CHAPTER 1

AN OVERVIEW OF POLYMER-IMMOBILIZED CHIRAL CATALYSTS AND SYNTHETIC CHIRAL POLYMERS

SHINICHI ITSUNO

1.1 INTRODUCTION

Polymer-immobilized chiral catalysts and reagents have received considerable attention in regard to organic synthesis of optically active compounds [1]. Use of polymer-immobilized catalysts has become an essential technique in the green chemistry process of organic synthesis. They can be easily separated from the reaction mixture and reused many times. It is even possible to apply the polymeric catalysts to the continuous flow system. Not only the practical aspect but also particular microenvironment created in the polymer network has sparked a fascination with their attractive utilization in organic reactions, especially in stereoselective synthesis. In some cases, the polymer-immobilized catalyst accelerates the reaction rate. In other cases, the polymer-immobilized chiral catalyst realizes higher stereoselectivity compared with its low-molecular-weight counterpart. These examples clearly show that the design of the polymeric catalyst is very important for understanding the efficient catalytic process. Chiral polymer synthesis that is directed toward the novel immobilization method of chiral catalysts also should be developed.

Most support materials used for the chiral catalyst have been cross-linked polystyrene derivatives, mainly because of their easy preparation. Various kinds of reactions have been used for the introduction of functional groups into the side chain of the polymer. However, there are so many different types of synthetic polymers, including both organic and inorganic polymers, which may be used as support material. Each polymer would provide a specific microenvironment for the reaction if it was precisely designed. Although the choice of solvent in organic reaction is

---

Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis, First Edition. Edited by Shinichi Itsuno.

limited, the choice of polymer network structure may be almost infinite. The most suitable polymer network for each reaction may be easily found.

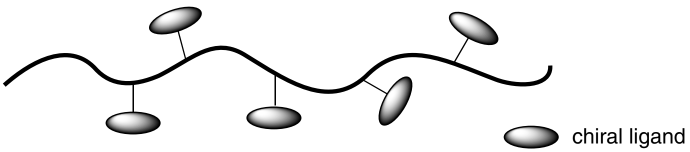
Although a substantial amount of work has been carried out using side-chain functionalized polymers for the preparation of a polymeric catalyst, only a limited number of investigations have been performed to elucidate the use of main-chain functional polymers. Recently, some main-chain chiral polymers including helical polymers have been successfully applied to a chiral catalyst in various kinds of asymmetric reactions. Because of the importance of main-chain chiral polymers in an asymmetric catalyst, this book also focuses on the synthesis of polymers that have main-chain chirality. Polymerization of enantiopure monomers simply produces optically active polymers. Although most enantiopure monomers involve a chiral carbon center, polymerization of some monomers consists of chiral heteroatoms such as silicon and phosphorous, which also have been studied. Asymmetric polymerization by means of a repeated asymmetric reaction between prochiral monomers has been applied to obtain optically active polymers. Several types of main-chain chiral polymers have been prepared by asymmetric polymerization.

Helicity is an important factor in characterizing a chirality of macromolecules. Helical synthetic polymers have gained increasing interest on the basis of recent progress in asymmetric polymer synthesis [2–4]. Efficient induction of the main-chain helical sense to macromolecules, such as poly(methacrylate)s [5], poly (isocyanate)s [6, 7], poly(isocianide)s [8], poly(acetylene)s [9], poly(quinoxaline-2,3-diyl)s [10, 11], and polyguanidines [12], has been achieved. Other types of chiral polymers such as chiral dendrimers and hyperbranched polymers are also involved. Major application of these chiral polymers should be focused on the polymeric asymmetric catalyst.

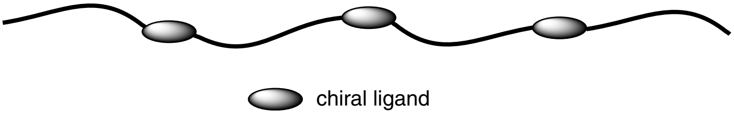
1.2 POLYMERIC CHIRAL CATALYST

Synthetic chiral polymers include (1) polymers possessing side-chain chirality (Scheme 1.1), (2) polymers possessing main-chain chirality (Scheme 1.2), (3) dendritic molecules containing chiral ligands (Scheme 1.3), and (4) helical polymers (Scheme 1.4). The use of polymeric chiral catalysts in asymmetric synthesis is an area of considerable research interest, and it has been the subject of several excellent reviews during the last decade. [13–21]

