12603
[3] Liu, Y.; Jiang, W.; Xu, L.; Yang, X.; Li, F. Materials Letters. 63 **(2009)** 2526
[4] Roberti, D.M.; Smyth, C.P. *J. Am. Chem. Soc*. 82**(1960)** 2106

BL10

Microwave assisted synthesis and characterization of polyimide/ functionalized MWCNTs nanocomposites

B. Govindaraj* and M. Sarojadevi
Department of Chemistry, Anna University, Chennai-600 025, India.
seenuchemist@gmail.com

Polyimide-MWCNT nanocomposites were prepared by the reaction of a heterocyclic diamine monomer of bis(4-amino-3,5-dimethylphenyl)-2-chloro-3-quinolylmethane (BACQM), pyromellitic dianhydride (PMDA) with unmodified MWCNTs (MWCNTs), acid-functionalized MWCNTs (Acid-MWCNTs) or amine-functionalized MWCNTs (Amine-MWCNTs) using microwave irradiation and as well as the conventional method. The structure of the monomer was confirmed by FT-IR, ^{1}H- NMR and ^{13}C-NMR. The glass transition temperature (T_g) of the MWCNTs/polyimide nanocomposite was found to be higher than that of the unfilled polyimide system. The T_g's of both systems were higher with the microwave method than the conventional synthesis. The T_g's of the nanocomposites using acid-MWCNTs and amine-MWCNT were greater than 300 °C, with both methods. This is attributed to the presence of hydrogen bond and strong covalent bond in the acid-MWCNT/polyimide and amine-MWCNT/polyimide systems respectively[1]. The morphological studies of the composites synthesized using microwave irradiation shows that a distinct MWCNT nano-fibrillar network is formed in the matrix when MWCNT or acid-MWCNT is used. A homogeneous morphology, without distinct nanotube domains is seen when the amine-MWCNT is covalently linked to the polymer [2,3].

References:

[1] Y. Siu-Ming.; M. Chen-Chi.; L. Yao-Yu.; K. Hsu-Chiang. *Comp Sci & Tech* 67 (**2007**) 2564-2573
[2] H. Yizhe.; W. Liping.; S. Jianfeng.; Y. Mingxing. *Journal of App Pol Sci* 110 (**2008**) 701– 705
[3] S. Singh.; Y. Pei.; R. Miller.; and P. R. Sundararajan. *Adv. Func. Materials* 13 (**2003**) 868- 872

BL11

Synthesis and Morphological Studies of TiO_2/Polyaniline Nano Composite

*B. Kavitha, D. Srinivasu, Ch. Srinivas, K. Siva Kumar, N.Narsimlu
Department of Physics, Osmania University, Hyderabad. 500 007 INDIA
Email:bkavithaou@gmail.com

Among the conducting polymers, Polyaniline (PANI) is a promising material with high environmental stability and electrical conductivity. It is a unique polymer which can be synthesized with tunable electrical conductivity, energy level splitting and morphology. Most of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, large number of papers published in the last five years would indicate the importance of polyaniline.

TiO_2/Polyaniline nanocomposite is synthesized by *In- Situ* chemical polymerization of aniline in presence of TiO_2 nanoparticles with hydrochloric acid as a catalyst and ammonium-peroxydisulphate [APS] as an oxidant. Morphological studies on PANI, TiO_2 and PANI/TiO_2 are performed with Small angle neutron scattering (SANS), X-ray diffraction (XRD), Scanning electron microscope (SEM) and Dynamic light scattering (DLS). The Guinier plots in SANS studies indicate that the shape of PANI is in fiber form, TiO_2 is in spherical form and their composite is in complex with compact. The physical parameters extracted from SANS data by using the Guinier equation $I(Q)= I(o)\exp [(-Q^2 (R_g{}^2)/3]$ are presented in the Table 1

Table1. Physical parameters of TiO_2/PANI nanocomposites calculated by SANS

S.No.	Particle	Correlationlength (nm)	Diameter Nm	Surface fractal dimension
1	PANI	11.919	52.09	2.65
2	TiO_2	49.433	77.58	2.31
3	PANI/TiO_2	03.820	16.97	2.82

The room temperature XRD studies are performed on PANI, TiO_2 and the composite with Cu K_α X-rays. The inter-planar distances are estimated with Bragg's law $2d \sin\theta = n\lambda$ and Crystallite size is calculated with the Debye Scherer equation $D = 0.89\lambda/\beta \cos\theta$. These results indicate that the polyaniline contains semi crystalline nature and composite is more compact than the individuals. The SEM studies of PANI shows that the morphology is in fiber form with diameter 50nm and length 550nm. The SEM image of TiO_2 indicates that the particles are in spherical shape with diameter 80 nm. Finally the composite SEM image indicates compact structure with minimum voids. DLS studies on PANI indicate fiber nature with diameter 150.1 nm and length 617.6 nm. Similarly DLS studies of TiO_2 reveal spherical shape with 400nm diameter. These results also indicate swelling of PANI and TiO_2 in aqueous medium.

Key words: PANI, XRD, SEM, SANS, DLS and Core/shell structure

Acknowledgments:

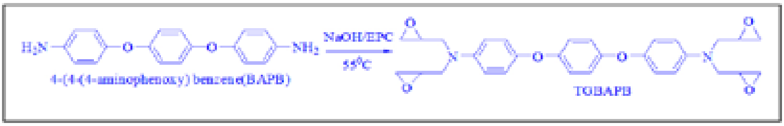
The Authors are sincerely acknowledges the UGC-DAE CSR Mumbai center for providing the research (CRS) project No. UDCSR/MUM/AO/CRS-M-181/12/035.

BL12

Synthesis and Characterization of Novel Ether containing Tetraglycidyl Epoxy Clay Nanocomposites

D.Duraibabu[a], P.Saravanan[a], M.Alagar[b] and S. Ananda Kumar[a]*
[a]*Deparment of Chemistry, Anna University, Chennai-600 025, India.*
[b]*Department of Chemical Engineering Anna University, Chennai-600 025, India.*
**Corresponding author: Dr. S. Ananda Kumar (sri_anand_72@yahoo.com)*

The TGDDM epoxy is widely used as matrix materials in advanced polymeric composites because of its versatile properties [1, 2]. However, TGDDM has a major drawback of brittleness, which restricts its many end-use applications [3]. To allivate the above deficient behaviour, an attempt has been made to develop ether containing tetra functional epoxy resin namely TGBAPB using skeletal modified diamine BAPB [4, 5, 6] and cured by DDM.



A new type of tetra functional epoxy resin (TGBAPB) was synthesized via 1,4'-bis (4-amine-phenoxy)benzene (BAPB) and epichlorohydrin. The molecular structure of TGBAPB epoxy resin was confirmed by FTIR and NMR spectroscopy and molecular weight determination by mass spectral study. The TGBAPPP epoxy resin was cured with diaminodiphenylmethane (DDM) curing agent. Octadecyl ammonium ion modified montmorillonite (OMMT) clay with varying weight percentages (1-5wt %) was reinforced with TGBAPB in order to study its effect towards improved mechanical properties of the resultant nano-composites. The thermo-mechanical behaviour of TGBAPB epoxy resin and its nano-composites was examined by dynamic mechanical thermal analysis (DMTA), and thermo gravimetric analysis (TGA). The surface morphology of the epoxy nanocomposites was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force of microscopy (AFM) studies. The TGBAPB epoxy clay nano-composite having enhanced thermo-mechanical properties appears to be an ideal candidate for advanced aerospace application.

References

[1] Lee, H.; Nevile, K. Handbook of Epoxy Resin, McGraw Hill, New York **(1967)**.
[2] Bauer, R.S. Epoxy Resin Chemistry, Advanced in Chemistry Series, ACS, Washington DC. (**1979**) 114.
[3] Park, S. J.; Jin, F. L.; Lee, J. R. *Materials Science and Engineering A,* 374 **(2004)** 109.
[4] Zhang, X. H.; Huang, L. H.; Chen, S.; Qi. G. R. *Exp.Poly.Lets,* 1 (5) **(2007)** 326.
[5] Yu Shao, Yan Feng Li, Xiao Long wang, Jin Shan Guo, Xin Zhao, *Chinese chemical letters,* 18 **(2007)** 762.
[6] Mustata, F.; Bichu, I. J. Appl. Polym.Sci, 77 **(2000)** 2430.

BL13

Percolation Driven NanoSilica Network Reinforcement of "Silicone" Elastomer

Anubhav Saxena,[*, a] Debarshi Dasgupta,[a] Shreedhar Bhat,[a] Sandip Tiwari,[a] Laxmi Samantara,[a] Dieter Wrobel[b]
[a]Global Research & Development Centre, Momentive Performance Materials Pvt. Ltd; Survey # 9, Electronic City West (Phase-1), Hosur Road, Bangalore-560100; India
[b]Research & Development Centre, Momentive Performance Materials GmbH; Building R20; 51368 Leverkusen, Germany
Anubhav.saxena@momentive.com

Silicone elastomers have come up as highly desirable performance polymers over synthetic organic elastomers because of their remarkable properties like superior elongation at break, wide operating temperature window, excellent weatherability, high dielectric constant, ease of functionalization and biocompatibility.[1-3] More often, platinum catalysed hydrosilylation reaction is used to vulcanize reactive poly(dimethyl siloxane) (PDMS) chains to produce highly cross-linked elastomeric network.[4] However, a cross-linked PDMS network cannot alone qualify on the mechanical parameters required for desirable elastomeric application and hence reinforcing fillers are compounded prior to thermoset formation.[5] In practice, colloidal silica or fumed silica nanofillers are compounded to improve upon tensile and tear strength properties.

The current contribution highlights the dominant effect of nanofiller morphology on elastomer properties. Tailor made nanosilica assembly (referred to as SS-Silica) was synthesized by sol-gel route and investigated for its reinforcement ability of high performance silicone elastomer systems. While commercial colloidal nanosilica (denoted by CS Silica) was used as benchmark filler, the beneficial effect of mesoscale network morphology of SS-silica in silicone elastomeric matrix was unravelled. Nanosilica reinforced liquid silicone rubber (LSR) sheets were fabricated using compression molding technology and characterized by standard analytical protocols. The mechanical properties of the elastomer sheets are found to be strongly dependent on the concentration and global morphological state of the particle fillers used. The mesoscale nanosilica network morphology of sol-gel nanosilica imparts efficient stress bearing ability on the formulated LSR. Thus, the interconnected tailor-made silica particulate networks offer a suitable replacement for fumed silica to remarkably reinforce mechanical properties for LSR sheets with no compromise on elongation when enforced into PDMS chains at and above 20% compared to those of the commercial colloidal silica nanocomposites under identical conditions. Moreover, the current methodology involves in-situ surface modification to avoid "creep hardening" of elastomer whereas commercial nanofillers always need to be surface treated additionally during industrial scale production.

References

[1] Mark J. E.; Erman, B.; "*Rubber-like elasticity: a molecular primer. 2nd ed.*" Cambridge: Cambridge University Press; (**2007**).
[2] Mark, J. E. Acc. Chem. Res., 37 (2004) 946.
[3] Saxena, A.; Markanday, M.; Sarkar, A.; Yadav, V. K.; Brar, A. S. Macromolecules, 44 (2011) 6480.
[4] Delebecq, E.; Hermeline, N.; Flers, A.; Ganachaud, F. *ACS Appl. Mater. Interfaces,* 4 (**2012**) 3353.
[5] Joshi, V.; Srividhya, M.; Dubey, M.; Ghosh, A. K.; Saxena, A J. Apl. Polym Sci. (2013) DOI: 10.1002/APP.39112

BL14

Graphene decorated with Ag deposited $Ni(OH)_2$: smart electrode material for supercapacitor application

Debasis Ghosh and Chapal Kumar Das*
Materials Science Centre, IIT Kharagpur, Kharagpur -721302, West Bengal, India
**E-mail: chapal12@yahoo.co.in*

In concern to the global warming and ecological balance, Supercapacitor has instigated a new era in the field of pollution free energy storage and conversion. Supercapacitors are the new generation energy storage device with the hybrid properties of conventional batteries and conventional capacitors in terms of high energy density and high power density. The other unique features associated with the supercapacitors stand as outstanding cycle stability, very fast rate of charge discharge and almost maintenance free, and find applications in hybrid electronic vehicles, space ship, portable electronics, fast acting short term power back up for UPS, laser pulsed, digital camera, etc [1-2]. Depending on the charge storage mechanisms supercapacitors can be classified into two categories: electrical double layer capacitors (EDLCs) and pseudocapacitors [3]. Graphene is an assembly of 2D honeycomb type arrangement of sp^2 hybridized C atoms having the highest conductivity and highest specific surface area amongst the carbonaceous materials and acts as EDLC source. $Ni(OH)_2$ is an important member of the pseudocapacitor family due to its well defined redox activity, relative low cost and ease to handle. In our present work, we have mainly focused on the increased utility of the pseudocapacitance of the redox active materials combining with the high surface area carbonaceous material. we have successfully synthesized $Ni(OH)_2$ via a hydrothermal route and UV assisted Ag deposited $Ni(OH)_2$ [$Ag@Ni(OH)_2$].We have also synthesized graphene based hybrid composite of the as prepared $Ni(OH)_2$ and $Ag@Ni(OH)_2$ and studied their electrochemical performances. Graphene increases the utility of the pseudocapacitive $Ni(OH)_2$ and Ag deposited $Ni(OH)_2$ as electrode material. Electrochemical characterizations in 6 M KOH electrolyte revealed superior electrode performance of the Ag deposited $Ni(OH)_2$/graphene composite over $Ni(OH)_2$/graphene composite with maximum specific capacitance of 496 F/g at 1A/g current density accompanying 93% specific capacitance retention at the end of 500 consecutive charge discharge cycles.

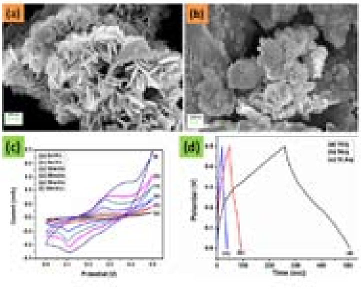


Fig. 1 FESEM image of (a) Ni(OH)2, (b)Ag@ Ni(OH)2/graphene, (c) CV plots and (d) CCD plots of Ag@Ni(OH)2/graphene nanocomposites.

References:

[1] H. Gao, F. Xiao, C. B. Ching, H. Duan, ACS Appl. Mater. Interfaces, 4 (2012) 2801.
[2] F. Marchioni, J. Yang, W. Walker, Fred Wudl, J. Phys. Chem. B, 110 (2006) 22202.
[3] Conway, B. E. Electrochemical supercapacitors: Scientific Fundamentals and Technological Application; Kluwer Academic/Plenum: Dordrecht, 1999.

BL15

Synthesis and Characterization of Eco-Friendly Chitosan Based Nano Composite Coatings for Corrosion Protection of Mild Steel in Saline Water.

G. Ruhi* and S.K. Dhawan
Polymeric & Soft Materials Section, (CSIR), National Physical Laboratory,
New Delhi, 110012, India
drgazala24@yahoo.co.in

In present work, Chitosan-polypyrrole nano composite of uniform diameters were synthesised by in situ chemical oxidative polymerisation of pyrrole in chitosan solution using $FeCl_3$ as an oxidant. Chitosan-polypyrrole nano coatings were developed on mid steel substrates using powder coating technique. FTIR spectroscopy of nanocomposites revealed the characteristic peaks of pyrrole and chitosan [1,2]. SEM and HRTEM studies (Fig. 1) revealed the homogenous distribution spherical nano particles (size ~ 50nm) of chitosan and polypyrrole arranged in a regular pattern. EDX and XRD analysis confirmed the presence respective elements and semi-crystalline nature of the nano powder, respectively. Thermo gravimetric analysis (TGA) was performed to analyse the thermal stability of the nano composite. TGA data showed a minimum weight loss of the chitosan-polypyrrole nano composite in the temperature range of 250^0-340^0C as compared to chitosan alone. It suggested a better thermal stability of the composite as a result of the synergistic interaction between chitosan and polypyrrole chains. The Differential Scanning Calorimetry (DSC) curve revealed the glass transition temperature of the nano composite to be 138.2^0 C. Coatings were developed by blending the synthesised nano composite powders with epoxy at different weight percent (1, 2, 3 and 4 wt %) and simultaneously spray coating on the mild steel substrates using electrostatic spray gun. Tafel polarisation curves and Bode plots of the coated and uncoated mild steel specimens in 3.5% NaCl solution exhibited a significantly less corrosion current (i_{corr}) and high modulus of impedance [3], respectively for the steel specimens coated with nano composite powder. Corrosion test of the steel panels (coated and uncoated) in accelerated conditions (as per ASTM standards) in high relative humidity and salt content shows significantly high corrosion resistance for the coated steel.

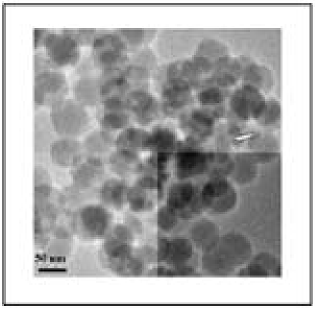


Figure 1. TEM image of Chitosan-polypyrrole nano composite.

References

[1] S. Radhakrishnan, N. Sonawane and C.R. Siju, *Prog. Org. Coat*. 64 (2009) 383.
[2] J. Lei, W. Liang, and C. R. Martin, *Synth. Metals*, 48 (1992) 301.
[3] J. O. Iroh, W. Su, *Electrochim. Acta*. 46 (2000) 15.

BL16

Nanostructured Polymeric membranes for Fuel Cell Application

R. N. Jana*, S. Mallick, A. Majumdar, and P. Singh
Department of Chemical Engineering, Haldia Institute of Technology,
ICARE Complex, Haldia-721657, Purba Medinipur, West Bengal, INDIA
**Corresponding author's e-mail: rabindrajana@yahoo.com*

In order to fulfill the increasing demand of power requirement from the advent of civilization, the fuel cells are nowadays, attractive because they provide an alternative power source with higher energy density. Again the fuels used in the cell are renewable, and have low environmental affects. Therefore, a considerable research work is focused on improving the efficiency of the fuel cells by different researchers [1-7]. However, till now, an overall efficiency for a methanol fuel cell is reported to be about 20 ~ 25%. The lower efficiency of the cell may be due to the critical factors, e.g. slow reaction kinetics at the anode and methanol crossover. Surprisingly, there are very limited reports on nanostructured membranes, which are rather simple to manufacture with different tunable compositions and are expected to allow only the proton permeation but not the methanol due to their molecular sizing effects and affinity to the membrane surface.

We have prepared nanostructured polymeric membranes by melt-mixing of polydimethyl siloxane rubber (PDMS) and ethylene methyl acrylate copolymer (EMA) (75:25 w/w) with different proportions (0 ~ 0.5 wt %) of functionalized multi-walled carbon nanotubes (f-MWNTs). The membranes were evaluated in terms of thermal stability, chemical resistivity, water absorption, proton conductivity, and methanol permeability (Fig. 1.). Fourier transform infrared (FTIR) spectroscopy showed that there was a covalent bond formation between PDMS and EMA. Phase morphology studied by SEM showed a good dispersion of f-MWNTs in the blend matrix (Fig.2). The proton conductivity and methanol permeability of the membranes were found to be dependent on f-MWNTs loading. There was a significant improvement in thermal stability of the composite membranes by using the f-MWNTs. There may be a significant cost savings by using the said composite membranes which contain less expensive polymers rather than the commercially available fuel cell membranes.

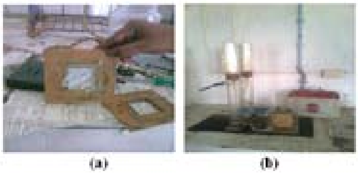


Fig 1. (a) Fuel cell membrane, (b) Fuel cell test set up

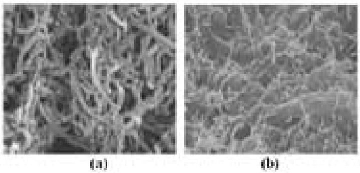


Fig 2. SEM Photomicrographs of (a) f-MWNTs and (b) Composite membrane

References

[1] Jana, R. N.; Bhunia, H. *Solid State Ionics*, 178 (**2008**) 1872.
[2] Sumner, M. J.; Harrison, W. L; Weyers, R. M.; Kim, Y. S.; McGrath, J. E.; Riffle, J. S.; Brink, A.; Brink, M.
[3] H. *J Membr Sci.,*239 (**2004**) 199.
[4] Scott, K.; Taama, W. M.; Argyropoulos, P. *J Membr Sci.,* 171 (**2000**) 119.
[5] Kim, B.; Kim, J.; Jung, B. *J Membr Sci* 250 (**2005**) 175.
[6] Kang, M. S.; Kim, J. H.; Won, J.; Moon, S. H.; Kang, Y. S. *J Membr Sci* 247 (**2005**) 127.
[7] Smit, M. A.; Ocampo, A. L.; Espinosa-Medina, M. A.; Sebastian, P. J. *J Power Sources*, 124 (**2003**) 59.
[8] Poltarzewski, Z.; Wieczorek, W.; Przyluski, J.; Antonucci, V. *Solid State Ionics*, 119 (**1999**) 301.

