

New directions in polymer chemistry research: Molecular design considerations in the synthesis of new polymer materials

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Increasing role of polymer materials for various advanced technology applications has created a special need for devising newer routes for obtaining polymers with tailored properties. Control of molecular and supramolecular architecture of polymers will make new demands on synthetic chemistry, molecular recognition concepts and surface chemistry, which would, in turn, lead to tailored materials with organized solid-state and solution properties.

THE relentless need for polymeric materials for a variety of specialty applications has resulted in increasing focus on synthesis of polymers with accurate control of molecular architecture¹. Today's synthetic polymers are, more often than not, collection of molecules with similar chemical compositions but widely varying molecular weights, microstructures, topologies and stereochemistry. In order to meet the demands for ever-increasing technological applications, extremely high degree of structural control is absolutely essential to achieve the ultimate desired properties. This has resulted in several synthetic approaches to control molecular and supramolecular architecture of polymer structures².

Initiator design and controlled polymerization approach

The major preoccupation in polymer chemistry research during the last decade has been to tame the reactivity of the polymerization chain end, may it be an anion, carbocation or radical, and to enable synthetic manipulation at the chain end. This approach has been successful to a great extent, giving unprecedented control on the growing polymer chain, in terms of molecular weight, molecular weight distribution, functionality and stereochemistry. Structure control, both at molecular and supramolecular level, has been mastered using these synthetic methodologies³.

Notwithstanding these spectacular advances, challenges facing polymer chemists are far from over. There are still a host of readily available monomers which do not lend themselves to synthetic control. A striking example is methyl acrylate and acrylonitrile,

whose controlled polymerization till recently was thought to be too difficult⁴. Vinyl chloride, a readily available commodity monomer, is even today incapable of being polymerized with any degree of structure control. Controlled synthesis of polymers from such reactive monomers and minimization of the myriad side reactions that normally complicate chain propagation require considerable fine tuning of the reactivity of the initiator and monomer. Only recently have the polymer chemists successfully learnt to use the otherwise well-known principles of physical organic chemistry for the control of polymerization reactions. Subtle manipulation of electronic and steric effects of the initiator and monomer, a deeper understanding of the role of ion pair association equilibrium, principles of selective complexation of the counterion and stabilizing reactive carbanions and carbocations using latent functionality or weak covalent and charge transfer interactions have contributed to the spectacular success in this area⁵⁻⁸. It is thus evident from these recent findings that this area of initiator modulation in polymerization chemistry holds great promise for future research. In addition to enabling controlled polymerization of reactive functional monomers, it enables manifestation of new and novel properties in macromolecules derived from inexpensive monomeric building blocks.

Metal and ligand tuning in transition metal complex catalyzed polymerization

The role of transition metal catalysis in polymer synthesis is another area of contemporary scientific as well as practical interest. Ever since the seminal discoveries of Ziegler and Natta, metal catalysis has had a major impact on the growth of both the science and industry of polymers⁹. The past two decades have witnessed spectacular accomplishments in organometallic chemistry and polymer synthesis as a result of their symbiotic relationship.

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Recent advances in organometallic chemistry are now opening newer horizons in polymer chemistry. Current excitements in Group IV metallocenes for stereospecific olefin polymerization and ring-opening metathesis polymerization are but two of the striking examples of the impact of transition metal organometallics in polymer synthesis^{10, 11}. In the case of olefin polymerization, unprecedented control of reactivity, regioselectivity, stereoselectivity and enantioface selectivity is now possible because of the understanding of the steric and electronic effects of the ligands around the transition metal as well as interaction of the growing chain with the metal centre¹²⁻¹⁴. Some noteworthy examples include (i) the synthesis of highly isospecific and syndiospecific polypropylene and polystyrene, chiral polyolefins with single configuration from achiral monomers, etc.^{15, 16}, and (ii) a deeper insight into the nature of surface-adsorbed organometallic complexes in fine-tuning reactivity of catalysis¹⁷.

Ring-opening metathesis polymerization resulting from the opening of strained cyclic olefins offers a route to prepare a variety of polymer structures¹⁸. A systematic study of the metal carbene metathesis catalyst has enabled the discovery of a number of interesting complexes that enable polymerization of such olefins in living manner, thus opening up the possibility to synthesize block, graft and a variety of well-defined polymer structures. Also, by choosing appropriate metal centres, the catalyst tolerance to functional groups has been increased, which further expands the scope of this polymerization method¹⁹. Controlling the reactivity of these catalysts for living ring-opening metathesis polymerization in more polar solvents (e.g. water) or controlled polymerization of reactive functional monomers is still a challenging goal.