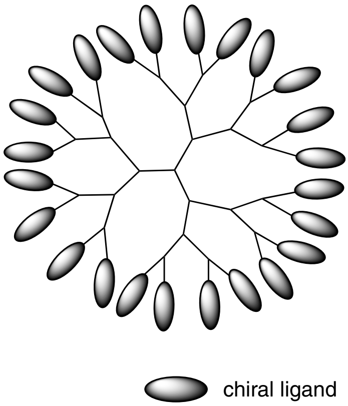
Polymeric catalysts obviously have considerable advantages over the corresponding low-molecular-weight counterparts. They can be easily separated from the reaction mixture, which can be reused many times. The catalyst stability is usually



SCHEME 1.1. Polymer having a side-chain chiral ligand.

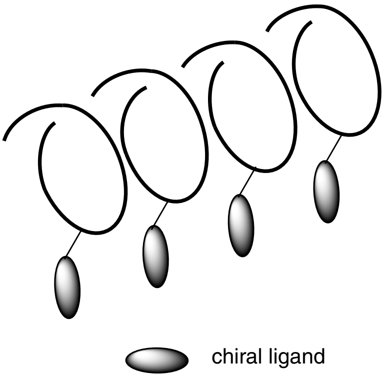


SCHEME 1.2. Polymer containing a main-chain chiral ligand.



SCHEME 1.3. Periferally modified chiral dendrimer.

improved in the case of a polymeric catalyst. Catalyst immobilization on a polymer sometimes results in the site isolation effect, which is also important when the catalyst molecule has a tendency to be aggregated to each other. Immobilization of the catalyst can prevent the aggregation of catalysts. The insolubility of the polymeric catalysts usually facilitates their separation from the reaction mixture. The application of the polymeric catalyst to the continuous flow system becomes possible when the insoluble polymer is used. Although many heterogeneous reactions using the polymeric catalyst suppress the reactivity, in some cases, even higher



SCHEME 1.4. Helical polymer catalyst.

stereoselectivity with sufficient reactivity in the asymmetric reaction is obtained by using well-designed polymeric chiral catalysts. The conformational influence of the polymeric chiral catalysts sometimes becomes a very important factor in the asymmetric reaction.

1.2.1 Polymers Having a Chiral Pendant Group

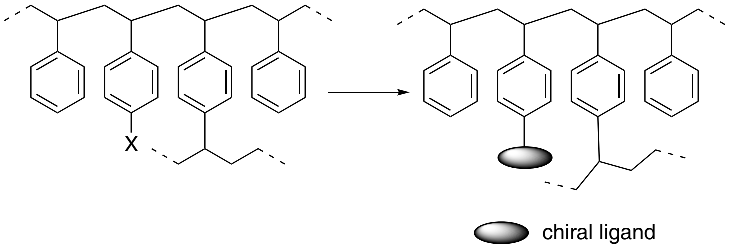
Polymer-immobilized chiral catalysts and reagents have received considerable attention in the organic synthesis of optically active compounds. A typical example of a polymeric catalyst is the polymer-immobilized catalyst. The achiral polymer chain possesses the chiral ligand as a side-chain pendant group. In most cases, polystyrene or cross-linked polystyrene has been used as the polymer support. Because phenyl groups in polystyrene can be easily modified to introduce functional groups, various kinds of chiral ligands are attached to the polystyrene supports (Scheme 1.5). Polyethylene fibers [22], polymeric monoliths [23, 24], poly(2-oxazoline) [25], polyacetylene [26], poly(ethylene glycol) [27], and poly(methylmethacrylate) [28] have also been developed.

An alternative method to preparing the polymer-supported chiral ligand is the polymerization of the chiral monomer with an achiral comonomer and cross-linking agent (Scheme 1.6). Styrene derivatives have been most frequently used as the chiral monomer because of their easy polymerizability with other vinyl monomers [29]. Acrylates and methacrylates have been sometimes used as the chiral monomer [28, 30].