BL17

Effect of MMT and OMMT loading on thermal, mechanical, physical and morphological properties of millable polyurethane (MPU) rubber

Harishchandra A. Sonawane, Ananda D. Mali, Navinchandra G. Shimpi, Satyendra Mishra
Department of Nanoscience and Technology, University Institute of Chemical Technology,
North Maharashtra University, Jalgaon, 425001, Maharashtra

MPU rubber: montmorillonite (MMT) and MPU rubber: organically modified montmorillonite (OMMT) nanocomposites were prepared on two-roll mill and moulded on compression moulding machine separately. The amount of loading of MMT and OMMT were from 0.5-2.5 wt % followed by addition of dicumyl peroxide (as a curing agent). The compounded matter was subjected to compression moulding so as to get a square sheet (130 x 130 x 3 mm). Mechanical (tensile strength, elongation at break (%) and abrasion resistance index), physical (hardness and swelling index) and thermal properties (flammability retardancy and degradation stability) of MPU nanocomposites were studied. The extent of dispersion of fillers was studied using field emission scanning electron microscope (FESEM). Meanwhile the surface modification of montmorillonite MMT was performed by ion exchange chromatography using Octadecyl amine as interfacial agent and confirmed by Fourier transfer infrared spectroscopy (FT-IR).The increased in interlayer spacing of OMMT was confirmed using X-ray diffraction (XRD), which was found to be ~31.5 Å, while for MMT it was 16 Å. MPU: OMMT nanocomposites shows improved mechanical, physical and thermal properties compared to pristine MPU and MPU: MMT composites. This improvement was due to uniform dispersion of OMMT within MPU rubber matrix. However higher loading of MMT and OMMT shows marginal decrement in properties due to agglomeration, especially at1.5 and 2.5 wt % respectively.

References

[1] Mishra, S.; Shimpi, N.G.; Mali, A.D. *Macromol Res.,* 20(1): **(2012)** 44-50.
[2] Mishra, S.; Shimpi, N.G.; Mali, A.D. *Macromol Res.,* **(2012)**. DOI: 10.1007/s13233-013-1035-4

BL18

Bionanocomposites Based on Agar and Cellulose Nanowhiskers Hydrolyzed from Onion Skin: Effect of Acid Concentration

Jeevan Prasad Reddy and Jong Whan Rhim*
Department of Food Engineering, Mokpo National University, 61 Dorimri, Chungkyemyon, Muangun, 534-729, Jeonnam, Republic of Korea
Corresponding Author: jwrhim@mokpo.ac.kr

Reduction of packaging waste has been a strong motivation for replacing plastic packaging materials by biodegradable materials from renewable sources during the last decades. Cellulose nanofibers are inherently a low cost and widely available material [1]. Moreover, they are environmentally friendly and easy of recycling by combustion, and require low energy consumption in manufacturing. All of this makes cellulose nanofibers an attractive class of nanomaterials for elaboration of low cost, lightweight, and high-strength nanocomposites [2]. Ligno-cellulosic agricultural waste materials have attracted considerable attention for producing bio-composites and bionancomposite materials [3]. With this motivation, the present work is aimed to extract cellulose nanowhiskers (CMF) from agricultural waste fibres from onion skin.

For the first time we used onion skin waste as a resource to extract cellulose and cellulose nanowhiskers. α-cellulose, hemi-cellulose and lignin contents of onion skin, onion stalk, garlic skin and garlic stalk were determined by alkaline extraction method. Cellulose nanowhiskers were prepared by sulfuric acid hydrolysis from onion skin cellulose microfibers which had previously been extracted fron onion skin by alkaline extraction method. The eefect of acid concentration (45%, 55% and 65% W/v H_2SO_4 on structural, thermal and morphological properties were investigated. Also cellulose nanowhiskers reinforced bionanocomposites prepaered with the agar biopolymer matrix. The mechanical, water vapour barrier and morphology properties of the bionancomposites were inestigated.

The result revealed that the α -cellulose content of the onion skin is 38%. The tensile properties of the cellulose nancowhisker reinforced agar composites higher than that of native onion skin fibre composites. The water vapor permiability (WVP) of the onion skin/Agar composite higher than that Agar biopolymer. Further the WVP of the cellulose nanowhiskers reinforced composites is same as Agar biopolymer. This study revealed that the onion skin waste is an interesting alternative as cellulose source for several applications. This research is also support that the cellulose nanowhiskers effctively enhanced tha mechanical bareier properties of the biopolymer film which can be used for food packgaing applications.

References:

[1] Gilberto, S.; Julien, B.; Alain, D. *Polymers,* 2 (2010) 728
[2] Satyanarayana, K.G.; Guilmaraes, J.L.; Wypych, F. *Compos. A-Appl. Sci. Manufact*. 38 (2007) 1694
[3] Bledzki, A.K.; Gassan, J. *Prog. Polym. Sci*, 24 (1999) 221

BL19

An Investigation on the State of Dispersion of Various Multiwall Carbon Nanotubes in Polypropylene Matrix

Joyita Banerjee[1], Arup R. Bhattacharyya[1]*, Ajay S. Panwar[1] and Kingsuk Mukhopadhyay[2]
[1]*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India*
[2]*Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur 208013, India*
** Arup Ranjan Bhattacharyya: e-mail id - arupranjan@iitb.ac.in*

This work involves the characterization of various types of multiwall carbon nanotubes (MWNTs), of different aspect ratio and purity. Several characterization studies viz. Raman spectroscopy, X-ray photoelectron spectroscopy, Fourier transfer infra-red spectroscopy and various other analytical techniques have been employed to characterize MWNTs. Scanning electron microscopic (SEM) analysis was carried out to analyse the surface morphology of the MWNTs and transmission electron microscopic (TEM) analysis was performed to characterize the diameter and the extent of entanglement associated with the respective MWNTs. A significant difference has been observed in MWNTs diameter (Figure1 and 2) and also the extent of purity as observed from the I_d/I_g values of MWNTs via Raman spectroscopic analysis [1]. MWNTs obtained from Nanocyl, Belgium have shown a lower value of I_d/I_g ratio as compared to D-MWNTs (DMSRDE synthesized MWNTs) which confers that N-MWNTs exhibit a higher graphitic content.

Furthermore, the isotactic polypropylene and MWNTs (PP/MWNTs) composites were prepared through melt-mixing by a conical twin screw microcompounder [2]. A comprehensive study was carried out to understand the state of dispersion of different types of MWNTs within the PP matrix through various morphological, spectroscopic and thermal studies. Further, in order to assess the interfacial interaction between the PP matrix and the different types of MWNTs, rigid amorphous fraction (RAF) [3;figure3] was calculated using modulated differential calorimetry (MDSC) and it was observed to be higher in case of PP/N-MWNTs as compared to PP/D-MWNTs composites. Moreover, an attempt has been made to improve the state of dispersion of MWNTs with the addition of a novel modifier; Li-AHA (Li-salt of 6-amino hexanoic acid), which could be assessed via microscopic studies and the mechanism of state of dispersion of modified MWNTs within the PP matrix has been validated through electrical conductivity measurements of the composites.

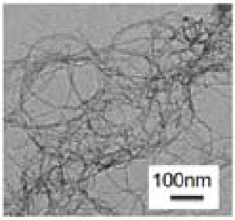


Figure 1. TEM micrographs of N-MWNTs

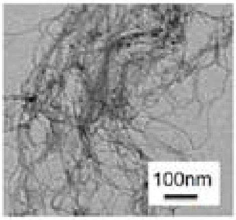


Figure 2. TEM micrographs of D-MWNTs

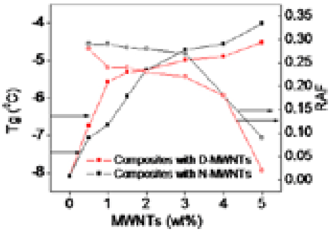


Figure 3. Variation of Tg and RAF with MWNTs

References

[1] Tambe P.B.; Bhattacharyya A.R.; Kulkarni A.R.; *J. Appl. Polym. Sci.* 127 (**2012**) 1017-1026
[2] Bhattacharyya A.R. ; Khare R.A.; Kulkarni A.R.; Panwar A.S.; *Polym. Engg. and Sci*, 51 **(2011)** 1891
[3] Zia Q.; Mileva D.; and Androsch R.; *Macromolecules, 41* (**2008**), 8095-8102
[4] Pötschke P.; Bhattacharyya A.R.; A. Janke A.*; Carbon*, 42 **(2004)** 965

BL20

Nano Modified Self-Cleaning Sol Gel Coatings

[ab]Ruchi Grover Wankhede*, [ab]Karan K Thanawala, [b]A. S. Khanna, [c]N. Birblis
[a]*IITB-Monash Research Academy, Mumbai, India*
[b]*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, India*
[c]*Department of Materials Engineering, Monash University, Victoria, Australia*
** Emai Id.: 123ruchi@gmail.com*

Combination of both low surface energy and surface roughness are the prime requirements to develop hydrophobic self cleaning surfaces. The present work focus on development of hydrophobic organic- inorganic hybrid sol-gel coatings using GPTMS and MTMS as silane precursors and HMMM as crosslinker followed by incorporation of nano-ZnO and HMDZ fume silica particles leading to enhanced surface roughness. Nano modified sol-gel coatings were then grafted by per-fluoro groups in order to achieve lowering of surface energy. As developed coatings showed excellent self cleaning and water repellent properties with C.A. of about 120° on aluminium and about 140° on several other porous substrates like cotton, wood, concrete and paper. Such coatings also exhibit enhanced U.V. blocking, corrosion resistant and mechanical properties.

Contact Angle (CA) Analysis was carried on various nano-modified sol-gel coated aluminium samples. CA of neat sol-gel coated sample was found to be only 70° whereas after nano-particle modification higher values of CA i.e. 105° and 110° for nano-ZnO and HMDZ fume silica, respectively were achieved due to enhancement in surface roughness which is the second important requirement for achieving water repellency along with lower energy. It was found that after addition of per-fluoro polymer, the contact angle further increased upto 120° for both the nano-particles, however, a very low sliding angle of 25° was achieved for HMDZ fume silica addition, whereas the sliding angle achieved for neat and nano-ZnO modified sol was 90° and 45° respectively

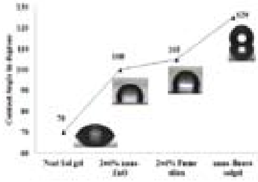


Figure 1. Variation of CA with nano-particle addition on aluminium substrate

References

[1] R.V. Lakshmi, T. Bharathidasan, P. Bera, B.J. Basu, Surface and Coatings Technology, 206 **(2012)** 3888-3894.
[2] D. Ebert, B. Bhushan, Langmuir, 28 **(2012)** 11391-11399.
[3] R.P.S. Chakradhar, V.D. Kumar, J.L. Rao, B.J. Basu, Applied Surface Science, 257 **(2011)** 8569-8575.
[4] A. Nakajima, K. Hashimoto, T. Watanabe, Monatshefte fuer Chemie, 132 **(2001)** 31-41.
[5] M. Hikita, K. Tanaka, T. Nakamura, T. Kajiyama, A. Takahara, Langmuir, 21 **(2005)** 7299-7302.
[6] J. Bravo, L. Zhai, Z. Wu, R.E. Cohen, M.F. Rubner, Langmuir, 23 **(2007)** 7293-7298.
[7] X.-k. Ma, N.-H. Lee, H.-J. Oh, J.-W. Kim, C.-K. Rhee, K.-S. Park, S.-J. Kim, Colloids and Surfaces A:
[8] Physicochemical and Engineering Aspects, 358 **(2010)** 172-176.
[9] Y. Xu, D. Wu, Y.H. Sun, Z.H. Li, B.Z. Dong, Z.H. Wu, Journal of Non-Crystalline Solids, 351 **(2005)** 258-266.
[10] K. Jeevajothi, R. Subasri, K.R.C. Soma Raju, Ceramics International, 39 (2013) 2111-2116.
[11] L. Musante, P. Vázquez, R. Torregrosa-Maciá, J.M. Martín-Martínez, Composite Interfaces, 17 (2010) 467-479.

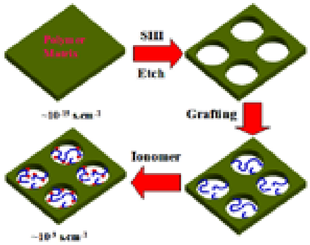
BL21

Piezoelectric polymeric hybrid membrane fabrication using swift heavy ions

Karun Kumar Jana[1], Biswajit Ray[2], D. K. Avasthi[3] and Pralay Maiti[*,1]
[1]*School of Materials Science and Technology, IIT-BHU, Varanasi 221 005, India*
[2]*Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India*
[3]*Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110 067, India*
Email: karun.jana@gmail.com

A modified poly(vinylidene fluoride) nanohybrids membranes have been prepared using swift heavy ions irradiation (Si^{7+} 80MeV) followed by suitable chemical etching and subsequent functionalization. The channel diameter is reduced to 40 nm in presence of nanoclay against 55 nm in pure *PVDF* making it suitable for membrane application. Through nano-channels were grafted with styrene or pyrrole using the active free radicals caused by *SHI* irradiation on the channel walls of the membranes [1]. Spectroscopic and chromatographic measurements have been performed to confirm the effect of irradiation on filled systems. Doping and sulphonation on the grafted species have been performed to introduce suitable functionalities membrane applications.

The effect of fluence on the channel dimension and functionalization study indicates larger diameter of channels and greater ionomer for higher fluence leading to enhancement of bulk electrical conductivity to 10^{-3} S.cm^{-1} (12 orders higher in magnitude as compared to pure *PVDF*). Activation energy of the modified membrane was calculated to be 26.9 KJ.mol^{-1} indicating greater stability of the membrane at higher temperature [2]. Nanohybrid conducting membrane produces current 46 nA against the value of almost zero for pristine *PVDF or NH* measured through *I-V* characteristics curves against the bias voltage of 10V making the nanoybrid suitable for electrochemical applications. The matrix *PVDF* crystallizes in piezoelectric β-phase in presence of nanoclay promoting the formation of smart membrane using the developed material.



References:
[1] Jana, K. K.; Ray, B.; Avasthi, D. K.; Maiti, P. *J. Mater. Chem.*, **2012**, 22, 3955-3964.
[2] Jana, K. K.; Ray, B.; Avasthi, D. K.; Misra, M.; Maiti, P. *RSC Adv.* **2013**.

BL22

Drug loaded Nanocomposite Fibers for Topical Drug Delivery

Kasturi Saha, B. S. Butola, Mangala Joshi*
Department of Textile Technology, Indian Institute of Technology Delhi,
New Delhi-110016 INDIA
**Corresponding Author: mangala@textile.iitd.ac.in*

At present 95% [1] of all new therapeutics have poor pharmacokinetics and biopharmaceutical properties. Therefore, there is a strong demand to develop suitable drug delivery systems that not only administer the active therapeutic agents to the action site without affecting healthy tissues but also release drug in appropriate amount and over prolonged periods. Recent developments in the field of nano-biotechnology are actively focused towards in vivo drug delivery technique [2] through nanoparticles to protect the drug entity in the systemic circulation, restrict access of the drug to the chosen sites and to deliver the drug at a controlled and sustained rate to the site of action. In topical system, drug is applied directly onto the skin and it is able to protect drugs from degradation during systemic circulation. Advantages of topical drug delivery through hybrid nanoparticles [3] include achievement of high efficacy with very little dose to a specific site, improving physiological and pharmacological response and patient compliance, convenience and ease of application and the option of termination of the medication when required.

Drug loaded hybrid nanoparticles were produced by ion exchange method in laboratory. Chlorhexidine Acetate (CA) is a cationic antibiotic drug is used for this study. This antibiotic is acting as a synthetic bacteriostatic as well as bactericidal with broad spectrum activity against both gram positive and gram negative microorganisms. This antibiotic has established application for treating nosocomial transmission of infections caused by the bacteria. It also acts as an antiseptic, pharmaceutical and cosmetic preservative and antiplaque agent [4, 5]. Drug loaded hybrid nanoparticle was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric (TGA) technique and Energy dispersive X-ray (EDX) technique.

Finally, bioactive nanofibers were produced by incorporation of hybrid nanoparticle using Electrospinning technique. About 1% of pure drug & hybrid nanoparticle were used for loading. The antimicrobial activity of hybrid nanocomposite fiber was determined against both gram positive and gram negative bacteria. Also in comparison with pure drug loaded polymeric fiber, nanocomposite fiber showed a very controlled release of the drug in the phosphate buffer solution. The produced nanocomposite fibers with controlled drug release and bioactivity against microbes can have wide application in the area of medical textiles and drug delivery applications.

References

[1] Brayden, D. J.; *Drug Discovery Today*, 8 **(2003)** 976.
[2] Wai, K. N.; Banker, G.S.; *Journal of Pharmaceutical Science*, 55 **(1966)** 1215.
[3] Hughes, G. A.; *Nanomedicine*, 1**(2005)** 22.
[4] Russell, A. D.; *Infection* 14 **(1986)** 212.
[5] Raso, E.; Cortes, M.; Teixeira, K.; Franco, M.; Mohallem, N.; Sinisterra, R.; *Journal of Inclusion Phenomena and Macrocyclic Chemistry* 67 **(2010)** 159.

BL23

Facile fabrication and characterization of Poly(tetrafluoroethylene)@polyurethane as alternatives to PTFE

Ch. Koti Reddy & D. Shailaja*
Polymers & Functional Materials Division
CSIR-Indian Institute of Chemical Technology
Hyderabad – 500007 India.

Polytetrafluoroethylene (PTFE) is widely used as blood-contacting device material in several biomedical applications mainly because it has excellent self-lubrication ability, low rate of water absorption, more importantly, it doesn't induce adhesion formation when used as an implant.[1] However, the high cost of this material impeded its use and encourages blending with another biocompatible material that can be used as a less expensive alternative without compromising on the properties which happens to be polyurethane (PU) another biocompatible polymer, in the present case.[2,3] Here, for the first time we report a new strategy to prepare PTFE, PU blends insitu by reacting isophorone diisocyanate with dodecanediol in the presence of PTFE using seeded emulsion polymerization method. The resulting PTFE/PU hybrid nanoparticles were characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS) analysis, Fourier transform infrared (FTIR) spectrometry, differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA). Formation of hybrid nanoparticles were confirmed by FTIR, TEM and DLS with changes observed in their structure, size and morphology. The water contact angle of PTFE/PU blends increased with increasing amount of PTFE in the blends. The glass transition temperature of PTFE/PU hybrid nanoparticles slightly increased upon increasing the content of PTFE and the thermal stability of hybrid nanoparticles improved, when compared to PTFE. Such blended composite materials are promising, cost effective alternatives to pure PTFE in several biomedical applications.

References

[1] Yang Xue, Xin Liu, Jiao Sun.Toxicology in Vitro 24 (2010) 404–410
[2] Jizhi Huang, Jianchun Zhang, Xinmin Hao, Yuhai Guo. European Polymer Journal 40 (2004) 667–671
[3] Xinmin Hao, Jianchun Zhang, Yuhai Guo. European Polymer Journal 40 (2004) 673–678

BL24

Expanded Graphite and Multiwall Carbon Nanotubes based Hybrid Polymer Composites

M. S. Sreekanth, Arup R. Bhattacharyya*, Ajay S. Panwar
Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay, Mumbai – 400076, INDIA
** Arup R. Bhattacharyya: e-mail: arupranjan@iitb.ac.in*

The concept of hybrid filler has been introduced to make use of excellent properties of individual fillers. The outstanding mechanical, electrical and thermal properties associated with carbon nanotubes (CNTs) attracted them towards its use in polymer nanocomposites. Expanded graphite (EG) exhibits excellent thermal and electrical properties. The hybrid composites in many cases showed synergistic properties than individual fillers [1,2]. Expanded graphite (EG) and multiwalled carbon nanotubes (MWNTs) based hybrid nanocomposites were prepared using polyamide6 (PA6) matrix via melt-mixing technique. EG+MWNTs based hybrid composites were prepared wherein EG:MWNTs ratio (wt/wt) was varied in 1:0.5, 1:1 and 1:4. MWNTs were modified with a novel modifier: Li-salt of 6-aminohexanoic acid (Li-AHA) in the ratio of 1:1 and 1:4 (wt/wt). The morphological studies of EG+modified MWNTs composites showed the existence of intercalated MWNTs in the galleries of EG [3] as shown in Figure 1A & 1B. The degree of exfoliation of EG was higher at higher MWNTs content as observed from the selected area electron diffraction (SAED) analysis. EG+modified MWNTs based PA6 composites were characterized through AC electrical conductivity measurements to investigate the 3D 'network-like' structure of the hybrid filler. State of dispersion of the hybrid filler was assessed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The nanocomposites exhibited the electrical percolation threshold between 2-3 wt% of EG+modified MWNTs (1:4, wt/wt) due to the formation of interconnecting network of the hybrid filler in the PA6 matrix as shown in Figure 1C. A significant improvement in glass transition temperature of PA6 phase was recorded (up to 10 °C) with increased EG+modified MWNTs concentration. The %crystallinity of PA6 phase of the composites increased (32% upto 40%) with increase in EG+modified MWNTs concentration. Morphology and electrical conductivity relationship studies in these hybrid composites were addressed in this study.

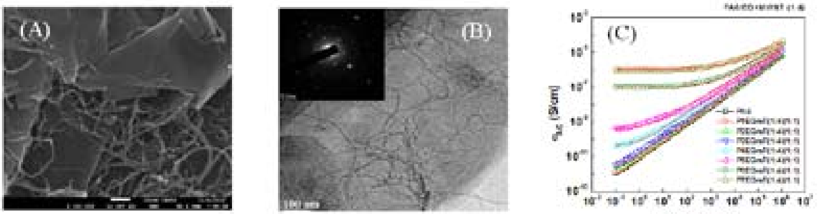


Figure 1. (A) SEM and (B) TEM of EG+mMWNTs(1:4) hybrid filler and (C) AC electrical Conductivity of PA6/EG+mMWNTs(1:4) composites

References

[1] Shin, M. K.; Lee, B.; Kim, S. H.; Gambhir, S. *Nature Communications,* **3** (2012) 1.
[2] Antar, Z.; Feller, J.F.; Noël, H.; Glouannec, P.; Elleuch, K. *Material Letters,* **67** (2012) 210.
[3] Sreekanth, M. S; Bhattacharyya, A. R; Panwar, A. S. *Proceeding Polymer Processing Society-28 Annual Meeting*, **07** (2012) 351.

