

Kaushal Kishore Memorial Award Lectures

AWARD LECTURE 1

Hierarchical Ordering of Poly (L-lactide) in Block Copolymers and Star-Shaped Polymers

by

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Date: December 22, 2018 | Time: 9.15 am

AWARD LECTURE 2

Crystalline Polyperoxides from Fatty Acid Containing Styrenic Monomers

by

Prof. Priyadarsi De

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Kolkata

Date: December 22, 2018 | Time: 9.45 am

Venue: MACRO-2018 at C.V. Raman Auditorium
Indian Institute of Science Education Research, Pune

Organized by:



The Society for Polymer Science, India

AWARD LECTURE 1

Abstract

Poly(L-lactide) (PLLA), the most common stereoisomer of the poly(lactic acid), is a widely used biobased polymer in degradable plastics. It is also used as a degradable biomaterial in many medical devices and tissue engineering. To overcome the limitations of polylactides and tailor its desirable properties, multiphase polymer systems have been developed.[1-5] The structural ordering process plays a key role in controlling the nanostructured morphologies of the multiphase systems. In the first part of the talk, the structural evolution of PLLA during heating of the amorphous ABA triblock copolymers will be discussed. For that purpose, two triblock ABA copolymers poly(L-lactide-b-dimethylsiloxane-b-L-lactide) and poly(L-lactide-b-ethylene glycol-b-L-lactide) containing poly(L-lactide) were synthesized. Upon heating of the glassy triblock copolymers, the amorphous PLLA transiently transformed to the mesophase just above the T_g of PLLA block before crystallizing into the regular form.[1-2] The formation of the mesophase was faster in miscible triblock copolymers due to the enhanced molecular mobility of the amorphous PLLA. In the second part of the talk, the role of polymer chain packing on the solid state emission properties of the star-shaped PLLA will be discussed. Using the blends of enantiomeric star-shaped polylactides, the structure formation process of stereocomplex will be discussed. Last part of the talk highlights the structure and morphology (superstructure) of the solvent-induced crystallized PLLA films in different length scales using wide-angle and small-angle X-ray scattering, atomic force microscopy, and polarized light microscopy.[4,5]

References

- [1] S. Nagarajan, E. B. Gowd, *Macromolecules* 2015, 48, 5367-5377.
- [2] S. Nagarajan, K. Deepthi, E. B. Gowd, *Polymer* 2016, 105, 422-430.
- [3] S. Nagarajan, E. B. Gowd, *Macromolecules* 2017, 50, 5261-5270.
- [4] P. Shaiju, N. S. Murthy, E. B. Gowd, *Macromolecules* 2016, 49, 224-233.
- [5] P. Shaiju, N. S. Murthy, E. B. Gowd, *Soft Matter* 2018, 14, 1492-1498.

About the speaker

Dr. E. Bhoje Gowd was born in Kummara Nagepalli, Anantapur district, Andhra Pradesh. He received his B.Sc. and M.Sc. (Tech) in Polymer Science and Technology from Sri Krishnadevaraya University, Anantapur, Andhra Pradesh and his Ph.D. from University of Pune, Pune (work carried out at CSIR-National Chemical Laboratory under the guidance of Dr. C. Ramesh). He worked as a post-doctoral fellow in Prof. Kohji Tashiro's group at Toyota Technological Institute, Nagoya, Japan and as an Alexander von Humboldt Fellow in Prof. Manfred Stamm's group at Leibniz Institute of Polymer Research, Dresden, Germany. After a short stay at Indian Institute of Science, Bangalore as a Centenary post-doctoral fellow in Prof. S. Ramakrishnan's group, he joined CSIR-NIIST, Thiruvananthapuram as a DST-SERB Ramanujan Fellow. In 2011, he accepted the senior scientist position at CSIR-NIIST. He was awarded IUSSTF research fellowship by Indo-US Science and Technology Forum in 2014 (Stony Brook University, Stony Brook, NY, USA) and the Raman Research Fellowship by CSIR, Government of India in 2018 (National Tsing Hua University, Hsinchu, Taiwan). He is the recipient of Materials Research Society of India (MRSI) Medal in 2016. He has authored more than 50 publications in peer-reviewed journals, edited a book and contributed 4 book chapters. He has been invited to deliver talks at different forums from countries like Japan, USA, Italy, France, Germany, China, and Taiwan. His research interests are in the areas of polymer self-assembly, nanostructured materials, polymorphic phase transitions in semicrystalline polymers, polymer/inorganic hybrid nanocomposites, polymer-solvent complexes and biodegradable polymers.