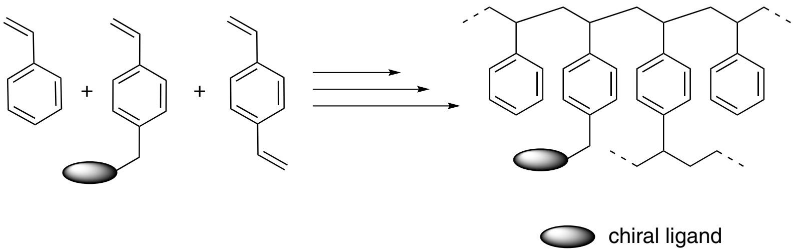
Various kinds of chiral catalysts have been immobilized on the polymer. Because enantioselective organocatalysis has become a field of central importance within asymmetric synthesis, Chapter 2 focuses on polymer-immobilized chiral organocatalysts. Proline and its derivatives are also important organocatalysts, which are discussed in Chapter 3. The use of polymer-imobilized peptides as enantioselective catalysts have been vigorously studied as well and are discussed in Chapter 4.

1.2.2 Main-Chain Chiral Polymers

Many naturally occurring polymers are optically active and have several functionalities. In 1956, Akabori et al. reported that silk-palladium was used as a chiral catalyst



SCHEME 1.5. Cross-linked, polystyrene-supported chiral ligand (polymer reaction method).



SCHEME 1.6. Cross-linked, polystyrene-supported chiral ligand (polymerization method).

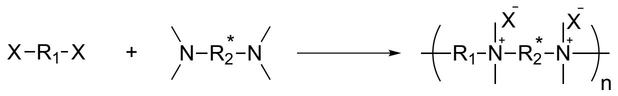
for asymmetric hydrogenation of 4-benzylidene-2-methyl-5-oxazolone [31]. The catalyst was prepared by adsorption of palladium chloride on silk fibroin fiber. This was one of the first examples of the polymer-immobilized chiral catalyst for an asymmetric reaction. Silk is a polymer that has main-chain chirality.

Instead of naturally occurring proteins, synthetic poly(amino acid)s have been applied to asymmetric catalysis. Investigations have been performed to elucidate the use of main-chain functional polymers. *N*-Carboxyanhydride (NCA) prepared from an optically active α-amino acid can be polymerized with amine as an initiator to produce poly(α-amino acid). Juliá et al. discovered that the use of poly(L-alanine) as a "polymeric chiral organocatalyst" produced high enantioselectivities in the epoxidation of chalcone [32]. Itsuno and coworkers also developed cross-linked polystyrene-immobilized poly(α-amino acid)s that allowed for easier workup and recovery [33]. Well-designed peptides have also been used as catalysts in many asymmetric reactions. Chapter 4 includes the important examples of peptide catalysts.

Other than peptides and poly(α-amino acid)s, various kinds of optically active compounds can be polymerized to produce optically active polymers that have main-chain chirality. For example, a reaction between disodium salt of tartaric acid and achiral diol in the presence of toluene-*p*-sulfonic acid produced chiral polyester [34]. The linear poly(tartrate ester) was used as a polymeric chiral ligand in the asymmetric Katsuki–Sharpless epoxidation.

Binaphthol and its derivatives are well-known efficient chiral ligands in asymmetric catalysis. Pu and colleagues studied the pioneering work of enantiopure binaphthol polymers. A class of rigid and sterically regular polymeric chiral catalysts has been developed [35]. Detailed discussion on binaphthol polymers is shown in Chapter 11. Hyperbranched polymers that have binaphthol units are also discussed in Chapter 13.

The polymeric chiral salen ligand was prepared with a polycondensation reaction and subsequently used as a polymeric chiral ligand of Zn [36, 37]. Most polymer-supported chiral zinc catalysts have been prepared by side-chain chiral ligand polymers. The polymeric chiral zinc catalyst derived from the main-chain polymeric salen ligand showed high catalytic activity in the enantioselective alkynylation of ketones. The same salen ligand–Mn complex was used for the enantioselective epoxidation [38]. The chiral organometallic catalysts consist of optically active ligands and transition metals. They often involve optically active



$$X{-}R_1{-}X \;+\; {>}N{-}\overset{*}{R_2}{-}N{<} \longrightarrow \left(R_1{-}\overset{X^-}{\overset{|}{N^+}}{-}\overset{*}{R_2}{-}\overset{X^-}{\overset{|}{N^+}} \right)_n$$

SCHEME 1.7. Chiral ionene polymer.

tertiary phophine ligands. Linkage of such phosphines to organic polymer backbones allows for the preparation of immobilized chiral catalysts.