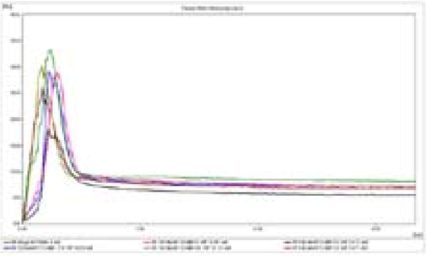
BL25

Preparation of wood flour/polypropylene composites using hyperbranched polyester as compatibilizer for improvement in processibility

Mahendra R. Nevare*, Pyush D. Tatiya, Pramod P. Mahulikar, Vikas V. Gite
Department of Polymer Chemistry, School of Chemical Sciences,
North Maharashtra University, Jalgaon- 425 001
Maharashtra, India
Phone No.: +91 257 2257432, Fax No.: +91 257 2257406
Email: mahendra.nevare@gmail.com

Maleated polypropylene (PP) is used as compatibilizer in wood/polypropylene composites[1,2]. But it is difficult to process the wood/PP composites by using MAPP. Processing challenges of wood flour/polypropylene composites has been overcome by using the hyperbranched polymer as processing aid. The wood/polypropylene composites were formulated using melt compounding on Brabender Plastograph EC. The hyperbranched polyester used as compatibilizer along with processing aid in wood/PP composites [3,4]. Comparative study between hyperbranced polyester and maleated polypropylene had been carried out with the change in properties [5]. The results were analysed by using Torque analysis, FTIR, mechanical properties, SEM and TGA.

The results obtained from the analysis shown that the hyperbranced polyester reduces the torque of composites than the maleated polypropylene.



References:

[1] Wang Z. M., Nakajima, H.: Manias, E.; Chung, T. C.; *Macromolecules*, 36, **(2003)**, 8919-8922.
[2] J. K. Kim and K. Pal, Recent Advances in the Processing of Wood–Plastic Composites, Engineering Materials, 32, **(2010)**, *DOI: 10.1007/978-3-642-14877-4-5*.
[3] Christopher J. G. Plummer, Laszlo Garamszegi, Yves Leterrier, Marlene Rodlert, Jan-Anders E. Manson, *Chem. Mater.* 14, **(2002)** 486-488.
[4] Marlene, R.; Christopher, J.G. P.; Laszlo, G.; Yves, L.; Henri, J.M. G.; Jan-Anders, E. M.; *Polymer* 45 **(2004)** 949–960.
[5] A.K. Bledzki, M. Letman, A. Viksneb, L. Rence, *Composites: Part A,* 36 **(2005)** 789–797.

BL26

Polymer-CNF Composites as Membrane Materials for Gas Separation

Manisha Dohade, Harshal Chaudhari, Ulhas Kharul*
Polymer Science & Engineering Division, National Chemical Laboratory, Pune-411008, India
uk.kharul@ncl.res.in

Polymeric membranes are used for gas separation due to their advantages like easy processability, modular in nature (high membrane surface area and easy scale up), cost effectiveness, etc. [1]. However, polymeric materials show a trade-off between permeability and selectivity [2]. On the other hand, inorganic membrane materials such as molecular sieving materials usually show extremely attractive gas permeation and separation performance on a laboratory scale, but it is difficult and expensive to fabricate large inorganic membranes. To overcome the trade-off limitation of polymer membranes and to address scale up issues of inorganic membranes, the concept of mixed matrix membranes (MMMs) had been proposed to combine the high performance of the inorganic fillers with the easy processability of the polymer membranes [3]. The porous fillers such as zeolites, carbon molecular sieves, metal organic framework (MOF), carbon nanotubes (CNTs) and nonporous fillers like SiO_2, TiO_2 nanoparticles are used for composite membranes preparation [4]. The zeolites and MOFs have compatibility issue with polymer matrix and forms brittle membrane with higher loading. In order to overcome these limitations and enhance permeation properties of polybenzimidazoles (PBI), hollow and open ended carbon nanofibers (CNFs) could be promising materials for hybrid membranes preparation.

The objective of present work is to fabricate of defect free composite membranes by using polymer material as a continuous phase and CNF as a dispersed phase, followed by investigations of their physical and gas separation properties.

The hybrid membranes were successfully fabricated with CNF loading of varying proportions with good flexibility. The TEM images proved defect free membranes formation, due to good compatibility between PBI and CNF. Appreciable thermal stability of membrane was obtained from TGA data. Gas permeability and selectivity variations in composite membranes obtained from chopped and unchopped CNFs showed distinctly different behaviour and will be presented.

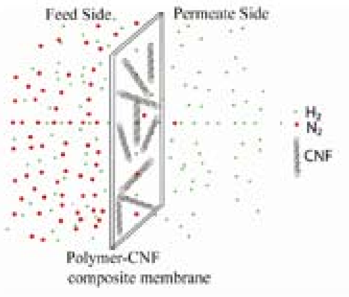


Figure 1. Schematic of gas molecules transport through composite membrane

References

[1] Prasad, R.; Notaro, F.; Thompson, D.R., *J. Membr. Sci.*, **(1994),** 94, 225-248.
[2] Robeson, L. M. *J. Membr Sci*., 62 **(1991)** 165–185.
[3] Noble, R.D. *J. Membr. Sci*., 378 **(2011)** 393–397.
[4] Chung, T.S.; Jiang, L.Y.; Li, Y.; Kulprathipanja, S. *Prog. Polym. Sci*. 32 **(2007)** 483–507.

BL27

Poly(ε-caprolactone)/ Graphene Nano-composites for Bone Tissue Engineering

Md. Dilkash Azam[a], K.S. Vasu[b], A.K. Sood[b], Kaushik Chatterjee[a]*
[a]*Department of Materials Engineering*
[b]*Department of Physics*
Indian Institute of Science, Bangalore, India
**kchatterjee@materials.iisc.ernet.in*

Tissue engineering is an interdisciplinary field which aims at replacing and regenerating diseased and injured tissues. Cells, a biodegradable scaffold and growth factors form the triad of any kind of tissue engineering. In particular for bone tissue engineering the scaffold should be mechanically robust and promote bone tissue generation in the scaffold.

Poly (ε-Caprolactone) (PCL) is a biodegradable polymer that is widely used for tissue engineering but has poor mechanical properties. The objective of the present work was to study the effect of graphene reinforcement in the PCL matrix. The nano-composites were prepared by solvent precipitation process by dispersing graphene oxide (GO) in PCL solution followed by precipitation in excess of a non-solvent. Physical properties were performed to characterize the nano-composite by scanning electron microscopy (SEM), x-ray diffraction, differential scanning calorimetry, contact angle measurement and infra red spectroscopy. Tensile tests indicated that modulus increased by 40% on addition of 0.5 wt% GO. Contact angle measurements indicated that the addition of GO nanoparticles increased the water wettability of the composite.

3D macro-porous scaffolds were prepared by salt leaching method and characterized by SEM imaging (figure 1). In vitro cell studies are currently underway to characterize biological response to the 3D scaffolds.

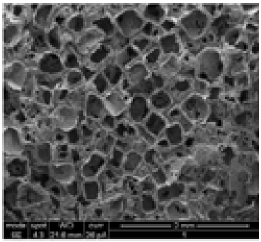


Fig 1: Scanning electron micrograph of a porous salt leached PCL-0.5% GO at 25X

BL28

Effect of Functionalized Halloysite Nanotubes as Compatibilizer in Syndiotactic Polystyrene/Thermotropic Liquid Crystalline Polymer Blend

Mrinal Kanti Kundu, Parthajit Pal, and Chapal Kumar Das*
Materials Science Centre, IIT Kharagpur, Kharagpur-721302, West Bengal, India.
** Email i.d: chapal12@yahoo.co.in*

Polymer-clay nanocomposites fascinated the scientific communities because of its various advantages such as enhanced thermo-mechanical properties, low gas permeability, chemical resistance, and flame retardancy induced due to the nanoscale effects and a large interface area in comparison with the conventional resources [1]. Halloysite nanotubes (HNTs) are naturally occurring nanotubular clay minerals having a basal spacing of 10Å distinguishing it from similar chemical composition of Kaolinite (7Å) [2].

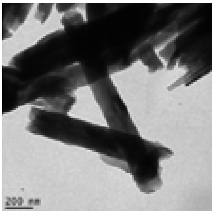


Figure 1. TEM image of APTMS modified HNTs.

In this study, compatibilizing ability of aminopropyltrimethoxysilane (APTMS) [3] modified HNTs for the incompatible Syndiotactic polystyrene (SPS)/liquid crystalline polymer (LCP Vectra A950) blend was investigated in detail. SPS/HNTs/Vectra A950 nanocomposites were developed through melt blending process in an internal mixer and then compression moulded. Successful surface modification of the HNTs with APTMS was confirmed by the Fourier Transform Infrared Spectroscopy (FTIR) as well as Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) images (Figure 1). The contribution of LCP as a processing aid due to its low melt viscosity was substantiated by the rheological study where, the viscosities of the binary and ternary blends were lower than the matrix polymer (SPS). However, in case of ternary blend systems including the modified nanofillers, viscosity was higher than the pure HNTs compounded blend systems signifying the modifier's hindrance to chain mobility [4]. FESEM analysis revealed a deformation in globular domains of the minor phase to elliptical shape and improved filler-matrix adhesion due to addition of pure and modified HNTs (mH) respectively (Figure 2). From X-Ray Diffraction (XRD) study, the crystallinity percentage associated with the augmented crystallite size is in well agreement towards the heterogeneous nucleation effect by the functionalized HNTs. Improved stress transfer between the dispersed phase and the matrix phase through the nanofillers were observed from the Dynamic Mechanical Thermal Analysis (DMTA) of the APTMS aided ternary blend systems, conceding better interaction among the polymer matrices and the tubular clay nanoparticles [5]. Enhanced rheological, morphological and thermo-mechanical properties of the immiscible thermoplastic SPS/Vectra A950 blend systems were observed in presence of functionalized HNTs substantiating its role as a compatibilizer.

Figure 2. FESEM image of SPS/LCP/mH ternary blends.

References

[1] Kim, M. H.; Park, C. I.; Choi, W. M.; Lee, J. W.; Lim, J. G.; Park, O. O.; Kim, J. M., J. App. Polym. Sci., 92 **(2004)** 2144.
[2] Du, M.; Guo, B.; Jia, D., Polym. Int., 59 **(2010)** 574.
[3] Yuan, P.; Southon, P. D.; Liu, Z.; Green, M. E. R.; Hook, J. M.; Antill, S. J.; Kepert, C. J., J. Phys. Chem. C, 112 **(2008)** 15742.
[4] Nayak, G. C.; Sahoo, S.; Das, S.; Karthikeyan, G.; Das, C. K.; Saxena, A.K.; Ranjan, A., J. App. Polym. Sci., 124 **(2012)** 629.
[5] Bose, S.; Pramanik, N.; Das, C. K.; Ranjan, A.; Saxena, A. K., Mater. Des., 31 **(2010)** 1148.

BL29

Synthesis and systematic characterization of cardanol based epoxy resin

S.C.Murugavel *and M. Natrajan
Department of Basic Sciences-Chemistry, PSG College of Technology Coimbatore, Tamil Nadu-641 004
psgmvel@yahoo.co.in

In recent years, the synthesis of polymers from renewable resources has attracted considerable attention of research workers throughout the world because of the escalating price of petrochemicals and high rate of depletion of the natural mineral resources. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry. In this respect, cashew nut shell, an agricultural byproduct abundantly available in the country, holds considerable promise as a source of unsaturated hydrocarbon phenol [1]. This monomer can be used for preparing phosphorus containing polyester and epoxy polymers.

In the present work the diol monomer, cardanol, was condensed with formaldehyde and epoxidized with epichlorohydrin[2]. The condition for synthesizing liquid resin was optimized. The synthesized resins were systematically characterized by spectroscopic techniques. Thermal properties were studied by TGA and DSC. The resins were cured with phosphorus containing diamines. The curing kinetics and thermal degradation kinetics were also studied. Flammability of the cured resins was studied with Limiting Oxygen Index analyzer chamber [3]. Thermal studies indicated that these resins undergo two stage degradations.

.

References

[1] Raju Pramod Kumar *J. Coat. Technol. Res. 8(5) 563-575,2011*.
[2] P.Jain, V.Choudhary and .K.Varma *Journal of Thermal Analysis and Calorimetry 67,761-772, 2002.*
[3] Pietro Campaner, Daniele D'Amico and Luigia Longo J. Appl. Polym Sci 114, 3585-3591, 2009

BL30

Effect of Modification, Compatibilization and Processing Strategy on the Morphology and Electrical Conductivity of Binary Blends of Polypropylene and Polyamide 6 Filled with Multiwall Carbon Nanotubes

Nabaneeta Mukhopadhyay, Arup R. Bhattacharyya* and Ajay S. Panwar
Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
** arupranjan@iitb.ac.in*

Blends of polypropylene (PP) and polyamide 6 (PA6) (50/50; wt/wt) were melt-mixed with varying amount of multiwall carbon nanotubes (MWNTs) with the intention to develop conducting composites. Simultaneous, sequential and masterbatch mixing strategies were used to study the effect of various processing strategies on the electrical conductivity of the composites. The state of dispersion of MWNTs in these blends was assessed through scanning electron microscopic analysis (SEM), AC electrical conductivity measurements and solution experiment. Electrical conductivity measurements indicated that blends prepared by simultaneous mixing protocol showed lower electrical percolation threshold as compared to corresponding blends prepared by either simultaneous mixing or masterbatch technique, which is due to the uneven distribution of the filler in the various phases. Blends where MWNTs were initially mixed with the PP phase (both in sequential mixing and masterbatch approach), exhibit better 'network-like structure' formation in terms of electrical percolation. To understand the role of compatibilizer on the morphology and electrical conductivity of the blends, polypropylene grafted maleic anhydride (PP-g-MA) was utilized in the blend system. Incorporation of MWNTs modified by an organic modifier leads to a transition of phase morphology viz. co-continuous to matrix droplet-dispersed type [1]. Change in phase morphology affects the network formation between MWNTs, resulting in a decrease in electrical conductivity. In order to improve the state of dispersion of MWNTs, an organic modifier: lithium salt of 6-aminohexanoic acid (Li-AHA) was used. Addition of the modifier gives rise to a drastic change in the electrical conductivity of the system indicating good dispersion of MWNTs in the blend phases [2]. An attempt has been made to understand the effect of MWNTs on the morphology and the electrical conductivity of the blends.

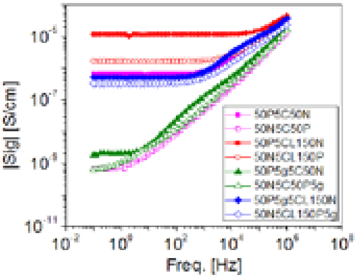


Figure 1. AC electrical conductivity measurements of 50/50 (wt/wt) PP/PA6 blends with unmodified and Li-AHA (1:1) modified MWNTs composites with and without compatibilizer (5wt% PP-g-MA) for PP based (filled symbol) and PA6 based (hollow symbol) sequence.

References

[1] R. A. Khare, A. R. Bhattacharyya, A. R. Kulkarni, *Journal of Applied Polymer Science,* 120 (**2011**) 2663.
[2] S. Bose, A. R. Bhattacharyya, A. R. Kulkarni, P. Pötschke, *Composite Science and Technology*, 69 (**2009**) 365.

BL31

Development of Low Density Thermal Insulation Material for Case Bonded Solid Rocket Motors

Nirmal.C*, Elbin George, Lakshmikanth.RV, Bhaskaran.AK, Mathew Daniel, Thomas.CR
Scientist, Rocket Propellant Plant, Vikram Sarabhai Space Centre, Trivandrum, Kerala-695 022, India.
** e-mail: nirmal.vssc@gmail.com, c_nirmal@vssc.gov.in*

Thermal insulation system of solid rocket motor protects the metallic case from hot gases and high temperatures, ranging from 2500°C to 4000°C, developed inside when the propellant burns for the generation of thrust. They are hybrid materials, containing different fillers or reinforcements in a matrix or binder [1]. NBR, SBR, EPDM, IIR, Polysulfide, Silicone and Urethane in combination with a wide variety of fillers like silica, asbestos, boric acid, carbon black, aramid/carbon/polybenzimidazole fibres etc finds widespread application as internal insulation material because of its excellent thermal properties and high strain capabilities.

Solid motors of ISRO's launch vehicles PSLV, GSLV and futuristic GSLV Mk-III rely on silica filled Nitrile rubber compound as internal thermal insulation material. The in-house developed compound, ROCASIN (Rocket Case Insulation), used in different thermal insulation applications; suffers from the disadvantages like high density, limited shelf life and inferior low temperature properties. The evaluation of elastomers like EPDM to replace Nitrile rubber in Indian space and missile programmes is in great progress, in view of EPDM's reduced specific gravity/density, wider operating temperature ranges and excellent weather resistance. EPDM insulation with density 15% lesser than conventional material can yield tremendous pay off, especially in gigantic solid booster motors, where the insulation weight contribution is about 1.3 to 1.5% of the propellant tonnage [2,3]. However the non polar nature of EPDM bestows these advantages and poses potent drawbacks due to inferior rubber-to-metal & rubber-to-propellant interface properties.

This paper discusses the development of a new low density insulation material based on EPDM. Though, this topic has been an area of fundamental research for the past several years in ISRO, none of the work has really matured to the level of attempting on sub-scale level motors, primarily due to EPDM's inferior interface properties [4]. In the present study, attempts were focused on blending EPDM and NBR to utilize the excellent interface, mechanical and chemical resistant property of NBR, coupled with low density of EPDM. Being EPDM and NBR non-compatible rubbers, a suitable compatibiliser was identified and attempted in different formulations in two roll mixing mill, for improved results. Compatibility of blend was studied using different characterisation/micrographic techniques. Later a promising blend was identified with excellent properties for further experimentation using different fillers (Kevlar pulp and precipitated silica) and other additives.

The newly developed insulation system is a blend of EPDM, NBR and liquid EPDM, in combination with highly erosion resistant fillers. The material shows rubber-to-metal and rubber-to-propellant interface properties four times better than earlier developed EPDM based systems. Mechanical properties achieved are well comparable with existing Nitrile rubber based insulation material. The compound also shows better surface finish, thermal and erosion resistance; at 10-15% lower density values.

References

[1] NASA space vehicle design criteria, *Solid rocket motor internal insulation* (**1976**).
[2] Bhuvaneswari, CM.; Kakade, SD.; Deuskar, VD.; Manoj Gupta. *Defence Science Jr*, 58 (**2008**) 94.
[3] Bhuvaneswari, CM.; Sureshkumar, MS.; Kakade, SD.; Manoj Gupta. *Defence Science Jr*, 56 (**2006**) 309.
[4] Muraleekrishnan, R.; Bhagawan, SS.; Raghavan, A.; Rao, SS; *Proceedings of the International Conference on - Rubbers*, (**1997**).

BL32

Crystallization, Polymorphism & Thermal Properties of Syndiotactic Polystyrene-Graphene/Carbon Nanotube Nanocomposites: A Comparative Study

P. Shaiju and E. Bhoje Gowd*
Materials Science and Technology Division,
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Trivandrum, Kerala, India – 695019
bhojegowd@niist.res.in

Syndiotactic Polystyrene (sPS), a stereoregular semicrystalline polymer, has drawn a lot of attention because of its high melting point, good thermal and dimensional stability, and rapid crystallization rate. sPS exhibits five major crystalline forms (α, *β*, γ, δ & ε) and some mesophases/ sub modifications. Among these crystalline forms *β* is the highly stable one and once formed, it will not undergo any transition in presence of solvents or before melting. If we can control the conditions to obtain pure *β* form, then sPS can be used for a wide variety of applications. In the present work, we studied the effect of both one-dimensional and two-dimensional nanoparticles on the crystallization, polymorphism and thermal stability of sPS. We successfully prepared the sPS nanocomposites using both multiwalled carbon nanotube (MWCNT) (1D) and graphene (2D) as nanofillers by solution blending method. The influence of nanofillers on sPS was studied by using differential scanning calorimetry (DSC), powder X-ray diffraction and thermogravimetric analysis (TGA).

Isothermal and non-isothermal crystallization studies using DSC revealed that the crystallization rate of sPS increases with the increase in filler content due to the heterogeneous nucleation effect induced by these nanofillers. But the nucleation ability of MWCNT was found to be better than that of graphene. Unlike graphene, MWCNT is hindering the crystallization at higher weight percentage. This may be due to the agglomerates formed at higher weight percentages. TGA measurements revealed that the thermal stability of the nanocomposites has been increased with the addition of filler. Compared to MWCNT, graphene is significantly enhancing the thermal stability of sPS. From the Wide angle X- ray Diffraction patterns of melt quenched samples, it was found that sPS crystallizes into the *β*- form in presence of graphene and the amount of *β*-form is increasing with the increasing graphene content (Figure 1a). Schematic representation of crystallization process of sPS in presence of MWCNT and graphene is shown in Figure 1b.

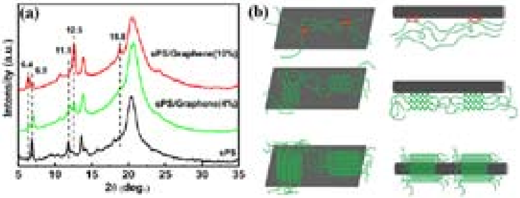


Figure 1: (a) Wide Angle X-ray diffraction patterns of melt-quenched sPS/graphene nanocomposites (b) Schematic representation of conformational ordering and crystallization of sPS in presence of 1D and 2D nanofillers.