AWARD LECTURE 2

Abstract

Vinyl polyperoxides, alternating copolymers of vinyl monomers and molecular oxygen, are highly viscous amorphous materials because of the flexible peroxy (-O-O-) bonds in their main chains.^{1,2} Polyperoxides show highly exothermic degradation in contrast to common polymers which generally degrade endothermically, and finds applications in various areas as; polymeric radical initiators, curators in molding and coating applications, dismantlable adhesives, auto combustible polymeric fuel, drug carrier, plastic waste management, etc. Although this class of polymers is known since 1922, till date there is only one report, where crystallinity was found in poly(α -phenyl styrene peroxide) (PAPSP).³ However, detailed mechanism of crystallization was never studied.

Side-chain crystallization occurs from long *n*-alkyl side chains of polymers with $C \geq 12$ of the side chain alkyl carbons.⁴ Thus, to prepare crystalline polyperoxides side-chain fatty acid based vinyl monomers of appropriate fatty acid chain length could be used, to restrict the main chain flexibility from the side-chain crystallization of long fatty acid moieties. Therefore, we have polymerized styrenic monomers having fatty acid moieties with different chain lengths at the *para*-position of phenyl group *via* oxidative polymerization in the presence of a free radical initiator at 50 °C in toluene. Indeed, crystalline polyperoxide forms when $C \geq 12$ of the side chain alkyl carbons in fatty acid moiety, as confirmed by differential scanning calorimetry (DSC), polarized optical microscopy (POM), powder X-ray diffraction (PXRD), transmission electron microscope (TEM) and density functional theory (DFT) calculations. Side-chain crystallinity imparts high thermal stability and powdery nature to these polyperoxides, despite their low molecular weight and highly flexible backbone owing to the main chain peroxy links.

References

1. Pal, S.; Das, A.; Maiti, S.; De, P. *Polym. Chem.* **2012**, 3, 182-189.
2. Pal, S.; De, P. *Chem. Commun.* **2012**, 48, 4229-4231.
3. Jayaseharan, J.; Kishore, K.; Nalini, G.; Gururao, T. N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 4033-4036.
4. Maiti, B.; De, P. *RSC Adv.* **2013**, 3, 24983-24990.

About the speaker

Dr. Priyadarsi De started his journey in Chemistry as an undergraduate student at Jadavpur University and completed his graduation in 1995, followed by post-graduation in 1997. Then, he went to Indian Institute of Science, Bangalore to pursue his doctoral studies under the supervision of Professor D. N. Sathyanarayana. After completion of the PhD program in 2002, he moved to the group of Professor Rudolf Faust at University of Massachusetts Lowell, USA, for postdoctoral training (2002-2006). He also worked as a postdoctoral fellow (2007-2008) with Professor Brent S. Sumerlin at Southern Methodist University, Dallas, USA. Later he joined as a Distinguished Scientist, PhaseRx Pharmaceuticals, Seattle, USA (2008-2009). On November 2009, Dr. De started his independent career as an Assistant Professor at Indian Institute of Science Education and Research Kolkata (IISER Kolkata), India, where he is currently working as a Professor. He is an Editorial Advisory Board Member of *Macromolecules* and *ACS Macro Letters* (2017-present), and *Polymer Chemistry* (2015-present). His research area includes synthesis of bio-inspired macromolecular architectures from naturally occurring amino acid and fatty acid; weak-link polymers; nonorthodox macromolecular luminogens and stimuli-responsive polymers for biological applications. Dr. De has published 120 papers in international peer-reviewed journals, 15 patents, 7 book chapters and 20 preprints.