Recently, chiral organocatalysts have received considerable attention as asymmetric reactions with a chiral organocatalyst meet the green chemistry requirements. One important chiral organocatalyst is optically active quaternary ammonium salt [39, 40]. Quaternary ammonium salts can be easily prepared by a reaction between tertiary amine and halide (Scheme 1.7). Polymerization of tertiary diamine and dihalide produces a quaternary ammonium polymer named “ionene” [41–44]. Polymers containing a chiral quaternary ammonium structure in the main chain can be easily prepared by this method. If the chiral quaternary ammonium compound has extra functionality such as the diol group, then the chiral diol is copolymerized with dihalide to produce chiral polymers that have a quaternary ammonium structure in their main chain [45]. These chiral quaternary ammonium polymers are discussed in Chapter 2.

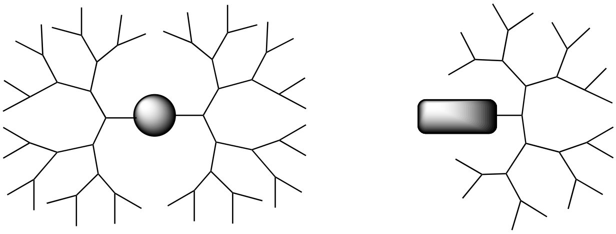
1.2.3 Dendrimer-Supported Chiral Catalysts

Dendritic molecules are a new class of polymers having well-defined, highly branched structures [46]. Several types of chiral catalyst immobilization on dendrimers have been reported. Core-functionalized chiral dendrimers, periferally modified chiral dendrimers, and solid-supported dendritic chiral catalysts are available (Scheme 1.8) [47]. In some cases, the dendritic chiral catalyst showed better performance compared with the corresponding low-molecular-weight catalyst. When a core-functionalized chiral dendrimer that has polymerizable groups on the peripheral site was copolymerized with an achiral monomer, a cross-linked chiral dendrimer was produced, which can be recycled many times [48].

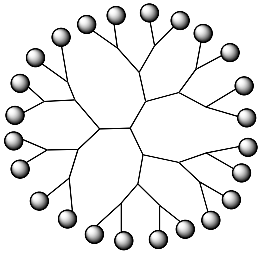
Optically active hyperbranched polymers have some structural similarity with chiral dendrimers. Synthesis of such polymers is relatively simple compared with the stepwise synthesis of a chiral dendritic molecule. Several types of optically active hyperbranched polymers have also been prepared and used as a polymeric chiral catalyst [49].

1.2.4 Helical Polymers

The conventional approach to the polymer-immobilized catalyst involves the introduction of the chiral ligand onto a sterically irregular polymer backbone, which sometimes results in less effective catalysts. A helix is one of the simplest and best-organized chiral motifs. Efficient induction of the main-chain helical sense to polymers produces optically active helical polymers. Several helical polymers with an excess of a preferred helix sense have been synthesized to mimic the structures



Core-functionalized chiral dendrimer Solid supported dendrimer



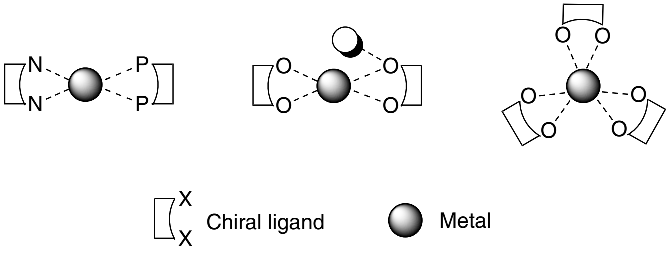
Periferally modified chiral dendrimer

SCHEME 1.8. Dendritic chiral catalyst.

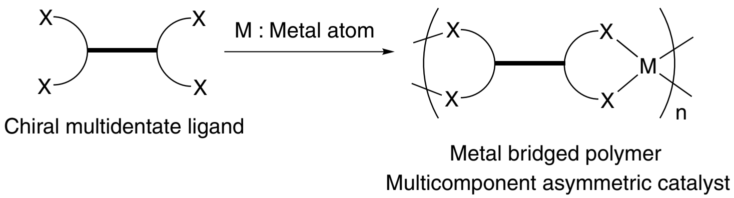
and functions of biological polymers such as proteins and nucleic acids [50–52]. Helical polymers with catalytic active sites have been developed and used as chiral catalysts. Some helical polymers have been used as catalysts for enantioselective reactions [53]. Chapters 7, 8, 9 involve some typical examples of helical polymer catalysts for asymmetric reactions.