References

[1] Gowd EB.; Tashiro K.; Ramesh C. *Prog. Polym. Sci.*, 34 (**2009**) 280
[2] Huang CL.; Wang C. *European Polymer Journal*, 47 **(2011)** 2087

BL33

Syntheses, Thermal Properties, and Phase Morphologies of Eugenol-based Benzoxazines Functionalized with Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites

P. Thirukumaran, M. Sarojadevi*
Department of Chemistry, Anna University, Chennai – 600025
E-mail: thiru.kumaran999@gmail.com

Octa-aminophenyl polyhedral oligomeric silsesquioxane (OAPS) was used as the reinforcing agent to prepare polybenzoxazine nanocomposites. Benzoxazine was synthesized using eugenol, paraformaldehyde and four different aromatic diamines through Mannich condensation. Polybenzoxazine-POSS hybrid nanocomposites were prepared by ring opening polymerization via thermal curing using benzoxazine precursors and OAPS. Increasing the POSS content in these hybrids improved their thermal and mechanical properties, relative to those of the neat polybenzoxazine, because of hydrogen bonding between the siloxane groups of the POSS core units and the OH groups of the polybenzoxazine moieties, as adjudged using FTIR spectroscopy. Thermal properties of these POSS-containing organic/inorganic polybenzoxazine nanocomposites have been improved over the pure polybenzoxazine analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Morphological characteristics were studied by scanning electron microscopy. The dispersion of POSS in polybenzoxazine and nanostructure of the composites were evaluated by transmission electron microscopic (TEM) analysis.

Keywords: Eugenol, Benzoxazine, POSS, nanocomposites

References

[1] Calo, E.; Maffezzoli, M.; Mele, G.; Martina, F.; Mazzetto, S.E.; Tarzia, A.; Stifani, C. Green Chem. 9 (2007) 754
[2] Agag, T.; Takeichi, T. Macromolecule 36 (2003) 6010
[3] Kai-Wei Huang; Shiao-Wei Kuo. Macromol. Chem. Phys. 211 (2010) 2301–2311
[4] Yi-Chen Wu; Shiao-Wei Kuo. Polymer 51 (2010) 3948-3955

BL34

Hexaferrite and MWCNT Based Nanocomposites for Supercapacitor and Microwave Absorbing Application

Pallab Bhattacharya and Chapal K. Das*
Materials Science centre, Indian Institute of technology, Kharagpur-721302, West Bengal, India
**Corresponding Author's Email: chapal12@yahoo.co.in*

The demand of suitable microwave absorber is very high for both commercial and military application. More precisely, the demand is to develop the thin microwave absorber with a high band-width [1, 2]. The present work concentrated on the synthesis and characterization of a hexaferrite of chemical formula $CuFe_{10}Al_2O_{19}$ by a simple chemical co-precipitation method and then its coating on the acid modified multiwall carbon nanotube (MWCNT). An in-situ approach was employed for the coating of $CuFe_{10}Al_2O_{19}$ on the surface of modified MWCNTs. Finally, thermoplastic polyurethane (TPU)/$CuFe_{10}Al_2O_{19}$/MWCNT nanocomposites, for the fabrication of microwave test plates, were prepared by solution mixing process. All the nanocomposites were characterised by different analytical techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). Microwave absorbing property was measured by Agilent vector network analyzer (ENA E5071C) in the X-band region (8–12 GHz). The nanocomposites exhibited a remarkable and improved microwave absorption property compared to the pristine MWCNT and $CuFe_{10}Al_2O_{19}$. This enhancement in microwave absorption property was correlated to the factors like high surface area, electrical conductivity and aspect ratio of MWCNT, good magnetic property of $CuFe_{10}Al_2O_{19}$, high interfacial interaction between MWCNT and $CuFe_{10}Al_2O_{19}$, good matching of dielectric and magnetic loss etc. We have measured the relative complex permittivity and permeability, which provided useful information to elucidate the improved microwave absorption property of the composites. We have also found that the synthesized $CuFe_{10}Al_2O_{19}$/MWCNT) showed a better specific capacitance of 269 F/g, and good electrochemical impedance property than that of the pristine MWCNT and $CuFe_{10}Al_2O_{19}$. This work can be extended effectively in future by making this type of composite materials with different magnetic materials for both supercapacitor and microwave absorbing applications.

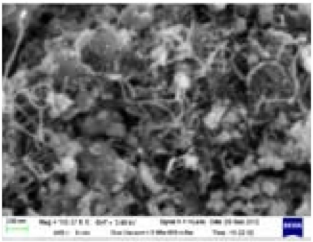


Figure 3. FESEM images of $CuFe_{10}Al_2O_{19}$/MWCNT nanocomposite

References

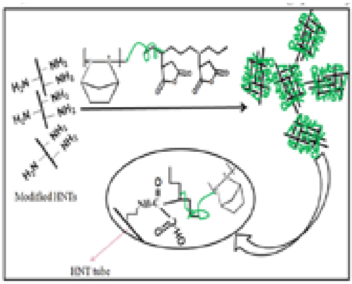
[1] Meshram, M. R.; Agrawal, N. K.; Sinha, B.; Misra, P. S. *J. Magn. Magn. Mater.*, 271 (**2004)** 207.
[2] Sugimoto, S.; Kondo, S.; Okayama, K.; Book, D.; Kagotani, T.; Homma, M. *IEEE Trans. Magn.*, 35 (**1999)** 3154.

BL35

Effect of Halloysite nanotubes on the mechanical and thermal properties of cyclic olefin copolymer based nanocomposite

Parthajit Pal, Mrinal Kanti Kundu, Chapal Kumar Das*
Materials Science Centre, IIT Kharagpur, India
Email: chapal12@yahoo.co.in

This work reports on the mechanism of compatibilization through addition of graft copolymer. Polymeric nanocomposite has been prepared by incorporation of raw and modified halloysite nanotubes into cyclic olefin copolymer (COC). It was a challenge to disperse polar halloysite nanotubes (HNTs) in nonpolar COC matrix. In this work we made the both polymer and HNTs polar. Surface treatment of raw HNTs was done organically by N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (APTMS) modifier which also brings a polar group (-NH_2) on the HNTs surface along with a long organic chain. Maleic anhydride grafted polyethylene (MA-g-PE) was melt blended with COC to bring polarity on COC chains and then modified HNTs incorporated to fabricated the nanocomposite. Fourier transform infrared spectroscopy (FTIR) indicates that the surface modification of HNTs was successfully done, also EDX result from TEM analysis support this modification. Surface morphology of nanocomposites studied by scanning electron microscope (SEM) whereas filler dispersion in polymer matrix observed by the transmission electron microscope (TEM). Modified HNTs exfoliated in polymer matrix which was confirmed by X-ray diffraction (XRD) analysis, also XRD result tells the modification of HNTs gives better exfoliation over unmodified one. Incorporation of modified nanoclays gives the better results on mechanical as well as thermal properties. Tensile strength, dynamic mechanical thermal analysis (DMTA) was performed for mechanical and thermo gravimetric analysis (TGA) was performed for thermal analysis. So from the above discussion it was clear that modification enhance the better interfacial interaction which was responsible for better performances of the nanocomposites where MA-g-PE acts as compatibilizer to combine the both of the modified HNTs and COC. A mechanism has been proposed on the basis of the above results and shown in the above figure.



References:

[1] Ruchatz, D.; Fink, G. *Macromolecules* 31 (**1998**), 4669.
[2] Rische, T.; Waddon, A. J.; Dickinson, L. C.; MacKnight, W. J. *Macromolecules* 31 (**1998**) 1871.
[3] Shin, J. Y.; Park, J. Y.; Liu, C.; He, J.; Kim, S. C. 77 (**2005**) 801.
[4] Scrivani, T.; Benavente, R.; Perez, E.; Perena, J.M. *Macromol.Chem.Phys.* 202 (**2001**) 2547.

BL36

Studies on the MWCNT/polysulfone composite membranes for efficient toxic metal removal

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

Functionalized multi-walled carbon nanotube/polysulfone (MWNT/PSf) composite membranes were synthesized by the phase inversion method using DMF as solvent and water with isopropanol as coagulant. The membrane characteristics when evaluated by capillary porometry showed reduced pore size depending on the type of functionalities on the nanotubes and the extent of functionalization. Different functionalities were generated on the nanotube surface i.e. oxidized, amide and azide. The MWNT/PSf composite membranes appeared to be more hydrophilic, with a reduced flux, and lower flow rate than the pure polysulfone (PSf) membranes. The amount of MWNTs in the composite membranes was observed to be governing factor affecting the morphology and permeation properties of the membranes. The composite membranes showed enhanced thermal stability as found from TGA analysis. Heavy metal rejection on the composite membranes gave interesting results. The percent rejection of heavy metal was found to increase with increase in amount of MWNTs and best results were obtained at pressure of 0.49MPa and in an acidic pH of 2.6. Amide functionalized CNT/PSf composite membranes gave 94.2% removal for Cr(VI) and 78.2% removal for Cd(II) which was just 10.2% and 9.9% respectively with unblended plain polysulfone membranes.

References

[1] Prachi Shah, C. N. Murthy, *J. Memb. Sci.,* **2013**.
[2] Y-H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, *Carbon*, **2003**.

BL37

Exfoliated PP/Pristine Na^+ nano-clay Nanocomposite Along With Improved Processability by Using Hyperbranched Polyester.

Pyus. D Tatiya*, Mahendra R. Nevare, Pramod. P. Mahulikar, Vikas V. Gite
Department of Polymer Chemistry, School of Chemical Sciences,
North Maharashtra University, Jalgaon, Maharashtra, India- 425 001
Email: pushpadeep1@gmail.com

Series PP/MMT nanocomposites with different hyperbranched polyester (HBPE) contents were fabricated by direct melt compounding using a Brabender torque rheometer in a simple process where all the components of the blend were fed simultaneously for mixing. The effect of HBPE on the processability of the composites has been investigated by Torque analysis. The results showed that the processability of the composites was greatly improved by an addition of as little as 5 wt % HBPE and a minimum torque observed at 15 wt % of HBPE. The dispersion capability of HBPE along with ease of processability in nanocomposite of PP with 5 wt % of pristine Na^+ montmorillonite clay has been investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results from this study showed that addition of HBPE is found to be beneficial to generate intercalated/exfoliated morphology of naturalMMT. The resultant nanocompositeswereshown better clay dispersion along with the extra benefit in the easy processability of compositewhen compared with PP/MMT nanocompositesprepared at similar condition with commonly used functional oligomer polypropylene graft- maleic anhydride (PP-g-MA).

References

[1] Chen, C.; Baird, D. G. *Polymer*, 53 (**2012**) 4178.
[2] Wang, Z. M.; Nakajima, H.; Manias, E.; Chung, T. C. *Macromolecules*, 36(**2003**) 8919.
[3] Plummer, C. J. G.; Garamszegi, L.; Leterrier, Y.; Rodlert, M.; Manson, J. A.E. *Chem. Mater*. 14 (**2002**) 486.
[4] Su, F. H.; Huang, H. X.; Zhao, Y. *Composites: Part B*, 42 (**2011**) 421.

BL38

Titania supported nickel nanoparticles for hydrogenation of p-nitrophenol

*R.K. Dhokale[a], H.M. Yadav[a,b], V.B. Koli[a,b] and S.D. Delekar[a,c]**
[a] Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University,
Aurangabad, Sub–campus Osmanabad–413 501 (M.S.) INDIA.
[b] Center for Interdisciplinary Research, D.Y. Patil University, Kolhapur – 416 005 (M.S.) INDIA.
[c] Department of Chemistry, Shivaji University, Kolhapur – 416 001 (M.S.) INDIA.
**E–mail: sddelekar7@rediffmail.com (S.D. Delekar)*

Titania supported nickel nanoparticles were synthesized via *in situ* sol–gel followed by reduction method. Nanocatalyts was characterized by X–ray diffraction (XRD), Transmission emission microscopy (TEM), UV–visible (UV–Visible), Fourier–transform infrared (FTIR), and Energy dispersive X–ray (EDAX) measurements. The crystallite size was investigated from XRD and TEM. Crystallite size was ranged between 8–30 nm. XRD analysis confirming the presence of the face-centered cubic (fcc) structure of metallic nickel nanoparticles. The UV-Visible absorbance spectra revealed the surface plasmon band of elemental nickel. FTIR analysis was carried out for studying the interaction between the nickel nanoparticles and the capping agent. The catalytic hydrogenation of p-nitrophenol to p-aminophenol was investigated using supported/elemental nickel nanoparticles [1]. The highly efficient catalytic activity of supported nickel nanocatalyts is attributed due to small particles size, and high surface area [2]. However, the catalyst performance increases for supported nickel nanoparticles. The higher concentration of nickel nanoparticles; the better anchoring of reactant molecules at surfaces of the supported nickel species leads to the enhancement of the catalytic performance [3].

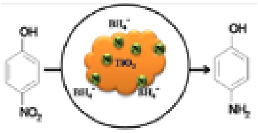


Figure 1. Titania-supported Ni NPs catalyst for reduction of nitro compounds in water.

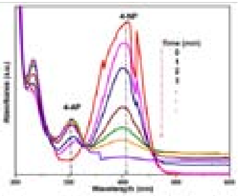


Figure 2. UV–visible spectra for catalytic reduction of p–NP to p–AP.

References:
[1] Jiang Z.; Xie J.; Jiang D; Wei X.; Chen M.; *Cryst. Eng. Comm.* 15 (**2013**) 560.
[2] Chen J.; Yao N.; Wang R.; Zhang J.; *Chem. Eng. J.* 148 (**2009**) 164.
[3] Antony Raj K.J.; Prakash M.G.; Mahalakshmy R.; Elangovan T.; Viswanathan B.; *Catal.*
[4] *Sci. Technol.* 2 (**2012**) 1429.

BL39

Fabrication of carbon /phenolic resin nanocomposite bipolar plates for PEM fuel cell

Rajeev K. Gautam[a] and Kamal K. Kar[a,b*]
[a]Advanced Nano Engineering Materials Laboratory, Materials Science Programme, Indian Institute of Technology, Kanpur 208016, India
[b]Advanced Nano Engineering Materials Laboratory, Department of Mechanical Engineering, Indian Institute of Technology, Kanpur 208016, India

The bipolar plate is an important constituent of a polymer electrolyte membrane (PEM) fuel cell [1, 2]. Nowadays, extensive research is being carried out for the development of new materials to create bipolar plates with low cost [3], good corrosion resistance and light weight for fuel cell applications [4, 5]. In this study, carbon / phenolic nanocomposite bipolar plates were developed using carbon filler (nano-carbon black and carbon fiber (fig. 1(a &b))) as reinforcement in resole type phenolic resin.

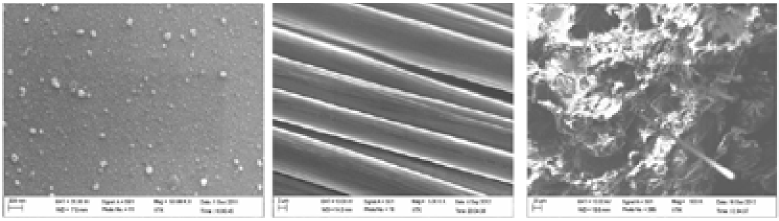


Figure 1: (a) Nano-carbon black, (b) carbon fiber, and (c) fractured surface of carbon/phenolic nanocomposites

The carbon / phenolic nanocomposite bipolar plates were prepared by compression moulding method with variation of nano-carbon black contents from 5 to 40 vol.% in polymer resin with fixed composition of carbon fiber and graphite powder. The prepared composite plates were then characterized for electrical, mechanical and thermal properties. It was observed that nanocomposite bipolar plates show optimum properties at 25 vol.% carbon filler contents. The prepared composite bipolar plates had the following achieved properties: bulk density ~1.79 g cm^{-3}, compressive strength ~76 MPa, flexural strength ~62MPa, Vickers microhardness ~833 MPa, storage modulus ~6.2 MPa and electrical conductivity ~155 Scm^{-1}. Additionally, it was observed that the nanocomposite bipolar plates were thermally stable up to 300°C. Also, the electrical conductivity of the carbon/phenolic nanocomposites was found to be increased by addition of carbon fiber (fig 1(c)).

References:
[1] Oh, M.H.; Yoon, Y.S.; S.G. Park, *Electrochim Acta* 50 (**2004)** 780.
[2] Cunningham, B.; Baird, D. G. *J Mater Chem* 16 (**2006)** 4388.
[3] Rio, C. D.; Ojeda, M. C.; Acosta, J. L.; Escudero, M. J.; Hontanon, E; Daza, L. *J Appl Polym Sci* 83 (**2002)** 2822.
[4] Kakati, B. K.; Yamsani, V. K.; Dhathathreyan, K. S.; Sathiyamoorthy, D.; Verma, A. *Carbon* 47(**2009)** 2418.
[5] Hermann, A.; Chaudhuri, T.; Spagnol, P. *Int J Hydrogen Energy* 30 (**2005)** 1302.

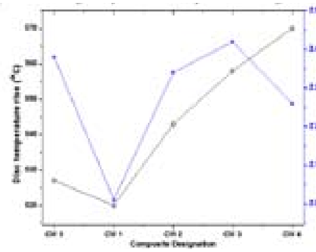
BL40

Dynamic Mechanical Response and Tribological Performance of Phenolic Composites: "Combinatorial Effect of Cenosphere and Tungsten disulphide"

Rakesh Kumar Kachhap and Bhabani K. Satapathy*
Centre for Polymer Science and Engineering, Indian Institute of Technology Delhi,
Hauz Khas, New Delhi-110016, INDIA

Increasing attention on the use of sustainable and environmemtal friendly resources, without depleting mineral resources, has allured lots of researchers [1, 2]. Cenosphere, a coal combstion byproduct, has been emerged as a potential candidate due to its inherent thermal stability, high specific heat and good abrasive characteristics [3, 4]. Friction composites based on the combination of cenosphere as filler (40-50 wt%) and tungsten disulphide as friction modifier (0-10 wt%) were fabricated via compression molding. Mechanical properties such as hardness and shear strength were found to be well above the desired range as per industrial practice for light commercial vehicles.

Dynamic mechanical analysis revealed improvement in storage modulus, loss modulus and loss tangent with increase in tungsten disulphide barring the composite containing 2.5 wt% of friction modifier. Krauss testing machine is used for the tribological evaluation conforming regulations-90 as per Economical Commission for Europe (ECE). The overall coefficient of friction was found to be decreased with an incorporation of 2.5 wt% of tungsten disulphide followed by a sharp increase with further addition. An increase in the recovery coefficient of friction has been observed whereas fade coefficient of friction showed the opposite trend with tungsten disulphide content. Improvement in the friction fluctuation has been observed with an incorporation of tungsten disulphide till 5 wt% followed by the deterioration of the same. A direct correspondence between wear in terms of weight loss and temperature rise of disc, as shown in the above *Figure*, has been emerged indicating the disc temperature rise induced wearing of the brake pads. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analyses have been found to be useful to unravel the associated wear mechanism and to study the counterface friendliness through elemental detection of friction film respectively.



References:

[1] Malhotra, V.M.; Valimbe, P.S.; Wright, M.A. *Fuel* 81 (**2002**) 235.
[2] Mohanty, S.; Chugh, Y.P. *Tribol Int* 40 (**2007**) 1217.
[3] Jaggi, H.S.; Satapathy, B.K.; Patnaik, A.; Mehra, N.C., Tomar, B.S. *J Eng Tribol* 227 (**2013**) 381.
[4] Satapathy, B.K.; Majumdar, A.; Tomar, B.S. *Mater Des* 31(**2010**) 1937.

BL41

Cure Kinetics Studies on Carboxyl Terminated poly(acrylonitrile-co-butadiene)-POSS Composites Using Differential Scanning Colorimetry

Raneesh Konnola* and Kuruvilla Joseph
[a]*Department of Chemistry, Indian Institute of Space Science and Technology, Thiruvananthapuram-695547, INDIA*
** raneeshkonnola@gmail.com*

Hybrid materials possessing both inorganic and organic components are interesting substances because of their potentially increased performance capabilities relative to those of either of their nonhybrid species [1]. Recently, novel classes of organic/inorganic hybrid materials have been developed based on polyhedral oligomeric silsesquioxane (POSS) with formula $(RSiO_{1.5})_8$, a cubic form of silica that is rigid, well-defined cage-like framework structure, and appended eight organic groups to the vertexes of the cage [2]. POSS have several advantages over conventional inorganic fillers, including monodispersity, low density, high thermal stability, and controllable functionalities. In addition, POSS monomers can be blended directly with polymers or copolymerized with other monomers to form polymer/POSS nanocomposites [3].

In this work, a new organic–inorganic hybrid material was prepared through reactive blending of Carboxyl Terminated poly(acrylonitrile-co-butadiene) (CTBN)) with Glycidyl Polyhedral Oligomeric Silsesquioxanes (Glycidylyl POSS). Triphenyl phosphine was used to catalyze the cure reaction. The structure of the composite (DSC).

The cure kinetics and the effect of catalyst on cure kinetics were investigated by using DSC at different heating rates. A single overall curing process by an nth-order function $(1\text{-}\alpha)^n$ was considered, and multiple heating rate models (Kissinger, Flynn–Wall–Ozawa, and Crane methods) were employed. The apparent activation energy (Ea) obtained showed dependence on the concentration of catalyst and the heating rate (β).

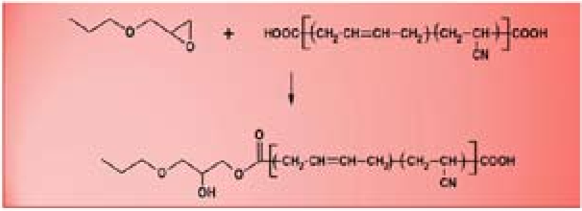


Figure 1: Reaction between Glycidyl group of POSS and Carboxyl group of CTBN

References

[1] Adam Strachota.; Irena Kroutilova.; Jana Kovarova.; and Libor Matejka *Macromolecules*, 37 **(2004)** 9457
[2] Caihua Ni.; Guifeng Ni.; Liping Zhang.; Jiaquan Mi.; Bolong Yao and Changping Zhu *J. Colloid Interface Sci.* xx **(2011)** xxxx
[3] Jieh-Ming Huang.; Hui-Ju Huang.; Yu-Xiang Wang.; Wen-Yi Chen and Feng-Chih Chang, *Journal of Polymer Science: Part B: Polymer Physiscs* **(2009)** 1927.

