

Special Invited Lecture
Inter-Disciplinary Explorations in Chemistry (I-DEC 2018)

**Immiscibility-driven Folding of Synthetic Polymers – Accessing
sub-10 nm scale microphase separation**

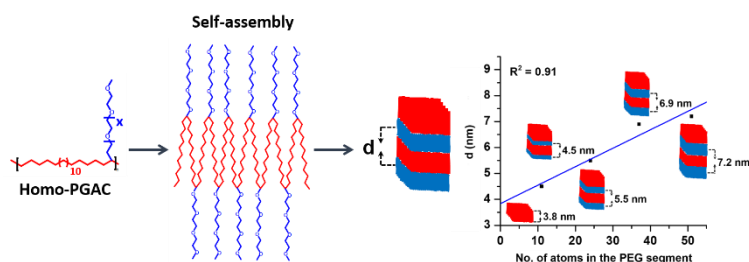
S. Ramakrishnan*

Department of Inorganic and Physical Chemistry

Indian Institute of Science, Bangalore 560012

E-mail: raman@iisc.ac.in

Abstract: Segmented polymers of different types carrying two or more immiscible segments tend to self-segregate leading to the emergence of several interesting properties, such as in thermoplastic elastomeric polyurethanes, liquid crystalline polymers, nanostructured polymeric films, etc. Such segmented polymers can be of several types, such as block copolymers (di-, tri- and multi-) and graft copolymers, in addition to other topological variations of these, such as star-block copolymers. When the length of the segments and the periodicity of their placement are precisely controlled, well-defined and predictable morphologies are seen; however, when both these features are not very precisely defined then randomly phase-separated systems emerge, which, despite the randomness, can yield remarkably useful properties, such as in the case of thermoplastic polyurethanes.



Scheme: Regulating bulk morphology by controlling the chain conformation at a single-chain level.

Periodically grafted copolymers form an interesting class of systems, wherein the immiscibility between the backbone segment that lies between the graft locations and the grafted chains could drive a zigzag folding of the polymer chain to facilitate the collocation of the two immiscible segments; crystallization of either one or both the segments could further reinforce the folded chains. I shall discuss two types of systems wherein self-segregation followed by crystallization leads to the stabilization of a specific reconfigured conformation and further leads to the formation of well-defined morphology in the solid state: in one case, by designing suitable periodically grafted amphiphilic graft copolymers, while in the other by generating Janus-type amphiphilic hyperbranched structures. The central theme in both these systems is the exploitation of the strong tendency for long alkylene segments to crystallize in a paraffinic-type crystalline lattice. I shall discuss these new designs to control the conformation at a single-chain level, provide evidences for their formation and discuss the consequences of such molecular-level control on their bulk morphology.

References and Notes:

1. Joydeb Mandal, S. Krishna Prasad, D. S. Shankar Rao and S. Ramakrishnan, "Periodically clickable polyesters: Study of intra-chain self-segregation induced folding, crystallization and mesophase formation" *J. Am. Chem. Soc.* 136, 2538 (2014)
2. Sananda Chanda and S. Ramakrishnan, "Controlling Interlamellar Spacing in Periodically Grafted Amphiphilic Copolymers" *Macromolecules*, 49, 3254 (2016)

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Bio-Sketch of Speaker

Dr. S Ramakrishnan

Professor

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012
Contact Number: +91-80-22932744
e-Mail: raman@iisc.ac.in



Biography: Ramakrishnan completed his BSc from the University of Bombay, MSc from the Indian Institute of Technology, Bombay and received his PhD from the University of Massachusetts, Amherst, in 1988. After a two-year postdoctoral stint at the Corporate Research Laboratory of Exxon Research and Engineering Company at Annandale, New Jersey, he took up a faculty position in the Department of Inorganic and Physical Chemistry at the Indian Institute of Science, Bangalore, where he is currently a Professor. He was awarded the S S Bhatnagar Prize for Chemistry in 2005 and is currently a J C Bose Fellow. His research interests are in the design and development of novel polymerization methods, hyperbranched polymers, conjugated polymers, polymerization in ordered media, internally functionalized porous polymers and conformational control in synthetic polymers. He currently serves as one of the Associate Editors of Chemical Communications.