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Education

Ph.D. from University of Massachusetts, Amherst, USA in 1988 (Advisor: J. C. W. Chien)

M.Sc. from Indian Institute of Technology, Bombay, India in 1982

B.Sc. from SIES College, University of Bombay, India in 1980

Academic Positions Held

April 2005 - To date	Professor, Indian Institute of Science
April 1999 - April 2005	Associate Professor, Indian Institute of Science
April 1993 - April 1999	Assistant Professor, Indian Institute of Science
Sept. 1990 - April 1993	Lecturer, Indian Institute of Science
July 1988 - July 1990	Postdoctoral Fellow, Corporate Research Laboratory, Exxon Research and Engineering Company, New Jersey, USA
Nov. 2000- Jan. 2000	Visiting Scientist, University of Florida USA
Feb. 2001 - May 2001	Philips Visiting Professor, Eindhoven University of Technology, Netherlands

Associate Editor - Chemical Communications (Royal Society of Chemistry)

Research Interests

Conjugated Polymers

Our efforts in this area are primarily directed toward PPV and its derivatives, specifically with the objective of controlling the molecular conjugation length and fluorescence quantum yield. A novel approach, wherein the sulfonium groups on the Wessling precursor polyelectrolyte precursor are competitively displaced by two different nucleophiles one that is readily eliminated while the other remains intact, yielded segmented dialkoxyPPV's with complete statistical control of the molecular conjugation length. Nucleophiles that have been used successfully are acetate, xanthate and more recently dithiocarbamate. Thus, the colour of emission from these was readily controlled over a 100 nm window. Utilizing soluble segmented MEHPPV's several interesting fundamental problems relating to the polymer conformation, intra-chain energy transfer and solvent-induced conformational collapse have been addressed. Our current focus is on developing novel routes to graft functional polymeric segments onto the PPV backbone for exploiting intra-chain energy transfer for colour control and also to develop approaches for preparing PPV-based gels.

Foldamers

Synthetic polymers that mimic the structure and function of their biological cousins have interested polymer scientists for many decades because of the intrinsic desire to emulate the sheer elegance of such control exercised by nature, on the one hand, and the immense potential technological applications that could result from success in such an endeavor, on the other. Foldamers represent a class of synthetic polymers, which can be coerced to adopt one particular conformation of the often numerous options that they have the entropic penalty that has to be paid as a result will have to be met by inclusion of appropriate inter-segment interactions that provide the requisite enthalpic stabilization. We are presently designing macromolecules that possess equispaced segments that can interact with each other via weak interactions, such as π -stacking, charge transfer and solvophobic exclusion, often times in tandem. We are also engaged in designing special experimental tools to examine such folding in solution.

Hyperbranched Polymers

Over the past decade our efforts have focussed on the development of new methodologies for synthesis of hyperbranched polymers, such as polyurethanes, polyesters, polyethers and more recently on polybenzyls. Apart from developing novel approaches, we have tried to address key issues, such as the effect of the nature and length of the spacer between branching points on the thermal properties of the resulting polymers, utilization of copolymerization of AB and AB₂ type monomers for control of the branching density, use of monofunctional monomers to incorporate mesogens etc. More recently, by the use of PEG segments to link the branching junctions, we are preparing branched PEO equivalents that should be very sluggish to crystallize and could be potentially useful as candidates for solid polymer electrolyte applications. Other applications such as terminal group modification to generate unimer micelles and also use of hyperbranched polymers for generating amphiphilic and ionically conducting gels are the focus of our current attention.

Polymerizable Surfactants

A large variety of polymerizable surfactants have been described during the past two decades. Most of these have polymerizable groups that form an integral part of the surfactants, while very few have them included as a counter-ion. Our focus during the last

couple of years has been the design and utilization of polymerizable surfactants, wherein the polymerizable group functions as the counter-ion. Such systems have the added potential of being able to generate nanostructured polymeric materials in which the aggregated long hydrocarbon tails function as supramolecular templates and can be removed after polymerization. Such polymeric materials may be considered as polymeric analogues of molecular sieves with the added advantage of being able to tailor the functionality by appropriate design of the surfactants. Studies to prepare surface-functionalized polymeric colloidal particles based on these surfactants are also currently being investigated.

Novel Polyethers

A novel melt condensation methodology for the synthesis of segmented polyethers, based on a transesterification reaction has been developed. This process was used for the preparation of segmented PEO's and hyperbranched polyethers. Approaches to design PEO-analogues that have very low propensity for crystallization are being currently examined as routes for the generation of materials suitable as solid polymer electrolyte applications. Extensive studies to understand the role of catalyst type and polymerization conditions has recently enabled the synthesis of polyethers with greatly improved molecular weights and polydispersity, thus permitting complete preclusion of the side reactions that plagued some of our early efforts.

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

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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.

Periodically grafted copolymers is 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

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3. 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)
4. Sananda Chanda and S. Ramakrishnan, "Controlling Interlamellar Spacing in Periodically Grafted Amphiphilic Copolymers" *Macromolecules*, 49, 3254 (2016)