BL42

Synthesis of Graphine Oxide from Different Precursors: Overview on Variation in Electronic Properties

Rini Rajesh Jain, Vijay Raman Chaudhari*
Department of Nano Science and Nano Technology, University Institute of Chemical Technology, North Maharashtra University, Jalgaon – 425 001, India
E-mail: (rinijain9@gmail.com), Cell Phone: 7709876006
***#:** Corresponding Author: – vijay.rchaudhari@gmail.com*

Graphine oxide (GO) have been prepared by improved Hummer's method using different precursors *viz*. graphite powder, activated charcoal. The samples were characterized by UV-visible, FTIR spectroscopy, X-ray diffraction, Filed Emission Scanning Electron Microscopy (FE-SEM) and Raman. The UV-visible and FTIR spectra suggest the presence of carbonyl, epoxy group on the GO sheets. Morphology of GO was confirmed using FE-SEM. Comparative study using UV-visible spectroscopy indicates the different relative absorbance for C=C and C=O of GO, suggest the impact of starting precursor on nature of GO. XRD pattern indicates lesser exploitation of graphene sheets of charcoal GO as compare to GPGO. From the Raman spectra it is observed that the D/G ratio lower for GPGO (0.84) is less than charcoal GO (0.88) indicating that GPGO has fewer defects due to larger size of SP^2 domain among both.

Electronic properties of GO prepared using these precursors were studied by recording ***I-V*** characteristic curve. Significant variation is observed in conductivity value for above GO samples which suggest the variation in the electronic nature of GO prepared using different precursors.

References

[1] F.Y. Ban1, S.R. Majid1,*, N.M. Huang2, H.N. Lim3,* *Int. J. Electrochem. Sci.,* 7 **(2012)** 4345 - 4351
[2] C. Brownson, D. K. Kampouris, and C. E. Banks, *J. Power Sources* 196 (**201**1) 4873.
[3] A. K. Geim, *Science* 324 **(2009)** 1530.
[4] P. Zhu, M. Shen, S. Xiao, and D. Zhang, Physica
[5] Daniela C. Marcano,† Dmitry V. Kosynkin,† Jacob M. Berlin, Alexander Sinitskii, Zhengzong Alexander Slesarev, Lawrence B. Alemany, Wei Lu, and James M. Tour* Improved Synthesis of Graphene Oxide,ACS Nano, VOL. 4 • NO. 8 • 4806–4814 • **2010**
[6] I.Pardes,*S. Villar Rodil,A. Martinez-Alonso,and J.M.D.Tascon,Langmuir 24, (**2008**), 10560-10564.
[7] C.-T. Hsieh, S.-M. Hsu, J.-Y. Lin, and H. Teng, *J. Phys. Chem*. C 115 (**2011**) 12367

BL43

Studies on Rheological Properties of PP/SEBS-g-MA Blend

Rishi Sharma* and S. N. Maiti
Centre for Polymer Science and Engineering, Indian Institute of Technology,
Delhi-110016 INDIA
Email:rishisharmaiitd@gmail.com

Polypropylene is known for its outstanding properties and it can be modified by melt mixing with an elastomer. These blends had some disadvantages of poor miscibility, low modulus, but they have some advantages of good impact strength and easy processibilty. In this study melt rheological properties of PP/SEBS-g-MA blends are studied up to 50% SEBS-g-MA content at three different temperatures 210^0, 220^0 and 230^0 C and shear rate range 100 to 3500 s^{-1}. Melt viscosity increased with increasing amount of SEBS-g-MA which showed that there is an interaction between PP and SEBS-g-MA. The blends follow power law behaviour for pseudoplastic fluids. The power law index value is increased with increasing amount of SEBS-g-MA but there is no change in the power law index value with temperature.

Parallel plate rheological studies also have been performed on the PP/SEBS-g-MA blends at 200^0 C. Complex viscosity decreased with increasing frequency. This may be due to ease of disentanglement of PP chains in presence of the blending copolymer at higher frequencies. At low frequency region storage moduli of the blends are higher than that of PP.

References:

[1] Gahleitner, M. *Prog.Polym.Sci.* 26 (**2001**) 895.
[2] Danesi, S. Porter, R. S. *Polymer* 19 (**1978)** 448.

BL44

Racemic drugs resolution by using polymer supported chiral selector

SachinT.Mane, S.Ponrathnam, N.N.Chavan*
National Chemical Laboratory,Polymer Science & Engineering Division, Pashan road, Pune-411008

Here,we synthesized the core-shell type of polymer by using suspension & solution polymerisation. Hydrophilic (MMA-EGDMA) & Hydrophobic (MMA-DVB) polymers of different crosslinked density were synthesized by suspension polymerisation.Because of high surface area & hydrophobicity, MMA-DVB polymer at 200 crosslink density was used as a core,while Poly(GMA) was synthesized using GMA by solution polymerisation & used as a shell.The shell polymer, poly(GMA) crosslinked 5 mole % by 1,6 hexadiamine crosslinker.Remaining 95 mole % reactive site was used for reaction with chiral selector.These steps was characterized by Fourier transform Infra red (FTIR),Scaning electron microscope (SEM),Elemental analysis,Surface area analyzer,particle size analyzer,Solid state NMR.

Racemic drug Atenolol was resolved by using D(-)Dibenzoyl tartaric acid as a chiral selector supported on a core-shell type of polymers.Enantiomeric excess was reported at different time intervals by HPLC.

BL45

A Strategy for Achieving Low Percolation and High Electrical Conductivity in Melt-Blended Polycarbonate (PC)/Multiwall Carbon Nanotube (MWCNT) Nanocomposites

Sandip Maiti and B. B. Khatua*
Materials Science Centre,Indian Institute of Technology, Kharagpur-721302, INDIA
E-mail address: khatuabb@matsc.iitkgp.ernet.in (B. B. Khatua)

In the last two decades, the electrically conductive polymer nanocomposites materials based on conductive carbon nanofillers or nanoparticles have become the subject of intensive research area [1, 2]. In general, polymer nanocomposites consist of two-phase systems containing polymers with high surface area of nanofillers or nanoparticles. The field of polymer nanocomposites has been greatly illustrated with the incorporation of carbon nanotubes (CNTs) to improve their electrical, mechanical and thermal properties. The electrical conductive properties of polymer nanocomposites reinforced with CNTs at low concentration make a great advantage in the different field of applications [3-5]. The homogeneous dispersion and distribution of CNTs throughout the matrix polymer is the main key that can help to decrease the filler loading concentration and improve the electrical, mechanical and thermal properties of the host polymer.

In this work, polycarbonate (PC)/multiwall carbon nanotube (MWCNT) nanocomposites were prepared by simple melt mixing at a temperature (~350 °C) well above the processing temperature of PC, followed by compression molding, that exhibited percolation threshold as low as of 0.11wt% and high electrical conductivity of $\sim 1.38\times10^{-3}$ S.cm^{-1} at only 0.5 wt% MWCNT loading. Due to the lower interfacial energy between MWCNT and PC, the carbon nanotubes are excellently dispersed and formed continuous conductive network structure throughout the host polymer. AC electrical conductivity and dielectric permittivity of PC/MWCNT nanocomposites were characterized in a broad frequency range, $\sim 10^{1}$-10^{7} Hz. Low percolation threshold (p_c) of 0.11 wt% and the critical exponent (t) of ~3.38 was resulted from scaling law equation. The linear plot of $\log\sigma_{DC}$ vs. $p^{-1/3}$ supported the presence of tunneling conduction among MWCNTs. The thermal property and storage modulus of PC were increased with the incorporation of little amount of MWCNTs. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) confirmed the homogeneous dispersion and distribution of MWCNTs throughout the matrix phase.

References:
[1] Spitalsky, Z.; Tasisb, D.; Papagelisb, K.; Galiotis, C. *Progress in Polymer Science,* 35 **(2010)** 357.
[2] Li, C. Y.; Li, L.; Cai, W.; Kodjie, S. L.; Tenneti, K. K. *Advanced Materials,* 17 **(2005)** 1198.
[3] Yoshimura, S. H.; Khan, S.; Maruyama, H.; Nakayama, Y.; Takeyasu, K. *Biomacromolecules,* 12 **(2011)** 1200.
[4] Geng J.; Zeng, T. *Journal of American Chemical Society,* 128 **(2006)** 16827.
[5] Tang, Y.; Allen, B. L.; Kauffman, D. R.; Star, A. *Journal of American Chemical Society,* 131 **(2009)** 13200.

BL46

Polyimide/Nanofiller based Modified EPDM Nanocomposites for Rocket Motor Insulation

[a]Sangita Singh, [b]P K Guchhait, [a]N K Singha, [a]T K Chaki*
[a]*Rubber Technology Centre, Indian Institute of Technology Kharagpur, India 721302*
[b]*Kalpana Chawla Space Technology Cell, Indian Institute of Technology Kharagpur, India*
**sangita.singh@rtc.iitkgp.ernet.in / tapan@rtc.iitkgp.ernet.in*

Insulation of rocket motor case is an important research topic for rubber/polymer composites to be developed in space applications. This is understood from space technology literature that the rocket case of solid propellant must be protected from the tremendous heat and high pressure generated during launch of a space craft. Elastomer chosen filled with different reinforcing fillers may be successfully laid on the rocket metal case to protect the same against hostile environment provided it meets desired insulation characteristics and interface properties. The technologies in aerospace insulation application demands light weight polymers of high specific strength, low modulus, high ablation and good thermal properties. Ethylene propylene diene terpolymer (EPDM) with all these above mentioned properties is emerging as an elastomer of choice in rocket motor insulation. Low density, high thermal resistance and good retention of properties even after six months of ageing are additional advantages. The present work deals with the introduction of polyimide (PI), as new filler in EPDM matrix along with nanosilica (NS) / carbon nanofiber (CNF). Because of its stiff aromatic backbone, polyimide is highly ablative and shows high thermal stability. More importantly, its availability in powdery state helps in ease of mixing into the rubber matrix as well as good dispersion in the EPDM matrix. Polyimide and nanosilica/CNF are having inherent polar groups on their surfaces. Hence to achieve compatibility and homogenous mix it is necessary and essential to modify EPDM by chemical grafting with maleic anhydride (MAH) [Fig 1]. The objective of this investigation is to achieve a low density material with better thermal performance based on EPDM-g-MAH. Thermal [Fig 2] and mechanical properties as well as morphology have been investigated for EPDM-g-MAH with PI/nanosilica and PI/carbon nanofiber.

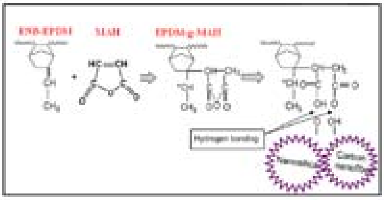


Fig 1 Modification of EPDM to EPDM-g-MAH

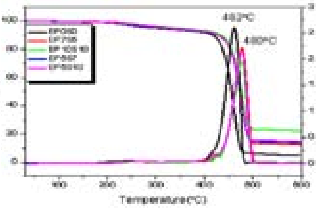


Fig 2 Thermo-gravimetric analysis of EPDM-g-MAH/ PI/nanosilica.

References:
[1] Harvey et al, US patent no. 6606852 **(2003)**
[2] Guillot et al, US patent no. 6787586B2 **(2004).**

BL47

Graphene oxide/polyaniline nanostructures: transformation of 2D sheet to 1D nanotube and *in situ* reduction

Sanjoy Mondal, Utpal Rana, Sudip Malik*
Polymer Science Unit, Indian Association for the Cultivation of Science,
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata, 700032
psusm@iacs.res.in

Graphene Oxide (GO) has produced a great attention among the researchers working in different areas because its superior electronic, optical, thermal and mechanical properties. However, GO is an electrically insulating material with a large number of defect sites that is generated by the presence of epoxide, phenoxides and carboxylic acids on its surface. Elimination of these defects either by chemical or thermal reduction technique subsequently produces reduced graphene oxide (RGO) and it simultaneously allows one to restore the electrical properties. RGO sheets have been used for many such as field effect transistors FETs, chemical sensors, organic solar cells, as well as transparent electrodes in photovoltaic devices.

Polyaniline (PANI) is one of the most fashionable conducting polymers due to its facile synthesis, exceptional solution processability, good environmental stability as well as simple doping/dedoping chemistry. In particular, making nanostructures of PANI could offer the exciting properties that will ultimately lead to potential applications in separation, sensors, batteries, electro-optic and electro-chromic devices, antistatic coating and correction protection. However, the control of size and morphology at the time of PANI nanostructures synthesis still remains a challenge. Taking the advantage of facile synthesis of PANI, hydrophilic nature of GO and the presence of carboxylic acid group which is requirement for polymerization of aniline in presence of an oxidant.

Here we report, the formation of unique PANI nanotubes in presence of graphene oxide (GO) which plays crucial dual role as dopant and soft template, simultaneously. GO in nanotubes is *in situ* reduced to reduced GO with restoration of electrical conductivities and enhanced thermal stabilities. Synthesized Graphene oxide/polyaniline composite are characterized by multiple techniques, such as electron microscopy, Fourier transformed infra-red (FTIR), Raman, UV-vis spectroscopy and XRD analysis. Cyclic voltametric analysis indicates that the good electrochemical stability with high capacitance value. Synthesize composite highly applicable also for super capacitor and nano device preparation.

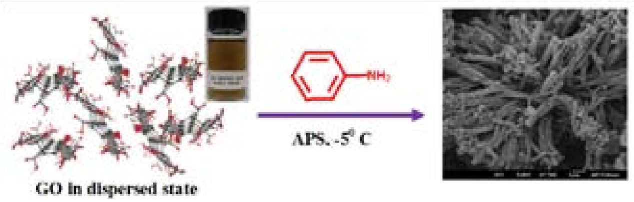


Figure1. Schematic view of Graphene oxide/polyaniline nanostructures preparation.

References

[1] Rana, U.; Chakrabarti, K.; and Malik, S.; *J. Mater. Chem.*, 21 (**2011**) 11098–11100.
[2] Rana, U.; Chakrabarti, K.; and Malik, S.; *J. Mater. Chem.*, 22 (**2012**) 15665–15671.
[3] Rana, U.; Malik, S.; *Chem. Commun.*, 48 (**2012**) 10862–10864.
[4] Wang, R; Wang, S.; Zhang, D.; Li, Z; Fang, Y. and Qiu, X., *ACS Nano*, 5 (**2011**) 408.
[5] Arif, M.; Heo, K.; Lee, B. Y.; Lee, J.; Seo, D. H .; Seo, S.; Jian, J. and Hong, S., *Nanotechnology*, 22(2011) 355709.

BL48

Evaluation of Ionic Liquids as Antistatic Agents for Polyurethane

Saori Tajima[a], Takuya Iwata[a,b], Akiko Tsurumaki[a,b], Hiroyuki Ohno[a,b,*]
[a] *Department of Biotechnology, Tokyo University of Agriculture and Technology,*
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[b] *Functional Ionic Liquid Laboratories,*
Graduate School of Engineering, Tokyo University of Agriculture and Technology,
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
** E-mail address: ohnoh@cc.tuat.ac.jp (H. Ohno).*

Ionic liquids (ILs), molten salts at ambient temperature, have received a great deal of interest due to their unique properties such as nonvolatility, nonflammability, designability, high ion density, and high ionic conductivity. Because of their high ionic conductivity, ILs are used as potential antistatic agents for insulating polymers. Antistatic agents such as carbon black and surfactants are considered to form successive conduction pathways to eliminate static electricity on polymer surfaces. Owing to the good designability of ILs, there is a strong expectation on ILs to be dispersed on polymer surfaces as antistatic agents. In this study, we have evaluated antistatic properties of ILs on insulating polyurethane (PU), and here we discuss the effect of ion structures on the antistatic properties of ILs.

Figure 1 shows structure of component ions of ILs used in this study. PU containing certain amount of IL (10~1000 ppm) was examined for surface resistance measurement. Surface resistance of the film was investigated using a Solartron Modulab system. A potential of ± 5 V was applied to the investigated film placed on the cell with gold comb-shaped electrodes to detect direct currents. Affinity of ILs with PU was examined with solubility test of linear PU. $[C_4mim][Tf_2N]$ was found to have better affinity with linear PU than $[P_{4448}][Tf_2N]$.

Figure 1. Structure of ions of prepared ionic liquids used in this study.

Figure 2 shows surface resistance verses IL concentrations in the PU film containing $[C_4mim][Tf_2N]$ or $[P_{4448}][Tf_2N]$. In order to obtain surface resistance of at least 10^{10} Ω/sq., addition of more than one per cent antistatic agent is generally needed. However, in this study, surface resistance of PU film without IL (>10^{14} Ω/sq.) decreased dramatically depending on the amount of ILs. The surface resistance of PU films with 10 ppm of ILs was about 1000 times less than that of PU film without ILs. Additionally, PU films with 1000 ppm of ILs showed surface resistance of 10^9 Ω/sq. Consequently, we found that ILs act as an antistatic agent at very low concentrations even below a concentration that forms a successive conduction pathway. In conclusion, we focused on the effect of ion structure on the antistatic properties.

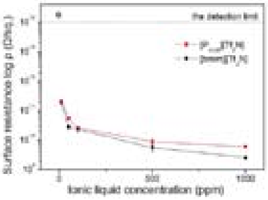


Figure 2. Surface resistance of concentration gradient polyurethane films containing [C4mim][Tf2N] and [P4448][Tf2N]. Surface resistance of PU film was higher than 1014 Ω/sq., withc was the detection limit of Solartron Modulab system.

BL49

Sonochemical Synthesis and Characterization of Calcium Sulfate Nano-Rods

Sarang S. Bari ,Aniruddha Chatterjee*, Satyendra Mishra*
Department of Plastics & Polymer Technology, University Institute of Chemical Technology, North Maharashtra University, Jalgaon – 425 001, (MS) India
***#:** Corresponding Author: – aniruddha _chatterjee2006@yahoo.co.in*

Nanoparticles of Calcium Sulfate ($CaSO_4$) were synthesized by sonochemical method using aqueous solution of Calcium Chloride ($CaCl_3$) and Ammonium Sulfate [$(NH_4)_2SO_4$], in order to acquire large surface area & high aspect ratio for the reaction. Size and shape of the nanoparticles were controlled by using different composition of anionic and cationic surfactants namely Sodium Dodyosyl Sulphate (SDS) and Cetyl Trimethyl Ammonium Bromide (CTAB) respectively as well as their combination. Sonication period was for 50 min, including the dropwise addition of the precursor, under controlled temperature condition. Chemical structure & elemental composition of the nanoparticles were characterized by Fourier Transform Infra-Red Spectroscopy (FTIR), X-Ray powder Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). Rod-shaped morphology and growth patterns of the nanoparticles were characterized by Field Emission Scanning Electron Microscopy (FESEM) while particle-size of the same was characterized by FESEM as well as Particle-size analyzer (DLS). $CaSO_4$ nanoparticles obtained with rod shaped morphology have lengths of 0.5–4 μm and mean diameters of about 150 nm. The combined effect of mixed surfactants assembly was found to have close relation with morphology of the final product which was discussed and possible growth and nucleation mechanism of the same was tentatively inferred.

Keywords: CaSO4 nanoparticles, Ultrasonication, Anionic & Cationic surfactants.

References

[1] Manoj Kumar Pal, Jaiswar Gautam, *Polymer Composites*- (**2012),** 515-523
[2] C. Saujanya, S. Radhakrishnan* Journal of Materials Science 33 (**1998**) 1063 -1068
[3] Yingqing Zhan • Yajie Lei • Fanbin Meng •Jiachun Zhong • Rui Zhao • Xiaobo Liu J Mater Sci
[4] 46(**2011**):824–8
[5] M. Sabzi, S.M. Mirabedini∗, J. Zohuriaan-Mehr, M. Atai *Progress in Organic Coatings 65* ***(2009)***
[6] 222- 228

BL50

Influence of moisture on mechanical properties of amino silane functionalized alumina in PVB nanocomposite films

Saravanan S[a,b], Satyajit Gupta[a,b], Praveen C Ramamurthy[a,b] and Giridhar Madras[b]
[a,b]*Department of Materials Engineering,* [b]*Centre for Nanoscience and Engineering*
Indian Institute of Science, Bangalore – 560012 INDIA

The recent progress in the development of organic conducting polymer and small molecule based materials are best regarded as an alternative to conventional silicon based solar cells and for in flexible-flat displays such as O-LEDs. Low band-gap material synthesis with better band-gap engineering and by various architectures such as stacked; tandem and inverted type cell models are proposed to increase the cell efficiency to compete with inorganic based solar cells [1]. But, these organic based materials are sensitive towards moisture and oxygen in the ambient, it needs hermitic protection (WVTR 10^{-6} g/m^2/d and OTR of 10^{-5} g/cm^2/d) [2]. Single and multilayer films of alternate polymer/metal oxide layers by ALD and MLD method of fabrication are available at higher manufacturing cost. The use of nano-fillers in polymer matrix acts as good moisture 'trapper' by providing long tortuous path at low production cost with flexibility [3].