About Professor Kaushal Kishore

Kaushal Kishore was one of the outstanding Polymer Scientists of our country. He was a professor at the department of Inorganic and Physical Chemistry at the Indian Institute of Science, Bangalore, till his untimely demise in 1999 at the age of 56. Kishore received his early education in chemistry from Lucknow University and his Ph.D. from the Gorakhpur University under the guidance of the distinguished physical chemist, Professor R. P. Rastogi. After a brief stint at Gorakhpur University as a



lecturer, he moved to the Department of Inorganic and Physical Chemistry, at the Indian Institute of Science, as an Assistant Professor in 1974; he rose through the academic ladder to become a full professor in 1984 and served as the head of the department during the years 1994-1998.

Kishore's formal training was in thermodynamics and combustion chemistry. His early work in collaboration with scientists at ISRO and DRDO led to several novel discoveries that shed light on the role of different components in solid propellants; one of the very significant findings was that the polymeric binders generated polyperoxides during aging and combustion, which in turn accelerated the combustion process. With this insight, he soon discovered a unique phenomenon that he termed "autopyrolysis", which catapulted him into fame. He contributed immensely to the field of polyperoxides, both in terms of understanding its formation and exploiting their potential for a variety of applications. Thus, in his early work, he brought to bear upon the phenomenon of combustion his deep understanding of chemical thermodynamics to formulate, quantify and provide a detailed mechanistic insight into this incredibly complex process. His early work on combustion steered him to several other important problems, namely flame retardancy, which led him to define a new dimensionless quantity he termed "Flammability Index", design of new additives that would retard/inhibit the flammability of polymeric materials, probing the molecular underpinnings of "plasticization", with a primary focus on the effect of molecular architecture on plasticizing efficacy. During his last years he studied a broad class of polymers he termed "weak-link" polymers; these were analogous to polyperoxides, such as polydisulfides and polyselenides; his main interest was to understand the degradation mechanism of these weak link polymers.

Kishore's work was always characterized by its ingenuity, depth and simplicity of analysis. He saw science in everything and had a strong conviction and motivation to understand all phenomena he observed at the microscopic and, if possible, at a molecular level. His solid foundation in chemical thermodynamics brought to polymer chemistry a much-needed "thermodynamic bias" – a term he often used to characterize his work. Using numerous tools, starting from thermal analytical methods, rheological measurements, NMR and computational methods, he attacked problems with passion and a characteristic zeal – which often culminated in nailing the issue on the head. His students and coworkers remember him with great fondness – for he was not only their research guide but also their friend and a confidant.

Recognition for his achievements came in many forms. Professor Kishore was awarded the Bhatnagar prize in 1988, was elected to the Fellowship of the Indian Academy of Sciences in 1991 and later to that of the Indian National Science Academy in 1999. Kishore served on several important decision-making bodies in the country – various assessment committees, research councils of national laboratories and in many others.

About Kaushal Kishore Memorial Award

The Kaushal Kishore Memorial Award was instituted in 2014 to recognize young outstanding polymer scientists of our country who have made outstanding research contributions and have demonstrated the potential to become global leaders in their chosen fields of research. The corpus fund for this award was donated to the Society for Polymer Science (India) after the successful conduct of the FAPS-MACRO 2013 conference in Bangalore. The award is open to researchers, under 45 years of age, who are working in India and will be awarded biannually during the MACRO conference held under the auspices of SPSI. The award will carry a cash prize of Rs 100,000, along with a citation.

Prof. K. Kishore Memorial Award Winners of The Society for Polymer Science, India

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| 2014 | 1) Dr. M. Jayakannan, IISER, Pune |
| | 2) Dr. Satish A. Patil, IISc, Bangalore |
| 2017 | 1) Prof. Suhrit Ghosh, IACS, Kolkata |
| | 2) Prof. Rabibrata Mukherjee, IIT, Kharagpur |