In addition to these two widely studied examples of catalysis in olefin polymerization, transition metal complexes have also been utilized to synthesize many interesting polymer structures. These include living polymerization of isocyanides to single-handed helical macromolecules, perfectly alternating copolymers of olefins and carbon monoxide generating polyketone structures and stereoregular polymers from heteroatom-functionalized cyclohexadienes²⁰⁻²².

Thus, rational design of structurally well-defined catalysts for the synthesis of olefin polymers with precise control of molecular structures and properties seems to be well within the reach of polymer chemists. The initial successes in this area have provided only a glimpse of the limitless possibilities in polymer synthesis.

Organic reagents in polymer synthesis

New polymer-forming reactions continue to hold the attention of synthetic polymer chemists. They include the wide gamut of reagents and catalysts that are

familiar to organic chemists, but require ingenuity when extended from traditional organic synthesis to polymer synthesis. Some of the examples are nucleophilic aromatic displacements on activated monomers as a synthetic route to high-performance materials²³, organosilicon and organoboron chemistry in polymer synthesis²⁴, protective group approach to polymer synthesis²⁵, organometallic coupling agents for polymer synthesis²⁶, in aqua synthesis of rigid rod polymers²⁷, facile ring-opening polymerization of cyclic oligomers²⁸ and solid-state polymerization of oligomers to high-molecular-weight polymers²⁹.

Supramolecular architecture and nanoscopic control of polymer structures

The ability to create ordered molecular arrays with specific chemical and physical properties opens the door to advances in novel materials for nanotechnology which would find applications as specific reagents, catalysts, components of integrated optoelectronic devices, patternable layers for nanolithography, molecular recognition systems, as active layers for bio and chemical sensors device fabrication, etc.³⁰. The need for materials as building blocks for such applications have led to new approaches for controlling the supramolecular architecture of organic polymer materials³¹. Different approaches adopted to such polymolecular assemblies are summarized below.

Cascade polymers or dendritic macromolecules

Synthesis of highly branched polymer structures (termed as starburst or cascade polymers) are receiving considerable attention, due to manifestation of a variety of new and improved properties in these topologically defined structures³². With precisely controlled size and spatially defined size, these polymers provide potentials as a unimolecular micelles to carry out constrained chemical reactions, preparation of electronic devices operating at quantum scale, etc. Although there is a sudden explosion in developing synthetic methodologies for preparing these polymers, all the approaches include a tedious step-by-step coupling of the building blocks to obtain homogeneous macromolecules³³. Thus, before the elusive goals of their applications are realized, the synthetic challenges to control of architecture and more precise location of the functionality on the surface of these polymers have to be adequately mastered.

Substrate-specific polymers through molecular imprinting

The process of molecular imprinting involves a molecular-recognition-based polymerization between a

polymerizable guest and an appropriate host, resulting in new polymers that can have structural precision of functional group arrangements in the range of few nanometers. These polymer-bound patterned functional group entities having structural precision at molecular level are capable of discriminating very closely analogous substrates and can be used as specific recognition materials for high-efficiency separation processes, biosensors, shape-selective catalysts³⁴. Furthermore, by choosing different types of intermolecular interaction forces (covalent and noncovalent) this method of polymerization offers materials with architectural features well below the size of current technology (submicron level).

Self-assembled and organized polymeric systems

Generation of polymeric assemblies with ordered functional groups and controlled microstructure in two dimensions provides materials of great scientific and technological importance. These organized systems such as liposomes, vesicles, Langmuir-Blodgett (LB) films, etc., have the special features of precise positioning of functional groups. Being part of a polymeric chain can enhance the stability of these otherwise unstable systems³⁵. The current synthetic efforts in this direction intend to incorporate functionalities exhibiting photochemical and electroactive properties, electrochromism, nonlinear optics, and pyroelectric properties. These designed materials have specific prospects for molecular electronics devices.