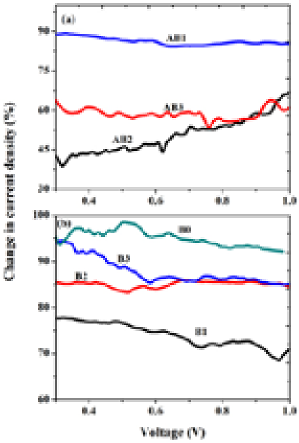


Fig.1 Change in current density with voltage

In the present study, a hybrid-polymer nanocomposite film, based on polyvinyl butyral/amino-silane functionalized nano alumina, is fabricated by melt processing. Functionalized nanocomposite films exhibit better moisture impermeation rate compared to non-functionalized alumina loaded films, as suggested from calcium degradation studies. Tensile, dynamic mechanical analysis and contact angle studies are also conducted to access the performance of the nanocomposite films. These films are encapsulated on Al/P3HT/ITO Schottky structured device to gain an insight over change in current density of the device before and after aging. Functionalized films exhibit 50% loss in current density after aging for 1 h, which is better than neat polymer and alumina loaded films (fig.1a,b, AB- fA/PVB, B- A/PVB, B0-neat polymer). These results indicate that PVB/f-alumina loaded films can be used as a single layer or as an interlayer barrier film for moisture sensitive electronic packaging applications.

References:

[1] Zhou, H.; Yang, L.; Wei, Y. *Macromolecules* 45 (**2012**) 607
[2] Park, J. S.; Chae, H.; Chung, H. K.; Sang, S. I. *Semicond. Sci. Technol* 26 (**2011**) 034001
[3] Gupta, S.; Ramamurthy, P. C.; Madras, G. S. Gupta, P.C. Ramamurthy and G. Madras, *Ind. Eng. Chem. Res* 50 (2011) 6585

BL51

Flexible Electron and Proton Conducting Composite Films Based on SBS Triblock Copolymer

Shankar P. Khatiwada, Santosh Adhikari, Rameshwar Adhikari
Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
E-mail: skradius33@yahoo.com, nepalpolymer@yahoo.com

Different conducting polymer films were prepared by introducing ionic groups *via* chemical modification of one of the blocks of the polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymer and by adding different amount of metal salts into the modified block copolymer. The butadiene part of the copolymer was partially sulphonated to prepare the proton conducting film while the epoxidized form (eBCP) was used to fabricate electron conducting films with different inorganic salts. The products were characterized by Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and potential as well as conductivity measurements. The mechanical properties of the samples were determined by microindentation hardness measurements. The formation of ionomer membrane was confirmed by proton conductivity measurement, the electron conductivity and SEM analysis. Some eBCP/metal-salts composite were electron conducting which may be attributed to the overlap of their respective energy bands, the latter being facilitated by co-continuous network of the composites. The ionic conductivity was found to increase with the increase in degree of sulfonation in the ionomer.

BL52

Investigations on Hydrocarbon Fuel Compatibility of Nitrile and Styrene-Butadiene Rubber Blends for Dynamic Application in Semi Cryogenic Engine

S.B. Singh, Suhas Mukherjee, Tushar Bhatt*, Ratheesh S, R.Muraleekrishnan and C.P. Reghunadhan Nair
Polymers and Special Chemicals Group, PCM Entiy, Vikram Sarabhai Space Centre,
Thiruvananthapuram 695 022 INDIA
*bhatt_tushar@vssc.gov.in

Rubber components like O-rings, gaskets, bellows, diaphragms, etc. used for aerospace applications are normally designed to withstand extreme thermal environments, vibrational fatigue loads, etc. during flight. However, there are reports on failure of even seemingly benign rubber components such as O-rings [1]. The present study is aimed at formulating a rubber compound that can withstand harsh conditions of hydrocarbon fuel jets at very high pressure and temperature levels under static and dynamic loading in a subsystem used in semi cryogenic engines being developed for heavy-lift satellite launch vehicles of *ISRO*.
\

A blend of two polymers, viz: acrylonitrile-butadiene rubber (NBR) and the styrene-butadiene rubber (SBR) was selected as the polymeric matrix for developing the formulation. A study was carried out by varying ratios of NBR and SBR in the polymer matrix and proportion of furnace black as the reinforcing filler. The rubber compounds with a sulphur based cure system were characterized for their rheological and dynamic-mechanical properties. It was observed that an increase in SBR content in the blend causes enhancement in plasticity of the rubber matrix which in turn results in increase in scorch as well as curing time [2,3]. Increased plasticity of the blend due to increase in SBR content can also be correlated to decreasing trend in mechanical properties and increase in Shore A hardness as shown in fig. 1. Desirable hardness levels could also be achieved to resist the high sealing loads, without compromising the processibility. Studies regarding change in response of NBR-SBR under various dynamic loading conditions were carried out for different percentage of styrene content in NBR-SBR blend. Dynamic response studies showed a decreasing trend of tanδ as the rubber was subjected to increased static strain along with frequency ramping in the range of 1 to 100 Hz. Compatibility aspects of the cured rubber compositions with the hydrocarbon fuel (a special grade of kerosene) were evaluated by controlled swell studies. With an increase in the styrene rubber percentage, exposure to hydrocarbon fuel resulted in swelling as well as deterioration in physical and mechanical properties, because of the obvious difference in the solubility of NBR and SBR in the hydrocarbon fuel [3].

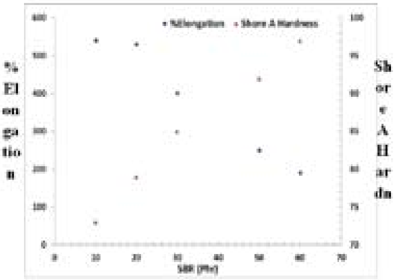


Fig.1: Effect of SBR content on Elongation and hardness

References:

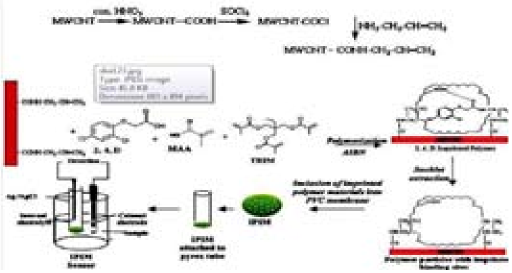
[1] Rogers Commission report (1986). "Report of the Presidential Commission on the Space Shuttle *Challenger* Accident", Volume 1, chapter 4, page 72.
[2] Mathew, M.; Thomas, S., "Compatibilisation of heterogeneous acrylonitrile-butadiene rubber/polystyrene blends by the addition of styrene-acrylonitrile copolymer: effect on morphology and mechanical properties.", *Polymer,* 44 **(2003)** 1295.
[3] Leblanc, J. L., "Rubber-filler interaction and rheological properties in filled compounds", Progress in Polymer Science, 27 (2002) 627.

BL53

Determination of 2, 4, D (2, 4, Dichlorophenoxyaceticacid) Using Imprinted Polymer Inclusion Membrane Derived from Surface Modified Multiwalled Carbon Nano Tube

Thayyath. S. Anirudhan*, Sheeba Alexander, Parvathy J.
Department of Chemistry, University of Kerala, Kariavattom, Trivandrum-695 581, India
E mail: tsani@rediffmail.com

2, 4, dichlorophenoxyaceticacid (2, 4, D) is generally used as a pesticide found in natural waters and its concentration in ground water is 20 µg L^{-1} [1]. Health effects of chronic or acute 2,4-D exposure reported for adults included blood, liver, and kidney toxicity[2], therefore its detection at low concentrations is a major problem.The potentiometric transduction approach is an easy type and on combining it with the imprinted polymer serves an approach for the sensing of analytes. Present work reports the fabrication of an ion imprinted inclusion membrane (IPIM) based biomimetic potentiometric sensor for routine monitoring of 2, 4, D in polyvinyl chloride (PVC) matrix using modified multiwalled carbon nanotube (MWCNT) as the supporting matrix. MWCNTs are initially functionalized with vinyl groups through nitric acid oxidation along with reacting by allylamine. MWCNT based imprinted polymer (MWCNT-MIP) was synthesized by means of methacrylic acid (MAA) as the monomer, trimethylol propane trimethacrylate (TRIM) as the cross linker, α, α′-azobisisobutyronitrile (AIBN) as the initiator and 2, 4, D an organochlorine pesticide molecule as the template. Organized material was characterized by means of FTIR, XRD and SEM analyses. IR spectroscopy results confirm the functionalization and formation of MIP. XRD results prove that the decrease of crystallinity in MWCNT-MIP compared to MWCNT and SEM results indicated that the surface of MWCNT-MIP became rough and porous. The sensing membrane was developed by the inclusion of 2, 4, D imprinted polymer materials in the polyvinyl chloride (PVC) matrix. Unlike the majority of other conventional sensors, the surface of the membrane sensor is able to be reused many times with no conditioning. The optimization of operational parameters normally used such as amount and nature of plasticizers sensing material, pH and response time was conducted. From the non-imprinted (NIPIM) and imprinted polymer inclusion membrane (IPIM) sensors the response behaviour of 2, 4, D was compared under optimum conditions. The IPIM sensor responds in the range 1×10^{-9}- 1×10^{-5} M and the detection limit was found to be `1.2×10^{-9} M. The stability of IPIM sensor was checked and it is found to be 3 months and it can be reused many times without losing its sensitivity. For the application of sensor experiments with ground and tap water samples were performed.



Scheme. 1 A schematic representation of imprinted polymer inclusion membrane-based field monitoring device for detecting 2, 4, D

References

[1] Bushway R J; Hurst H C; Perkins L B; Tian L; Cbanillas G C; Young B E S; Ferguson B S and Jennings H S. Atrazine, alachlor, and carbofuran contamination of well water in central Marine. Bull. Environ. Contam.Toxicol., 49 (**1992**)1-9.

[2] Howard, P H E. "2, 4-D." Handbook of Environmental Fate and Exposure Data for Organic Chemicals Lewis Publishers (Chelsea MI), (**1991**) 145-156.

BL54

Poly(ether sulfone)/Graphene Oxide and Poly(ether sulfone)/Graphene Composites: A Comparative Study on the Thermal, Electrical and Mechanical Properties

Shikha Singh, Kheyanath Mitra, Biswajit Ray*
Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi – 221005, India
*Corresponding author: Email: biswajitray2003@yahoo.co.in

Poly(ether sulfone) (PES) is one of the high performance engineering thermoplastic owing to its excellent mechanical, biological and thermal stability and chemical resistance to hydrolysis and pH. In order to improve its different physical properties, several groups have reported its composites with layered clay, [1] Al_2O_3, [2] ZrO_2, [3] TiO_2, [4] Ag, [5] Au [6] etc. Here, we report first time the preparation of novel PES/Graphene oxide (GO) and PES/Graphene (G) composites with 0 – 5.0 wt% GO / G loading by solution mixing method. Resultant composites have been characterized by FTIR spectroscopy, Raman spectroscopy, X-Ray Diffraction, Thermo Gravimetry and Differential Scanning Calorimetric methods. Moreover, the mechanical, resistivity and thermal conductivity properties have also been studied. All these results will be compared.

Reference:

[1] C. Dizman, S. Ates, T, Uyar, M.A. Tasdelen, L. Torun, Y. Yagci. *Macromol. Mater. Eng.*
[2] 296(2011)1101-1106.
[3] M. Wara, I.F. Francis, B.V.Velamakanni. *J.Membr. Sci.* 104(1995)43.
[4] L. Genne, S. Kuypers, R. Leysen. *J. Membr. Sci.* 113(1996)343.
[5] J.B. li, J.W. Zhu, M.S. Zheng. *J. Appl. Polym.* Sci. 103(2006)3623.
[6] W.L. Chou, D.G. Yum, M.C. Yang. *Polym. Adv. Technol.* 16(2005) 600.
[7] M. Sangermano, I. Roppolo, V.H.A. Camara, C. Dizman, S. Ates, L. Torum, Y. Yagci. *Macromol. Mater. Eng.* 296(2011)820-825.

BL55

Proton Exchange Membrane Based on Polybenzimidazole/ Silica Nanocomposites

Shuvra Singha and Tushar Jana*
School of Chemistry, University of Hyderabad, Hyderabad 500046, INDIA.
Email: tjsc@uohyd.ernet.in

Poly(4,4′-diphenylether-5,5′-bibenzimidazole)(OPBI) is an aryl ether linked polybenzimidazole which, because of its unique materials properties like high thermal stability, glass transition temperature, modulus, etc, is widely studied for application in high temperature proton exchange membrane fuel cells (HT-PEMFC). Phosphoric acid (PA) doped OPBI exhibits high proton conductivity (1.17×10^{-1} Scm^{-1}) at 160°C. However, the chemical and mechanical stabilities of PA doped OPBI tend to deteriorate significantly at higher temperatures. Hence, there is a trade-off between the PA doping level of the polymer and its performance [1].

We prepared nanocomposite membrane based on OPBI and long chain amine functionalised silica nanoparticles to resolve the issue. Interaction between the polymer and nanoparticles at different weight loadings of the latter was studied by FTIR and ^{13}C solid state NMR. WAXD and TEM showed that the introduction of the functionalised silica in OPBI matrix altered the morphology of the nanocomposite membrane that led to the formation of well ordered interconnected arrays (Figure 1). And this ordering of the nanoparticles was found to improve the properties of the polymer [2, 3]. For instance, the nanocomposite membrane containing 15wt% of silica showed the highest proton conductivity (1.8×10^{-1} Scm^{-1}) at 160°C, a value almost twofold than that of pristine OPBI under identical conditions(Figure 2). The result was higher than that reported earlier [4]. The dimensional, thermal, mechanical and oxidative stability were enhanced and there was decrease in the water uptake of the nanocomposites membranes [5].

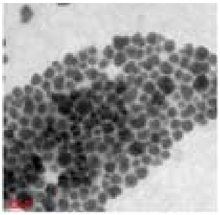


Figure 1. TEM image of OPBI/ 15% silica nanocomposite

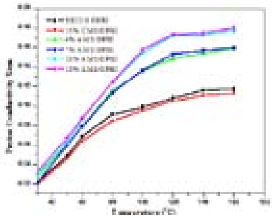


Figure2. Proton Conductivity as a function of temperature of OPBI nanocomposites

Acknowledgement
We thank CSIR for the senior research fellowship.

References

[1] Zhang, S.; Shen, P.K. *Chem. Rev,* 112 **(2012)** 2780.
[2] Suryani.; Chang, Y. N.; Lai, J.Y.; Lui, Y.L. *J. Memb. Sci.* 403 **(2012)** 1.
[3] Narayanan, S.R.; Yen, S.P.; Liu, L.; Greenbaum, S.G. *J. Phys. Chem. B* 110 **(2006)** 3942.
[4] Ghosh, S.; Maity, S.; Jana, T. *J. Mater. Chem.* 21 **(2011)** 14897.
[5] Singha, S.; Jana, T. *(Manuscript under preparation)*

BL56

Design and fabrication of high moisture barrier materials

Sindhu Seethamraju, Praveen C. Ramamurthy,* and Giridhar Madras
Department of Materials Engineering, Indian Institute of Science,
Bangalore-560012 INDIA

The development of high gas barrier materials, viable economically, is critical for all packaging applications. Recent progress in the field of organic electronics [1] has led to the increased flexible barrier material requirements towards moisture and oxygen for their encapsulation [2]. Active organic layers and the electrodes used in organic photovoltaics and organic light emitting diodes are prone to photo-oxidation in the presence of oxygen and moisture [3]. In order to protect the devices from environmental conditions, a flexible barrier material with water vapour transmission rate (WVTR) $< 10^{-6}$ g m^{-2} day^{-1} and oxygen transmission rate (OTR) $< 10^{-5}$ cm^3 m^{-2} day^{-1} is required.

The gas permeation through polymers follows the solution-diffusion mechanism. In rubbery polymers with polar groups, the permeation of polar molecule is solubility dominant whereas in glassy and non polar polymers, it is diffusion dominant. The penetrant molecules first get adsorbed onto the polymer surface dissolving in the matrix and followed by diffusion through the matrix based on concentration/pressure/temperature gradient. Due to the chemical nature of O_2 and H_2O, H_2O plasticizes polar, high oxygen barrier materials like poly (vinyl alcohol), making them poor H_2O vapor barriers at moderate humidities. Similarly, O_2 permeates more rapidly through the non-polar, low oxygen barrier materials, due to the relative smallness of the molecule. Therefore, the fundamental interactions between the polymer, environment and the permeant, the size of the permeant, connectivity of the system, free volume available, thermodynamic factors and environmental parameters determine the permeability behavior for a system.

In order to design better polymer-based low permeation, high barrier materials, solubility dominant permeation system with poly (vinyl alcohol-co-ethylene) (EVOH) as the base matrix [4] and diffusion dominant permeation system with poly (ethylene-co-methacrylic acid) (PEMA) ionomer as the base polymer [5] have been studied for organic device encapsulation. Calcium degradation test is used to determine the WVTR of these barrier materials.

References:

[1] Choi, M. C., Kim, Y., Ha, C. S. *Progress in Polymer Science* **33** (2008) 581
[2] Norrman, K., Gevorgyan, S. A., Krebs, F. C. *Applied Materials and Interfaces* **1 (2009)** 102
[3] Kawano, K., Pacios, R., Poplavskyy, D., Nelson, J., Bradley, D. D. C., Durrant, J. R. *Solar Energy Materials & Solar Cells*, **90** (2006) 352
[4] Sindhu, S., Ramamurthy, P. C., Madras, G. *unpublished data* (2013)
[5] Sindhu, S., Ramamurthy, P. C., Madras, G. *Applied Materials & Interfaces* under review, 2013.

BL57

Synthesis and characterization of functional polyhedral oligomeric silsesquioxanes and its composites with vinyl polydimethyl siloxane

Smitha C. Sukumaran*[a], Lekshmy M G[b], Prasanta Kumar Behera[a], Pravin R[a], Indulekha K[a], R.S. Rajeev[a],
[a]*Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram-695 022*
[b]*Udaya School of Engineering, Kanyakumari*
** Correspondence: smitha_sukumaran@vssc.gov.in*

Polyhedral oligomeric silsesquioxanes (POSS) are a class of important nanosized cage-like molecules, derived from hydrolysis and condensation of trifunctional organosilanes. A typical POSS molecule possesses a structure of cube-octameric frame work represented by the formula $(RSiO_{1.5})_n$ with an inorganic silica-like core (Si_8O_{12}) (~0.53 nm in diameter) surrounded by eight organic corner groups, one (or more) of which is reactive. Incorporation of nano sized POSS macromers into polymers has produced significant improvement in thermal and oxidative resistance as well as reduction in flammability of several POSS-based polymers; these systems then being suitable candidates in high-temperature and fire-resistant applications.

In the present work, we report the synthesis and characterization of polydimethylsiloxane (PDMS) containing completely and partially condensed POSS with mono and multifunctionalities. Monoallyl heptaphenyl POSS was synthesized by the hydrolysis and alkali catalysed condensation of phenyl triethoxy silane followed by capping with allyltrichlorosilanes. It was characterized using IR, ^{1}HNMR and TGA. Figure 1 shows the addition curing of Monoallyl heptaphenyl POSS and vinyl terminated PDMS with Si-H crosslinker. Incorporation of different weight loadings of the POSS into vinyl terminated PDMS and curing via platinum catalyzed addition cure mechanism using poly(dimethyl-co-methylhydrogen) crosslinker resulted in PDMS compositions with enhanced thermal stability with respect to decomposition that increased from 370 °C to 450 °C. DMA studies revealed that presence of POSS causes a change in the viscoelastic properties of vinyl PDMS. Usage of fully condensed monofunctional POSS in vinyl PDMS systems displayed enhancement in thermal stability compared to partially condensed multifunctional POSS.

There was a significant increase in the char residue of partially condensed POSS resin containing methyl and vinyl units, which increased from 80% to 89% on condensation curing. The studies have shown that the POSS incorporated PDMS systems are potential high temperature resistant coatings for aerospace applications.

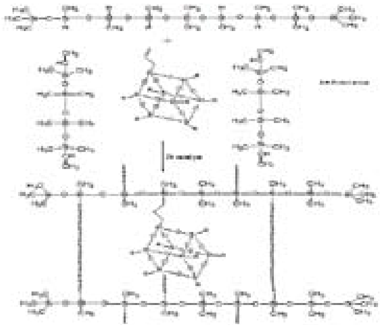


Fig 1. Preparation of the vinyl PDMS-POSS hybrid polymers

References
[1] Y.R. Liu,; Y.D. Huang,; Polymer Degradation and Stability 91 (**2006**) 2731-2738
[2] Shiao-Wei Kuo,; Feng-Chih Chang,; Progress in Polymer Science 36 (**2011**) 1649–1696

BL58

Growth of Vertically Aligned Tunable Polyaniline Nanofibers on Graphene/ZrO_2 Nanocomposites for Supercapacitor Energy-Storage Application

Soumen Giri and Chapal Kumar Das*
Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302 INDIA.
** Email: chapal12@yahoo.co.in*

With the mounting progress of global economy and industry, consequently, the impending energy crisis has stimulated intense research on the low cost, environmentally friendly and renewable energy resources [1]. Therefore, great efforts have been devoted to develop highly active electrode materials with enhanced energy density, while maintaining high power density, good specific capacitance and cycling stability accompanied with low fabrication costs. Supercapacitors, one of the most promising energy storage/conversion systems with the ability to store energy in a fraction of second, and the advantage of delivering the stored energy much more rapidly than batteries, can be coupled with batteries or fuel cells to deliver the desired high power density [2]. So, we need to develop their performances to meet the higher requirements of future systems, by developing new materials and advancing the interfaces of the materials at the nanoscale. For this purpose, we have synthesized *in-situ* reduced graphene oxide/ZrO_2 nanocomposite by hydrothermal method. Herein, we have successfully synthesized vertically aligned tunable polyaniline on this binary composite (Figure 1) by varying percentage of binary composite and monomer ratio keeping the oxidant concentration unchanged. We have also measured the conductivity and band gap of the as prepared nanocomposites. All the composites were characterized by UV-visible, FTIR, Raman, XRD, XPS, FESEM and TEM analyses. The formation mechanism of vertically aligned polyaniline nanofibers was also elaborately discussed in this paper by "Nanofiber Seeding" mechanism [3,4]. All electrochemical characterizations were performed by three electrode systems in terms of Cyclic Voltammetry (CV) (Figure 2), Electrochemical Impedance Spectroscopy (EIS), Galvanostatic Charge-Discharge (GCD) and cyclic stability test using 1 (M) H_2SO_4 as supporting electrolyte. The highest specific capacitance obtained was 1336.37 F/g from the composites at particular ratio and concentration. The small charge transfer resistance and high retention of specific capacitance after 1000 cycles showed promising electrode behavior in the field of electrochemical energy storage materials.

