

‘Trends in Polymer Science’

Chiral polymers

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1. Introduction

Most naturally occurring macromolecules, such as nucleic acids, proteins, and polysaccharides, are chiral and optically active. Because of their chirality, nature produces many smaller chiral, optically active compounds. This situation can be very clearly seen if we look at the chirality of nearly 800 drugs derived from natural sources. Only 2% are racemates and only 1% are achiral. The remaining 97% of the drugs are optically active. We are certainly living in a chiral world.

In the history of polymer science, both naturally occurring and synthetic, optically active polymers (OAP) have received much attention in conjunction with their stereochemistries, and extensive studies have been conducted on their syntheses, conformations and functions. The simplest method of synthesizing OAPs involves the polymerization of optically active monomers. However, this is often less attractive from the viewpoint of the polymerization reaction. Asymmetric polymerization, which produces configurationally or conformationally specific optically active polymers starting from optically inactive monomers, is much more attractive and challenging, and remarkable advances, particularly on helical polymers, have been made over the past two decades. Chiroptical techniques such as optical activity, circular dichroism (CD), and vibrational circular dichroism measurements are characteristic probes for OAPs and these have been extensively utilized for studying the configurations and conformations of the polymer chains. Progress in CD instrumentation significantly contributed to advances in the conformational study of OAPs. In recent years, asymmetric reactions and catalysis with chiral reagents have become remarkably advanced, and some of these reagents have been introduced onto polymer supports to be used as immobilized reagents. However, polymer-specific chiral agents or catalysts with high selectivities like enzymes have not yet been developed. The only successful application of synthetic OAPs for practical use has involved the separation of enantiomers by high-performance liquid chromatography using these polymers as chiral stationary phases.

Therefore, what new trends can we expect in the field of OAPs for the coming 21st century?

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2. Synthesis

Recent advances in asymmetric reactions and catalysis as well as in chiral separations have afforded a rapid increase in the number of commercially available optically active compounds and reagents. This situation will influence new methodologies for the preparation of OAPs in the coming century. We now have a variety of tools for the synthesis of novel chiral monomers and polymers. Many chiral monomers will be prepared from these chiral chemicals, and many new OAPs will be directly prepared by means of asymmetric bond formation reactions devised in the field of asymmetric synthesis.

Helix-sense-selective polymerization, which affords OAPs with stable helical conformations from a prochiral (achiral) monomer, has been realized for several monomers over the last two decades. This asymmetric polymerization will be extended to many newer monomers logically designed with the aid of computer simulation. Computational methods will be more frequently involved for a better understanding and innovation of polymer stereochemistry including synthesis, conformation and function.

Asymmetric synthesis polymerization and copolymerization affording configurationally chiral polymers have been performed with various prochiral monomers such as cyclic olefins and dienes. However, the degree of asymmetric induction has scarcely been evaluated. A theoretical approach to optical activity or CD band intensities and the synthesis of logically designed model compounds must be advanced for the estimation of the degree of chiral induction in polymer systems.

From the viewpoint of polymer stereochemistry, it is possible to prepare optically active homopolymers with only configurational main chain chirality from common vinyl monomers such as styrene and MMA, and polymers with very low optical activities have been obtained by the derivatization of their analogues bearing optically active groups. Polymers with clear optical activities will be directly prepared from these vinyl monomers with novel chiral initiator systems. Optically active copolymers with only configurational main chain chirality may be prepared by chemical reaction of an atactic homopolymer by using a stereospecific catalyst or biocatalyst that reacts only with side groups existing at configurationally specific main chain positions.

Enantiomer-selective (stereoselective) polymerization is a kind of kinetic resolution of a racemic monomer in which one of the enantiomers is preferentially polymerized to give an optically active polymer along with unreacted monomer. This kind of asymmetric polymerization has been examined only for several olefinic and cyclic monomers, and should be expanded to include polycondensation reactions with chiral acids, amines and alcohols. The highest enantiomer selectivity so far observed is nearly 95%ee starting from a racemic vinyl monomer. In the near future, higher and nearly perfect enantiomer selection as characteristically observed in enzyme systems as well as in some asymmetric reactions with chiral organometallic reagents will be attained with polymerizations using well-designed monomers and improved catalyst systems. Biocatalysts are likely to be good candidates for future studies in this area.