Molecular engineering through noncovalent interactions

Another approach to generate supramolecular arrays of polymeric assemblies is the use of noncovalent interactions that are selective, directional and strongly attractive and which can induce spontaneous self-assembly of molecular components in a predictable manner, leading to supramolecular aggregates. Thus, use of complementary hydrogen bonding and metal coordination interactions have produced polymeric two and three-dimensional ordering, showing unusual properties such as liquid crystallinity, helicity, molecular laminates, molecular wires, etc., properties not shown by the individual components. This chemical collectivism offers a fundamentally new approach to design novel polymeric materials with unusual supramolecular structures and properties^{36, 37}.

Biocatalytic approach for polymer synthesis

Synthesis of polymeric materials with well-defined molecular architecture with the help of chemical methods needs scrupulously careful experimental

manipulations. Nature, on the other hand, makes biopolymers with great precision of molecular parameters under much milder and less rigorous conditions. However, most of such reactions occur in aqueous medium, thereby limiting their utility to a very small segment of monomer systems. Furthermore, high specificity of biocatalysts towards substrates enables only a limited number of such monomers that can be polymerized. Recent developments in enzyme-catalysed organic transformations in nonaqueous media demonstrate the possibility of polymerization reactions catalysed by enzymes³⁸. The techniques of genetic manipulation of biological organisms (site-directed mutagenesis) enable engineering of structure and hence properties of the native enzymes expressed in their modified forms (mutants). The altered properties that can be expressed include stability and activity to variation of solvent polarity, recognition of unusual substrates and initiation of new chemical transformations³⁹. Thus, use of engineered biocatalysts would enable carrying out synthesis of a variety of functional polymers (e.g. polyamides) from unnatural multifunctional amino acids, polyester, under mild reaction conditions. The polymers thus obtained are likely to be uniform in molecular weight, have high degree of structural and stereochemical purity, be contaminant-free and biodegradable⁴⁰.

Surface functionalized polymers: Organic chemistry in two dimensions

The general importance of interface in polymer materials stems from the fact that most of the critical properties of materials involve their surface. The interfacial characteristics of bulk polymer systems (e.g. films, fibres, etc.) determine their wettability and influence adhesion among other properties. For example, the surface of a biomedical material determines its biocompatibility. The surface lubricity of Teflon underlines its use in bearings. Similarly, the local surface character of a resist polymer that defines the patterning is obviously a key factor in the fabrication and function of an integrated circuit⁴¹.

Only rarely does it happen that a material has valuable bulk properties and ideal surface properties for a particular application. For example, most of the elastomers that are candidates for use as heart pump or blood vessel prostheses have surface properties that favour protein deposition, trigger thrombus precipitation and provide a foothold for bacterial colonization. This is why large areas of biomedical materials research revolve around the testing and retesting of five or six long-existing off-the-shelf commercial polymers. In the absence of a better approach, materials scientists and biomedical engineers are constantly forced into a compromise in order to balance bulk materials advantages against unwanted surface characteristics.

Polymer surface modification chemistry is a viable technique for maximizing the properties of the existing polymers. This would offer a facile route to new types of polymer-derived functional materials. In this approach, a material is chosen for its bulk property and the surface is then altered by interfacial organic chemistry. In many respects, the chemistry of surface is a more complex process than solution chemistry. Factors such as the hydrophilic or hydrophobic interactions at the interface, or the tendency for certain side groups to concentrate at the surface may play a controlling role in the reaction chemistry. Moreover, a change in surface structure generated by a chemical reaction in the outer few angstroms of the material may bring about only a temporary change in surface properties because the motion of polymer molecules may bury the new surface within minutes after exposure to air or to a different liquid medium. However, progress is being made in the development of an underlying understanding of these processes in ways that are likely to aid rational surface design in the future⁴².

Conclusions

Synthetic tool box developed by polymer chemists (highlighted above) demonstrates the power of polymerization chemistry to custom-design new polymeric materials. The challenges faced today to design new materials for advanced technologies certainly testify to the need for developing more and more sophisticated chemistry for rational design of polymers for specific properties. Furthermore, as polymers will be used as molecular components of more complex systems rather than as stand-alone materials, attempts to follow one approach while neglecting the other would lead to disappointing progress. Hence, future efforts in design of polymer materials would require close collaboration between diverse specialists ranging from molecular biologists to surface scientist, with synthetic polymer chemists as mediators.

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