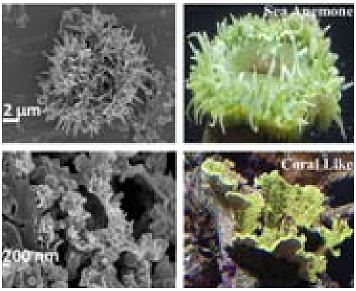


Figure 1. Different types of vertically aligned polyaniline with structure resembles

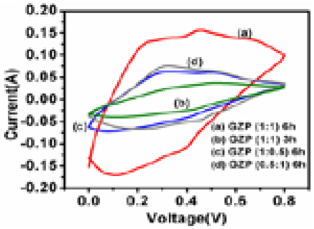


Figure 2. Cyclic Voltammetry curve of nanocomposites at 1 mV/s

References

[1] Simon, P.; Gogotsi, Y.; Nature Materials 7 (**2008**) 845
[2] Liu, C.;Yu, Z,.; Neff, D.;Zhamu, A.; Jang, B.; Nano Letters 10 (**2010**) 4863.
[3] Zhang, X.; Goux, WJ.; Manohar SK.; *J. Am. Chem Soc.* 126 (**2004**) 4502 .
[4] Chiou, NR.; Lu, C.; Guan J.; Jameslee, L.; Epstein AJ.; Nature Nanotechnology 2 (**2007**) 354.

BL59

Morphological and Dynamical Properties of Carbon Nanotube in Polycarbonate Carbon Nanotube Composite from Dissipative Particle Dynamics Simulation

Souvik Chakraborty[a], Sudip Roy*[a]
[a]*National Chemical Laboratory, Pune, India*
s.roy@ncl.res.in

Carbon nanotube is highly demanding material due to their chemical and physical properties and wide applications in material science. Polycarbonate is industrially important and widely used polymer. Small amount of nanotube when incorporated in polymer matrix can improve physical properties like strength, stiffness, thermal and electrical conductivity etc. Classical molecular dynamics (MD) simulation is a useful tool to study morphology and dynamics of polymer composites. We have performed atomistic simulation first to explore local structural and dynamical properties of nanotubes in composite and then meso-scale simulation is carried out to study morphology and dynamics in experimental length and timescale. In atomistic simulation bundle formation of CNTs is observed and the mechanism and energetics of bundle formation are investigated. Bundle formation of nanotubes is found to be energetically favourable [1]. As atomistic simulation is restricted in terms of length and timescale, simulation of long polymer chains with long nanotubes is difficult. So Dissipative Particle Dynamics simulation is performed to study the morphology and dynamics of CNTs in long chain polycarbonate matrices with different concentrations of CNT. Necessary parameters for DPD simulation of nanotube polymer composite is obtained from all-atomistic MD and Flory-Huggins theory. Three different concentrations (2, 5, 10 wt. percentages) of nanotube loading in polycarbonate matrix are simulated to investigate morphology and dynamics of nanotubes. Bundle formation of nanotubes in polycarbonate matrices has been observed. In case 10% mixture, percolation morphology by nanotubes is found to be formed. To explore the dynamics of bundle formation in different mixtures we have calculated mean square displacements of nanotubes and bundle size distribution is explored to investigate relative bundling efficiency of nanotubes in different concentrations.

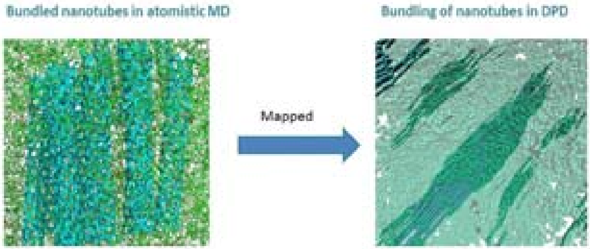


Figure1: Mapping from atomistic to meso-scale simulation

References

[1] S. Chakraborty, S. Roy, *J. Phys. Chem. B* **2012**, 116, 3083-3091.

BL60

A novel nanoparticle based matrix for targeted drug delivery

Sridhar Sanyasi[a], Silpa Panda[a], Chandan Goswami[b], Luna Goswami[a*]
[a]KIIT School of Biotechnology, KIIT University Campus-XI, Patia
Bhubaneswar-751024, Orissa, India
[b]School of Biological Sciences, National Institute of Science Education and Research, Institute of Physics Campus,
Sachivalaya Marg, Bhubaneswar 751005, India
[*]Email: lbh_1975@yahoo.co.in

Abstract: Recent advancement in nanotechnology has offered several novel and safer nanomaterials for human welfare particularly in the field of catalysis, electronics, molecular diagnostics, sensors and drug delivery [1]. However, the classical synthesis of nanoparticles by physical or chemical methods involve toxic chemicals and harsh reaction conditions emphasizing the need for novel strategies for "green synthesis" of nanoparticles which are clean, non-toxic, bio-compatible and environment friendly. Recently, polymers have been used to synthesize different nanoparticles made of silver, gold, platinum, palladium, iron, cobalt, etc. These polymer assisted synthesized nanomaterials are comparable with chemically synthesized nanoparticles in terms of size, shape and also exhibit advanced properties. In this work we have used Carboxy Methyl Tamarind Polysaccharide (CMT), a naturally occurring gum to synthesise different colloidal nanoparticles and stabilize these particles further by a "green approach". We report the successful use of CMT for the synthesis of gold, silver and cobalt colloidal nanoparticles by in situ reduction. These nanoparticles synthesized by this approach remain stable for a prolonged time as confirmed by UV visible spectroscopy and different microscopic methods. The sizes of these synthesized particles are in the range of 20-40 nm and are present as monodispersed form for longer period. We aim to use these nanoparticles for further preparation of tarnary system by using Hydroxy Ethyle Methacrylate (HEMA) as a grafting agent. We aim to use this for potential device for targeted drug delivery.

Key words: Nano based Devices , Carboxy Methyl Tamarind, Drug Delivery, Ternary system.

References

[1] Sankar R, Karthik A, Prabu A, Karthik S, Shivashangari K S, Ravikumar V. *Colloids and Surfaces B: Biointerfaces*, 108 (2013) 80–84.

BL61

Carbon Nanotube Induced Nucleation in Polypropylene/ Multi-Wall Carbon Nanotube Composites and its Influence on Crystallization Kinetics and Structural and Thermal Behaviour

Suchitra Parija[a], Arup R. Bhattachryya*[a], Ashok Misra[b]
[a] *Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay, Mumbai-400076 INDIA,*
[b] *Intellectual Ventures India LTD No. 701 Raheja Paramount, 138 Residency road,*
Bangalore-560025 INDIA.
** arupranjan@iitb.ac.in*

This study is aimed to investigate the role of multi-wall carbon nanotubes (MWNTs) as a nucleating agent and its influence on crystallization kinetics, micro-structural and thermal behaviour of MWNTs reinforced polypropylene (PP) composites. PP and MWNTs were prepared by melt mixing technique using a conical twin screw microcompounder with varying concentration of MWNTs. The structural analysis of the prepared samples was examined through X-ray diffraction analysis. The effect of MWNTs addition on the thermal transition of the PP was investigated by differential scanning calorimetric analysis (DSC) and thermo gravimetric analysis (TGA).

The result presented in this paper clearly shows that MWNTs nucleate crystallization of PP. Isothermal crystallization kinetics through differential scanning calorimetry (DSC) of PP/MWNTs composites demonstrate that rate of crystallization and relative crystallinity were affected by the presence of MWNTs, showing a significant increase in both the parameters. This indicates the existence of nucleating effect on the crystallization of PP due to presence of MWNTs in polypropylene melt. The X-ray diffraction data showed that the MWNTs act as a hetero-nucleating agent in PP, maintaining the monoclinic crystalline structure of PP. Degradation temperature of the samples obtained from thermo gravimetric analysis (TGA) showed an increase in thermal degradation behaviour for the PP/MWNTs composites with increase in the MWNTs concentration. Overall, it can be concluded that MWNTs based PP composites showed a significant improvement in degree of crystallinity, rate of crystallization and thermal stability as compared to the pristine polymer due to hetro-nucleating effect of MWNTs.

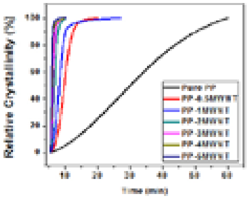


Figure 1. Relative crystalinity vs time of PP/MWNTs composites

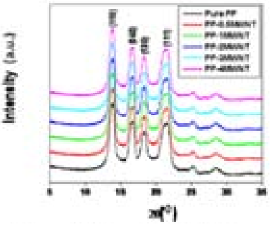


Figure 2.XRD of PP/MWNTs composites

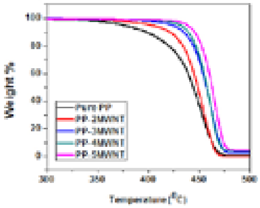


Figure 3. TGA of PP/MWNTs composites

References

[1] Grady B. P.; Pompeo F; Shambaugh R. L.; Resasco D. E. *J. Phys. Chem. B*, 106 (**2002**) 5852.
[2] Donghua X.; Zhigang W.;. *Polymer,* 49 (**2008**) 345.
[3] Bhattacharyya A. R., Sreekumar T. V., Liu T., Kumar S., Ericson L.N., Hauge R. H., Smalley R. E.; *Polymer, 44,* **(2003),** 2373

BL62

Advanced Characterisation Techniques for Nanomechanical Characterisation of P(VDF-HFP) /TiO_2 Piezoelectric Nanocomposite Thin Films

E.P Suhas[a,*] and Navin Kumar[b]
[a]*Department of Mechanical Engineering, R.V College of Engineering,*
Bangalore-560059 INDIA
[b]School of Mechanical, Materials and Energy Engineering, Indian Institute of Technology (IIT) Ropar,
Rupnagar- 140001, Punjab INDIA
(*email Id: suhas.ep@gmail.com)

Fluoropolymer thin films of PVDF [polyvinylidene fluoride] and its copolymer P(VDF-HFP) [polyvinylidene fluoride- hexafluoropropylene] have drawn considerable scientific and technological attention because of their excellent mechanical, piezoelectric, and pyroelectric properties as well as their exceptional biocompatibility[**1**]. Polymer thin films are being used for a large number of applications such as sensors and actuators in Micro-Electro-Mechanical Systems (MEMS) and non-volatile memories [**2**]. For many of their applications as actuators, they are used in the form of cantilever or membrane devices. The operation of these devices is determined by their electromechanical properties, which includes their elastic properties [**3**]. The properties of thin films can be quite different from bulk materials because of the high texture and residual stresses in the thin films. Nanomechanical Characterisation of the polymer thin films was carried out mainly by Nano Indenter (Hysitron Inc.) and AFM (Veeco Nanoscope). Nano-mechanical testing helps analyse materials at scales smaller than micro-indenters can provide, with higher resolution and smaller forces [**4**]. In contrast, nano-mechanical testing uses much smaller diamond-tipped probes and specially developed force transducers for quantitative nano-scale information [**5**]. Tests and imaging yield surface property information with very high spatial resolution. (**Fig 1**)

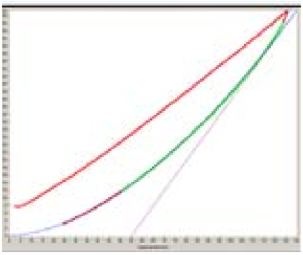


Fig 1: Nano Indentation results for thin film

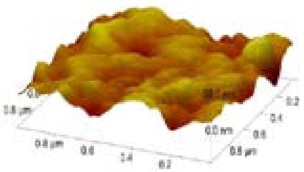


Fig 2: 3D plot of doped sample

Thin films of P(VDF-HFP), both pristine and doped (with TiO_2) prepared by solution casting ,were subjected to XRD (X-ray diffraction Analysis) , SEM (Scanning Electron Microscopy) , FTIR (Fourier Transform Infrared Spectrum) and EDS (Energy Dispersive Analysis) for phase confirmation of the polymer nanocomposites[**6**][**7**]. The tapping mode was employed during AFM (*Atomic force microscopy*) studies with frequency range of 324-368 kHz. Average roughness (Ra), Root mean square roughness (Rq) and Maximum roughness (R_{max}) were calculated for both pristine and doped thin films. It was found that both these values were higher for the doped film because of the titanium oxide nano particles embedded in the polymer matrix. The roughness values for both the polymer thin films did not exceed beyond 7 nm for a scan size of 1µm × 1µm. (**Fig 2**)

References:

[1] Marcel, B. and Euler, B. W. *J. Appl. Polym.Sci.*, **2003**, 89, 1093.
[2] Ramer, N. J.,Marrone, T., and Stiso, K. A. *J. Polym.*,**2006**, 47, 7160
[3] V.Ostasevicius *et al*; ISSN *1392-1207, MECHANIKA, **2010**. Nr.6 (86)*
[4] H. J. Lee *et al; &7803-7976-4/03 8 **2003** ,IEEE proceedings*
[5] Kristin Arlt and Michael Wegener, *IEEE Transactions Vol. 17, No. 4; Aug-**2010***
[6] Sajkiewicz *et al ; European polymer journel 35 (**1999**) 423-429*
[7] Xiaohong Gu *et al ; JCT Research, Vol. 1, No. 3, July **2004***

BL63

KOH modified graphene/polypyrrole nanocomposite for supercapacitor applications

Sumanta Sahoo* and Chapal Kumar Das

Graphene is a transparent single layer of carbon atoms, arranged in a "honeycomb" fashion. Owing to its high aspect ratio, surface area, extraordinary electrical and electrochemical properties, it has been considered as an efficient component for the construction of supercapacitor electrode. However, to achieve improved electrical as well as electrochemical properties, incorporation of graphene into polymer matrices needs some type of modification. Among different polymers, Polypyrrole is one of the most widely investigated conducting polymers because of its easy synthesis, enhanced thermal stability, high electrical conductivity, excellent chemical stability etc.

The electrochemical performances of the supercapacitor electrode materials based on KOH modified graphene and Polypyrrole was investigated in 1M KCl solution. The modification was carried out in a simple, inexpensive chemical route. Nanocomposite was prepared by *in situ* polymerization process using ammonium persulfate as oxidant. KOH treatment of graphene enhanced the electrochemical performances of nanocomposite. KOH modified Graphene/ Polypyrrole nanocomposite showed non-linear I-V characteristics, which is favourable for device application. The nanocomposite also exhibited enhanced electrochemical performances like high specific capacitance, high energy density, superior cyclic stability etc. The electrochemical impedance spectra showed low equivalent series resistance of the nanocomposite, indicative of high conductivity of the electrode material.

References

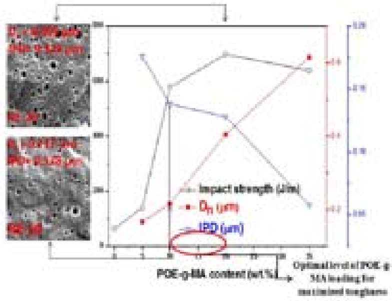
[1] Sahoo, S.; Dhibar, S.; Hatui, G.; Bhattacharya, P.; Kumar Das, C. K. *Polymer*, 54 **(2013)** 1033-1042.
[2] Sahoo, S.; Karthikeyan, G.; Nayak, G. C.; Das, C. K. *Synthetic Metals*, 161 **(2011)** 1713-1719.
[3] Sahoo, S.; Dhibar, S.; Das, C. K. *eXPRESS Polymer Letters*, 6 **(2012)** 965–974.

BL64

Morphological, Rheological and Thermal Properties of Polyamide-612 / Poly (Ethylene-Octene Elastomer) Blends

Sunil Kumar, Bhabani K. Satapathy* and S. N. Maiti
Centre for Polymer Science and Engineering, Indian Institute of Technology Delhi,
Hauz Khas, New Delhi-110016, INDIA

Polyamide-612 is well known for its low moisture uptake, dimensional stability and good wear resistance [1, 2]. Melt blending of polyamide-612 and maleic anhydride grafted poly-ethylene-octene elastomer (POE-g-MA) as an impact modifier with varying composition were done by co-rotating twin screw extruder. Structural, morphological, rheological, fracture and thermal properties of PA-612/POE-g-MA blends were studied. X-ray diffraction showed a decrease in percentage crystallinity. Significant increase in the impact strength (~11 fold) with an incorporation of POE-g-MA has been observed, which is further correlated to the domain size (D_n) of the dispersed phase [3] and their inter-particle distances (τ) as presented in *Figure* below. Scanning electron microscopy showed uniform distribution of POE-g-MA.



Further the toughening mechanism were analysed by Essential work of fracture (EWF) approach. Parallel plate rheometry results revealed the storage modulii (G′) and loss modulii (G″) of the blends are higher compared to the neat PA-612 at low frequency. Reduction in the extent of increase has been observed at higher frequencies. Increase in the complex viscosity was observed with POE-g-MA content. Differential scanning calorimetry (DSC) showed that the melting point of PA-612 and its blends were found to be broadly unaffected.

References:

[1] Majumdar,B.; Keskkula H.; Paul, D.; R.; Polymer 35 **(1994)** 1399.
[2] Pegoretti, A.; Ricco, T.; Engineering Fracture Mechanics 73 **(2006)** 2486.
[3] Bucknall, C. B.; Paul, D. R.; Polymer 50 **(2009)** 5539.

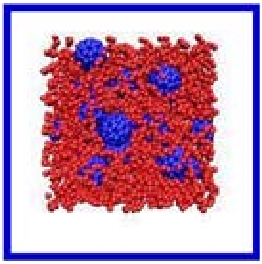
BL65

Effect of Aggregation and Dispersion of Nanoparticle on Tensile Strength of Polymer/Fullerene(C_{60}) Nanocomposite: Molecular Dynamics Simulation

Sunil Kumar, Sudip K. Pattanayek*
Department of Chemical Engineering,
Indian Institute of Technology, New Delhi-110016
**sudip@chemical.iitd.ac.in*

Polymer nano-composite with fullerene nano particle have attracted researchers because of its improved mechanical properties [1] and found wide range of applications from aerospace material to biomedical applications [2]. We have simulated the above system using LAMMPS [3] to estimate it's the mechanical properties from the molecular parameters such as polymer-polymer interaction parameter(ε_{pp}), polymer-nanoparticles interaction parameter(ε_{pn}), nanoparticle - nanoparticle interaction parameter(ε_{nn}), molecular weight of polymer (i.e. number of beads, N) etc. At a constant ε_{pp},and $\varepsilon_{nn,}$ we can have three different cases: (a) $\varepsilon_{pn} > \varepsilon_{pp,}$ (b) $\varepsilon_{pn} = \varepsilon_{pp}$ (c) $\varepsilon_{pn} < \varepsilon_{pp}$. We found that tensile yield strength during uniaxial deformation is the highest in case (a), due to favourable interaction between surface of nano-particle and polymer segment.

Radial distribution function clearly shown that nanoparticles are well dispersed in regime (a), so that tensile yield strength is found higher in regime (a). In regime (b) and (c), nanoparticles have tendency to aggregate and system separate in two phases and finally decreases tensile yield strength.



References:

[1] S. J. V. Frankland, V. M. Odegard and T. S. Gates, Comp. Sci. Tech., **63**,1655(2003)
[2] J. H. Koo, Polymer Nanotechnology, McGraw-Hill, (2006)
[3] D. Hossain et al., Polymer, **51**, 6071 (2010)

BL66

The use of Phosphonium Modified Organoclay for the Preparation of Optically Transparent Polycarbonate/clay Nanocomposites

SupratimSuin, Nilesh K. Shrivastava, Sandip Maiti and **B.B. Khatua***
Materials Science Centre,Indian Institute of Technology, Kharagpur
Kharagpur 721302, India
** Correspondence to: Dr. B. B. Khatua (email: khatuabb@matsc.iitkgp.ernet.in)*

The present work deals with the retention of optical transparency of polycarbonate (PC) in PC/clay nanocomposites using phosphonium modified organoclay by industrially feasible melt blending technique. The organic modification of the clay (Na-MMT) was done by ion exchange reaction and the resulting organoclay was characterized by X-ray diffraction study, FTIR spectroscopy etc. to ensure the proper modification of the clay. The prepared organoclay was melt mixed with PC and the resulting PC/clay nanocomposites were characterized by wide angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), dynamic mechanical analysis etc. The morphological analysis revealed a highly exfoliated morphology in the PC/clay nanocomposites. Considerable enhancement in mechanical properties of the PC was evidenced at very low loadings (0.5 phr, 1phr) of the clay in the nanocomposites. Moreover, the thermal analysis revealed an increase in thermal stability of the PC in the nanocomposites. The stability of the phosphonium modified organoclay at the processing temperature (280 °C) for processing time (15 min) helped to retain the optical transparency of the PC in the PC/clay nanocomposites.