1.2.5 Multicomponent Asymmetric Catalysts

The highly organized multicomponent asymmetric catalysts shown in Scheme 1.9 have been developed and used as catalysts for several asymmetric transformations [54]. Some of these catalysts were attached to a polymer support by using the catalyst analog method. After copolymerization of a catalyst analog with a monomer



SCHEME 1.9. Multicomponent asymmetric catalysts.



SCHEME 1.10. Metal-bridged chiral polymeric catalyst.

in the presence of a cross-linker, the connecting group was exchanged by the catalytically active metal. The polymer-supported multicomponent asymmetric catalysts have been successfully used in some asymmetric reactions such as the Michael reaction [55]. Typical examples are summarized in Chapter 10.

The combination of the chiral multidentate ligand with a metal atom forms metal-bridged polymers (Scheme 1.10) [56]. Multicomponent asymmetric catalysts have been developed as efficient immobilization of the chiral catalyst in the polymer. Compared with the conventional approach, multicomponent asymmetric catalysts involve the regularly introduced catalyst sites. Moreover, this approach provides a simple and efficient method for immobilization without the need for a polymer support. For example, Al-Li-bis(binaphthoxide) and μ-oxodititanium complexes have been used as catalysts for the asymmetric Michael addition and the asymmetric carbonyl–ene reactions, respectively.

1.2.6 Continuous Flow System

One of the most common methods of simplifying isolation has been to attach one reactant to an insoluble polymer bead. Once the reaction is complete, the species supported on the polymer will be easily separated from the others by simple filtration [57]. The polymer-immobilized catalysts are used not only for the batch system but also for the flow system when the catalyst is packed in a column. The advantage of the continuous system in organic synthesis is that it allows the products of the reaction to be isolated more quickly and easily than traditional methods. The flow system can eliminate the stirring that sometimes causes damage on the polymer beads. Application of the flow system to an asymmetric reaction was initiated by Itsuno et al. in asymmetric borane reduction of ketones [58]. The continuous flow system has been applied to various asymmetric reactions, including asymmetric Michael reacions [59] and alkylation [60, 61]. Glyoxylate–ene reaction [62], α-chlorination [63], Michael reaction [59], and cyclopropanation [64] facilitate the reaction process. Important examples of flow system are summarized in Chapter 5.

1.3 SYNTHESIS OF OPTICALLY ACTIVE POLYMERS

Most naturally occurring macromolecules, such as proteins, DNA, and cellulose, are optically active, and a well-controlled polymer chain configuration and conformation makes it possible to realize highly sophisticated functions in a living system.

Considerable attention has been paid to their unique properties and functions. Optically active, higher ordered structures of these macromolecules would be essential in their functions, including molecular recognition, catalytic activity, and substrate specificity. These considerations have motivated considerable interest in the synthesis and application of optically active polymers [65]. The synthetic chiral polymers have many applications, such as separation of chiral compounds and polymeric catalysis in asymmetric reactions. Considerable effort has been devoted toward the synthesis of optically active polymers. A simple method to prepare optically active polymers is polymerization of enantiopure monomers. This method produces optically active polymers that have main-chain chirality. When some chiral functionality is introduced as a pendant group of the nonchiral polymers, the optically active polymers with side-chain chirality are available. Most polymeric chiral catalysts are classified as a side-chain chiral polymer. Chirality can also be created on a polymer by an asymmetric reaction. A highly stereoselective asymmetric reaction on a polymer produces a chiral polymer. Several applications are discussed in Chapter 6. Another method for preparing optically active polymers is a repetitive asymmetric reaction between prochiral monomers. Various asymmetric reactions can be used to synthesize optically active polymers with the asymmetric polymerization of prochiral monomers (Chapters 12 and 14) [8, 50, 52, 66–68].

1.3.1 Asymmetric Reaction on Polymer

An asymmetric reaction by using a polymer-immobilized catalyst and reagent has recently received a great deal of attention, as mentioned, for establishing green chemistry processes in organic synthesis of optically active compounds. However, asymmetric transformations on polymer support is also an important strategy for obtaining various kinds of optically active compounds. This methodology is especially useful in diversity-oriented synthesis, which involves the preparation of compound libraries [69, 70]. These libraries display a wide range of physical and biological properties, which can be useful in assays to identify novel lead compounds. Enantioselective catalysis is also used in diversity-oriented synthesis of optically active compounds. Achiral or chiral substrate molecules attached on the polymer support were transformed into a chiral product [71]. Synthesis of a variety of natural products using combinatorial chemistry methods also has been demonstrated [72].