3. Conformation

The chiroptical properties exhibited by OAPs are very useful for understanding their configurational and conformational characteristics. Helical structure is chiral and characteristic for polymers. There exist two different types of helical conformations; one is a rigid helix and the other is a more dynamic helix. Optically active, rigid one-handed helical conformations can be constructed through a polymerization

process. However, one-handed helical structures with dynamic features have been realized in several different ways in solution as known for the polyisocyanates, polysilanes, and polyacetylenes. Their dynamic properties may have a connection with their conformations in the solid state. Chiral compounds usually exist in two different types of crystals, racemate and conglomerate. In racemates, enantiomers exist in pairs, while in the conglomerate, each enantiomer forms a crystallite. In the latter case, the resolution of enantiomers is possible through preferential crystallization. A similar phenomenon is possible for polymer systems. However, this type of optical resolution of polymer chains has never been attained. A chiral polymer with high degree of crystallinity may be a good candidate for this type of resolution. In an ideal case, adding a proper nucleating agent might form a completely one-handed helical polymer. A few stereoregular polymers are known to form double-stranded helical structures. The one-handed double-stranded helix could be induced in the presence of a chiral stimulant. As already pointed out, a computational approach for conformational analysis is a very useful and essential technique; and a plausible conformation can be predicted for various polymers. The application of this method to better understand the arrangements of polymer chains in the solid state remains to be explored.

Many achiral organic molecules are known to give chiral crystals due to their arrangements. This had been shown by X-ray analysis. However, more recent advances in chiral instrumentation are dramatically changing this situation. Optical activity and CD spectra can sometimes be successfully measured in the solid state. Particularly, the High Accuracy Universal Polarimeter (HAUP) will likely become a powerful tool for probing the chirality of many OAPs in the solid state. For instance, isotactic polypropylene produced with an optically active metallocene catalyst may be constructed with single-handed polymer chains immediately after polymerization. To prove this, a measurement of the optical activity in solid polypropylene must be attained. A better substantiation may be accomplished by the direct observation of one-handed helical structure by atomic force microscopy (AFM) or scanning tunnel microscopy (STM). Such an observation has already been done for a large macromolecule like DNA, and hopefully it will become possible for smaller polymers.

4. Function

Due to the chirality of proteins, polysaccharides and lipids, our bodies often discriminate pairs of enantiomers. For developing new chiral drugs and also for efficiently performing asymmetric syntheses, classical polarimetric analysis of chiral compounds is not suitable because of its low sensitivity. Reliable expeditious analytical methods with high sensitivities are required. In recent decades, the analysis of chiral compounds by gas and high-performance-liquid chromatographies (HPLC) with chiral stationary phases (CSP) has become remarkably advanced and is now among the practical analytical methods. HPLC methods can also be used for large-scale industrial separations. CSPs are key components for this technique and these materials have been prepared from both optically active small compounds and polymers. Among them, CSPs derived from polysaccharide derivatives, particularly phenylcarbamates of cellulose and amylose, are useful materials because of their excellent resolving characteristics and easy availability. It is extremely important and interesting to clarify the origin of this high chiral recognition from the viewpoint of not only molecular recognition but also for the design of new CSPs with high chiral recognition abilities. Many of these polymers are likely to have a helical

conformation with a groove or other unique geometrical features. X-ray analysis, computer simulation or direct microscopic observations are likely to confirm this possibility.

Molecular imprinting methods will be more precisely done and gels or films with high chiral recognition and high efficiency will also be prepared. Supramolecular chemistry may allow for the development of polymeric materials with chiral holes regularly arranged in a gel or film. These materials may exhibit high chiral recognitions that can be exploited for chiral separations and for sensing technologies.

To develop biodegradable or biocompatible materials, the incorporation of chiral residues may be useful and attractive because biosystems often exhibit different actions towards enantiomers. The logical design and practical applications of OAPs with optoelectronic properties should also be explored.

Chemistry is moving from small molecules to larger ones and from simple systems to more complex ones. Under these circumstances, the problem of chirality automatically arises. Is it essential that life be formed only with optically active macromolecules? Optically active systems at a low entropy level would have been involved in biological systems that feature high molecular recognition abilities that are essential for maintaining life. To answer these significant questions, we must study new directions in chirality from both macromolecular and bioscience viewpoints.