BL67

Development of Polymer-Ceramic Nanocomposites as Pressure Sensitive Dielectric Elastomer

Suryakanta Nayak, Tapan Kumar Chaki*, and Dipak Khastgir*
Rubber Technology Centre, Indian Institute of Technology Kharagpur, W.B. 721302, India
*E-mail: suryakanta99@gmail.com

In recent years, polymer-ceramic nanocomposites have attracted great interest of many researchers due to their novel electrical and electronic properties [1-3]. These nanocomposites show better performance compared to individual polymer and ceramic materials [4-6]. In the present investigation, we have taken polydimethylsiloxane (PDMS) elastomer as base matrix and titanium dioxide (TiO_2)/prepared barium titanate ($BaTiO_3$) as ceramic fillers. Different mechanical and dielectric properties of these nanocomposites have been studied in order to find the effect of filler on these properties and found that both dielectric constant and dielectric loss increases with filler loading and the increase is more pronounced at low frequency region. The effect of moisture/filler heat treatment is also studied for PDMS-TiO_2 composites and found that composites with heat treated titania show lower dielectric constant than composites with normal titania. The particle size of titanium dioxide and barium titanate was analyzed by transmission electron microscope (TEM) and dynamic light scattering (DLS) technique. The dispersion/distribution of filler (TiO_2/$BaTiO_3$) particles in PDMS matrix was studied by field emission scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM), and scanning probe microscope (SPM). The effect of pressure on all the nanocomposites was studied in order to find out their piezoelectric behaviour. From the above study, it was found that these nanocomposites are sensitive to external pressure as dielectric constant and conductivity increases with the applied pressure.

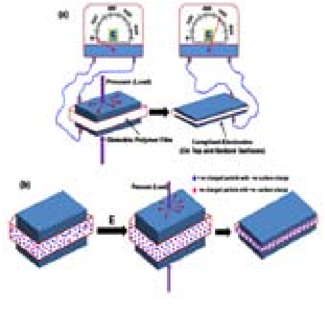


Figure 1. Schematic representation of (a) signals (C=capacitance/conductivity) before and after the application of stress/pressure to piezoelectric polymer-ceramic composite, (b) positions of charged particles inside the composites before and after the application of electric field/pressure.

References:

[1] S. Nayak, M. Rahaman, A.K. Pandey, D.K. Setua, T.K. Chaki, D. Khastgir, Journal of Applied Polymer Science, 127 (1) (2013) 784–796.
[2] Y. Rao, S. Ogitani, P. Kohl, C.P.Wong, in: International Symposium on Advanced Packaging Materials, 2000, pp. 32-37.
[3] S. Nayak, B. Sahoo, T.K. Chaki, D. Khastgir, RSC Advances, 3 (2013) 2620-2631.
[4] J.R. Webster, in: Electrical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1998, pp. 95.
[5] X. Liang, S.M. George, A.W. Weimer, Chemistry of Materials, 19 (2007) 5388-5394.
[6] Y. Bai, Z.-Y. Cheng, V. Bharti, H.S. Xu, Q.M. Zhang, Applied Physics Letters, 76 (25) (2000) 3804–3806.

BL68

Microindentation Hardness Studies of Polymer Composites Containing Nanofillers of Different Dimensionalities

Sushant Ghimire, Binita Neupane, Sharmila Pradhan, Rameshwar Adhikari
Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal
E mail: nepalpolymer@yahoo.com

The microindentation hardness has found in recent years widespread applications in polymer research. The technique has been increasingly used in the characterization of homopolymers, copolymers, polymer blends and polymer composites. A very attractive feature of this technique is its ability for the micromechanical characterization of the polymeric materials. In addition, this technique, being very simple and sensitive to the phase behaviour, may serve as an important tool to gain a straightforward and deeper insight into the morphology-mechanical property correlations in heterophase systems. In this work, the microhardness behaviour of different nano-structured polymeric systems, particularly thermoplastics based polymer nanocomposites (PNCs), has been investigated with the aid of a Leitz Microhardness Tester equipped with a square based pyramidal Vickers indenter. This work mainly focuses on the influence of filler content and filler dimensionality on the mechanical properties of the polymers investigated. A clear dependence of microhardness on filler content and dimensionality, loading time (creep effect) and annealing temperature has been shown. The main conclusions drawn from this work were as follows.

- Microhardness and other mechanical properties are significantly affected by the filler content and filler dimensionality. It was found that high aspect ratio fillers show the most remarkable reinforcement effect on mechanical properties of PNCs.
- The results obtained from model PNCs reflect significantly enhanced creep performance and thermal stability of the composite as compared to the neat matrix.
- The results from tensile testing and microindentation hardness measurements demonstrate the following reinforcing ability of the fillers having different dimensionalities: 1D filler > 2D filler > 3D filler. The higher reinforcing effects of 1D and 2D fillers can be attributed to the high aspect ratio of those fillers.

BL69

Aminophthalonitirle –Graphene Oxide Composites; Synthesis and Co-reaction Mechanism

Temina Mary Robert*, Dhanya Augustine, Satheesh Chandran M., Dona Mathew,
C. P. Reghunadhan Nair
Polymers and Special Chemicals Group
Vikram Sarabhai Space Centre, Trivandrum, India
* temirobert@gmail.com

Phthalonitrile polymers constitute a family of high performance thermosetting matrix resins, exhibiting outstanding thermo-oxidative stability, excellent mechanical properties, low water absorptivity and superior flame resistance. However, their wide applicability is limited due to poor processability and the need for curing at temperature > 300°C for prolonged duration [1]. Among the various methods reported for reducing the cure temperature, incorporation of amine functional groups has some acceptability. Reinforcement of the resins by graphene nanoplatelets is expected to lead to nanocomposites. To facilitate the interaction of resin with graphene, graphene oxide appeared better as it is gifted with groups capable of reacting with amino and nitrile groups[2]. Thus the present study is an attempt to synthesize and characterize epoxy- and hydroxyl- functional graphene nanoplatelets (GO) and to investigate the interaction of these functionalized graphene nanoplatelets with the amino novolac phthalonitrile polymers (APN). The study is also aimed at simulation and establishment of their probable co-reaction mechanisms. Amino Novolac Phthalonitrile (APN) and monolayer of functionalized graphene (GO) were synthesized by appropriate synthesis strategies and characterized. Reactive blends of APN and GO, with GO content varying from 0.05-2.00 (weight ratio) were prepared. Chemical interaction of the functional groups on GO with those in APN led to a low temperature curable route and nearly complete conversion of nitrile group in the APN-GO blends. Based on FTIR spectral evidence, it was found that both –OH and epoxy groups of GO reacted with the phthalonitrile groups to form structures including triazines, phthalocyanins, isoindoline, oxazolines, etc in the cured network. The minimum amount of GO required to obtain complete conversion of nitrile groups was estimated as 0.4 wt%. Theoretical modeling using M06L/6-311+G (d,p) level of DFT revealed that the hydroxyl and epoxy groups of GO facilitated the curing of the nitrile functionalities. Thermal stability of APN was found to decrease with increasing GO content in the blend. It is established that, GO alters the cure characteristics of the APN resin by changing the network structure and cure dynamics. The APN-GO nanocomposites are expected to have potential applications in high performance structural composites.

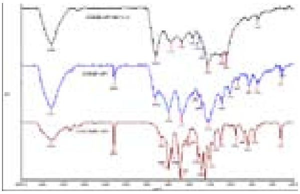


Figure1. FT-IR spectrum of uncured APN, cured APN and APN-GO (1:1) blend

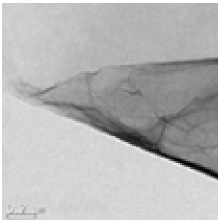


Figure 2.TEM image of single folded GO sheet

References

[1] Keller T M. J Polym Sci Part: A Polym Chem; 26(1998): 3199–3212.
[2] Z.M. Dang, J.K. Yuan, J.W. Zha, T. Zhou, S.T. Li, G.H. Hu, Prog. Mater. Sci., 57 (2012) 660–723.

BL70

Methyltriphenylphosphonium permanganate as Novel Oxidant for Aniline to Polyaniline-Manganese(II, IV) oxide for Pseudocapacitor

S. Palaniappan,[a,b,*] B. Rajender,[a] U. Susmitha[a]
[a]*Polymers & Functional Materials Division,CSIR- Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b]*CSIR – Network Institutes for Solar Energy (NISE). India*
email : palaniappan@iict.res.in

Supercapacitors have the highest available capacitance values per unit volume and the greatest energy density of all capacitors. Electrical double-layer capacitors (EDLC) are, together with pseudocapacitors, part of a new type of electro-chemical capacitors [1] called supercapacitors, also known as ultracapacitors. Supercapacitors are divided into three families, based on the design of the electrodes: double-layer, pseudo and hybrid capacitors. Composites of polyaniline salt with manganese(II,IV) oxide (PANI-Mn_5O_8) are prepared by aqueous, emulsion and interfacial polymerization pathways using methyltriphenyl-phosphonium permanganate as novel organic oxidant. Polyaniline composites are characterized by FT-IR, FE-SEM, EDAX, XRD, TGA and conductivity measurements. PANI-Mn_5O_8 shows nano fiber morphology (fig.1) with high conductivity (9.4 S/cm). These composites are used as electrode materials in psedocapacitor in symmetric configuration. Psedocapacitor systems are characterized by cyclic voltammograms, galvanostatic charging/discharging, and electro-chemical impedance spectroscopy. The result shows that the obtained polyaniline composites shows a capacitance value of 220 F/g and this composite material could be beneficial to the development of energy storage.

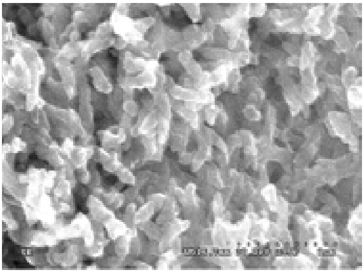


Figure 1. SEM image of PANI-Mn5O8

References:

[1] Conway B.E. Google Books *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Berlin: Springer, (**1999**) pp.1–8

Acknowledgments
The authors thank Dr. K.V.S.N. Raju, Head, PFM Division and Dr. Ahmed Kamal, Acting Director, IICT, Hyderabad for their support. The authors also thank CSIR, New Delhi under the TAPSUN program (NWP-0056) for funding. One of the authors (Rajender) thanks UGC for SRF fellowship.

Additional Abstracts

New Elastomers for Optimal Vision: the Light-Adjustable Intraocular Lens

Julie Kornfield
California Institute of Technology, USA

As the lenses in our eyes age, they frequently become cloudy—develop a “cataract.” Over 14 million surgeries are done each year to remove cataracts and implant a synthetic lens to take its place. Current intraocular lenses leave approximately one third of cataract patients needing spectacles to achieve optimal distance vision. To achieve the desired refractive outcome without spectacle correction demands that the lens be capable of adjustment after wound healing has stabilized. New materials developed at Caltech enable post-operative, non-invasive adjustment of lens power. Kornfield will present collaborative work with Bob Grubbs in Chemistry and eye surgeon Dan Schwartz of UCSF, developing a material capable of *in vivo*ajustment using safe levels of light. The Light Adjustable Lens (LAL) is performing well in clinical trials, providing reproducible and predictable *in situ*power change up to ± 2.0 diopters. The talk will conclude with a parameter-free predictive model of the reaction-diffusion-deformation process; the model successfully describes both the transient response and the final state of the lens after an arbitrary adjustment.

Enhancing the Performance of Optoelectronic Devices by Rational Design of Molecular Semiconductors

Satish Patil
Solid State and Structural Chemistry Unit
Indian Institute of Science, Bangalore

E-mail: satish@sscu.iisc.ernet.in

The development of molecular semiconductors for optoelectronic devices has tremendous impact on energy production. However, a major challenge to attain widespread implementation of this technology would be to develop materials by cost effective methods and achieve high stability. Although this can pose a great challenge, the concept of bulk heterojunction has provided the record breaking efficiency of as high as **9.2%**. However, a clear relationship between the material properties and stability is still lacking. In this talk, the role of torsional defects in molecular semiconductor shall be discussed. Moreover, our recent results of ambipolar molecular semiconductors for organic field-effect transistors (**OFET**) will be highlighted.

References:

[1] Influence of Side-Chain on Structural Order and Photophysical Properties in Thiophene Based Diketopyrrolopyrroles: A Systematic Study, Mallari A. Naik, N. Venkatramaiah, Catherine Kanimozhi, and **Satish Patil*, Journal of Physical Chemistry-C, 2012, 116, 26128–26137**

[2] Diketopyrrolopyrrole-Diketopyrrolopyrrole-Based Conjugated Copolymer for High-Mobility Organic Field-Effect Transistors, Kanimozhi, C.; Yaacobi-Gross, N.; Chou, K. W.; Amassian, A.; Anthopoulos, T. D.; **Satish Patil, *J. Am. Chem. Soc.* 2012**, *134*, 16532

Control of Critical Molecular Design Parameter for Conjugated Polymers via Flow Syntheses

Anil Kumar,
Department of Chemistry, National Center for Photovoltaic Research and Education (NCPRE), Center for Excellence in Nanoelectronics (CEN), IIT Bombay, Mumbai, INDIA

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 electronic 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. Polythiophene, polyphenylenes, polycarbazoles and polyfluorenes are some of the prominent examples for use in printable electronic applications. In this direction, large scale syntheses of these polymers with complete control over Critical Molecular Design Parameters **(CMDPs)** such as chemical purity, regioregularity, molecular weight and polydispersity, still remains a challenge. Flow chemistry provides an attractive route in this direction. Recently, we have initiated a program to design new synthetic routes via flow chemistry, which are amenable for large scale syntheses. Our recent results in this direction will be highlighted in this presentation.

Electromagnetic Interference Shielding Effectiveness of Barium Hexaferrite–Graphene hybrids

M. Verma[a]*, S.K. Dhawan[b] and V. Choudhary[a]
[a]Centre for Polymer Science & Engineering, Indian Institute of Technology- Delhi,
New Delhi,110016,India
[b]Polymeric & Soft Materials Section, (CSIR), National Physical Laboratory,
New Delhi, 110012, India
meenakshi.iitd@gmail.com

Here, we report a simple method to fabricate a hybrid of barium hexaferrite nanoparticles well dispersed on electrically conductive graphene nanosheets. The morphology, crystal structure and magnetic properties of as-prepared hybrid materials have been characterized using Scanning Electron Microscopy, Transmission Electron Microscopy, Fourier transmission infrared spectroscopy, Raman spectroscopy, thermogravimetry/ differential thermal analysis, powder X-ray diffraction, vibrating sample magnetometer. The morphological characterization clearly shows that the graphene sheet is homogeneously decorated by barium hexaferrite nanoparticles. XRD and SAED suggest that each barium hexaferrite nanoparticle decorated on the graphene has a polycrystalline structure. VSM studies reveal that these hybrids are ferromagnetic at room temperature. Electromagnetic interference shielding effectiveness of hybrids of varying sample thickness were studied in the frequency range of 8.2 to 18 GHz. Shielding effectiveness up to -30 dB in the frequency range 12.4 – 18 GHz was achieved for a sample thickness of 2.38 mm.

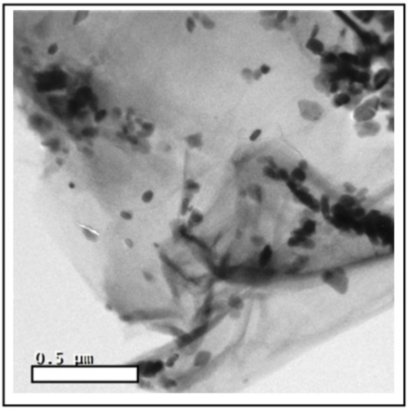


Figure 1. TEM of Barium hexaferrite-Graphene hybrid

Hyperbranched Polyurethanes Nanocomposites for Advanced Surface Coating to Biomedical Applications

Niranjan Karak*
Advanced Polymer & Nanomaterial Laboratory, Department of Chemical Sciences Tezpur University, Tezpur 784028, Assam, India
** Corresponding author's email : karakniranjan@yahoo.com*

Development of high performance right polymeric materials is the demand of the material society to fulfill the stringent requirements for many advanced applications. In this context, polyurethane, the most versatile polymer, because of inherent structural in-homogeneity within the same molecular chain, may be the right choice to delve into. The design of suitable structural architecture such as hyperbranched polymers with long segment through molecular engineering offers a new golden feather in the performance of such polyurethanes. In addition to this, the utilization of renewable bio-based product as one of the components for synthesis of such polyurethanes resulted environmentally acceptable biodegradable polymer. These hyperbranched polyurethanes are superior in performance to their linear analogs due to their unique architectural features. Further, the unison of blessing of nanomaterials with such hyperbranched biodegradable polyurethanes resulted the right polymeric materials for today's society by the help of nanotechnology [1]. In this endeavor, the advance polymer and nanomaterial laboratory at Tezpur University developed a few vegetable oil based hyperbranched polyurethanes and their nanocomposites by incorporation of different nanomaterials like organically modified nanoclay to reduced grapheme oxide including metal nanoparticles [1- 3]. The developed materials are also tried to utilize in different domains of applications from binder of advanced surface coatings to biomaterials for biomedical applications including intelligent stimuli responsive shape memory materials. The overview of all the results obtained through this study from synthesis to properties evaluation including characterization for the above applications will be discussed in this conference.

In all the above cases, the concept of 'green chemistry' tried to follow as much as practicable, as well as the products are developed by maintaining the 'Triple bottom line' approach. The spectroscopic and analytical techniques like UV-visible, FTIR, ^{1}H NMR and ^{13}C NMR, XRD, SEM and TEM are used to know the insight of their physico-chemical structures.

The property evaluation indicated the improvement of the most of desired properties from mechanical to thermal including chemical and biodegradability [1, 3]. This investigation thus indicated that the studied materials have potential to be used as advanced surface coating materials, biodegradable biomaterial, shape memory materials, etc. for today's material society.

References

[1] Deka, H.; Karak, N.; Kalita, R.D.; Buragohain, *Carbon*, 48 (**2010**) 2013.
[2] Thakur, S.; Karak, N. *Prog. Org. Coat.* 76 (**2013**)157.
[3] Das, B.; Mandal, M.; Upadhyay, A.; Chattapadhya, P.; Karak, N. *Biomedical Materials*, (Proof corrected, **2013**).

Sponsors

سابك
sabic

3M | 25 years of 3M in India 1988-2013

Reliance Industries Limited

SOLVAY
asking more from chemistry

MOMENTIVE

JUBILANT
Agri & Consumer Products

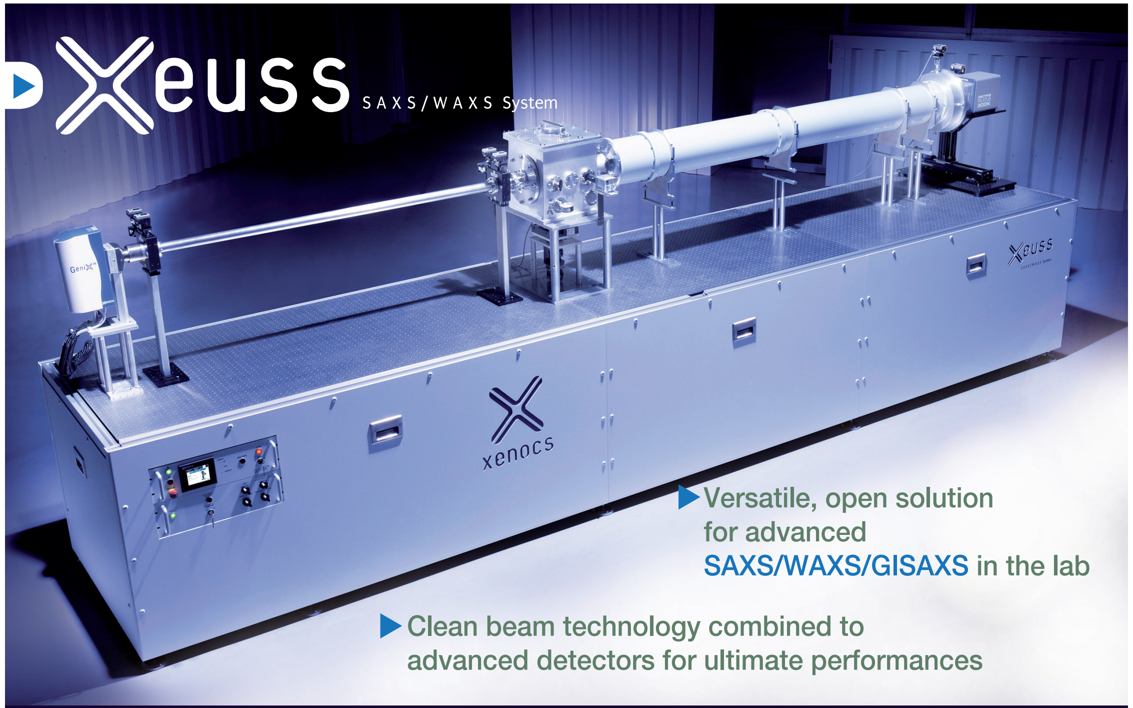
Xenocs
Brighter solutions

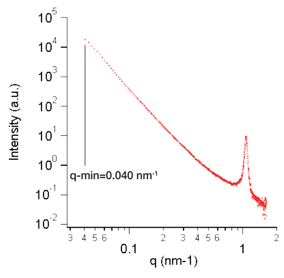
Dr.Reddy's

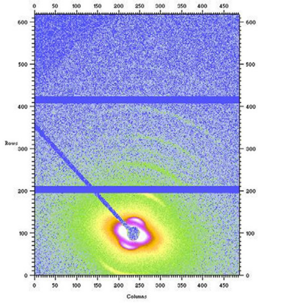
सत्यमेव जयते
Government of India
Department of Science & Technology

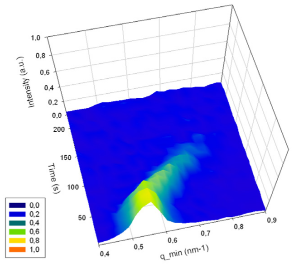
CSIR-INDIA

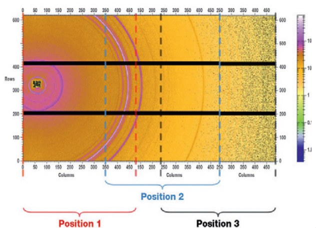

Look twice


Xeuss SAXS/WAXS System
xenocs


Intensity (a.u.)
q-min=0.040 nm⁻¹
0.1
1
q (nm-1)




Intensity (a.u.)
Time (s)
q_min (nm-1)


Position 1
Position 2
Position 3