1.3.2 Helical Polymers and Hyperbranched Polymers

Helical structures in polymers are among the most fundamental and important features of macromolecules [3, 52, 73]. Optically active helical polymers can be obtained by (1) polymerization of an optically active monomer, (2) asymmetric polymerization of an achiral monomer, and (3) enantiomer-selective polymerization of racemic monomers. Various kinds of helical polymers containing poly(isocyanate)s [74, 75], poly(isocyanide)s [76], polychloral [77], poly(alkylmethacrylate), polysilanes [78], poly(acetylene)s [79, 80], poly(thiophene)s [81], and polyguanidines [82, 83] have been synthesized.

One of the most impressive studies on optically active helical polymers has been Yashima et al.'s discovery of the memory of helicity. When the chiral inducer was replaced with achiral compounds, the helicity was completely reproduced by the memory of the macromolecular helicity [84–89]. These helical polymers are described in Chapter 7.

Other important examples of helical polyacetylenes include chiral poly(*N*-propargylamide) [90] and poly(phenylacetylene) derivatives [91]. The helical structure in the polymer is stabilized by means of intramolecular hydrogen bonds. Helix-sense-selective polymerization of achiral and bulky phenylacetylene monomers was performed in the presence of $[Rh(cod)Cl]_2$ and enantiopure 1-phenylethylamine [92]. Chiral π-conjugated polymers from phenylacetylenes are sumamrized in Chapter 15.

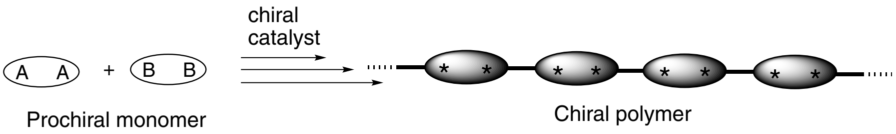
Polymerization of maleimides having optically active *N*-substituent produces one-handed helical polymers. Asymmetric polymerization of achiral *N*-substituted maleimide also has been investigated [93]. Details on asymmetric polymerization of maleimide derivatives are described in Chapter 12.

Helix-sense-selective polymerization of isocyandie was initiated by Nolte et al. [76]. Optically active amine-nickel(II) complexes catalyzed the polymerization of achiral isocyanide to produce helical polyisocyanide [76]. Another helix-sense-selective polymerization of achiral isocyanide was performed by using a single-handed helical oligomer complex [94]. Structurally related poly(quinoxaline-2,3-diyl) was developed by Ito and Suginome and Coworkers [10, 11, 95]. Highly screw-sense-selective polymerization of quinoxaline has been achieved by using optically active binaphthylpalladium(II) [96]. Recently Suginome et al. showed that high-molecular-weight, polyquinoxaline-based helically chiral phosphine was successfully used as a chirality-switchable, reusable, and highly enantioselective monodentate ligand in catalytic asymmetric hydrosilylation of styrene [97]. Related topics are detailed in Chapter 8.

1.3.3 Heteroatom Chiral Polymers

Polymers containing inorganic elements in the main chain have been widely synthesized. However, only a few optically active polymers containing chiral heteroatoms in the main chain have been reported. One typical example is a silicon containing chiral polymers. Although a silicon atom is not a stereogenic center, polysilanes adopt screw-sense helical structures [74]. Polycabosilans [98, 99], polysiloxans [100], polyc(siloxane)s [101], and oligosilanes are other examples of optically active polymers containing silicon as chiral heteroatoms.

An interesting approach to heteroatom chiral polymers is the incorporation of P-stereogenic centers into the polymer main chain. Chujo et al. have synthesized optically active polymers containing chiral phosphorous atoms in the main chain [102–105]. Because various types of P-stereogenic phosphimes have been used as chiral ligands for transition-metal–catalyzed asymmetric reactions, development of the corresponding polymeric catalysts is highly expected. Several recent reviews on chiral polymers with heteroatoms as chiral centers are described in Chapter 16.



SCHEME 1.11. Asymmetric polymerization of prochiral monomers.

1.3.4 Asymmetric Polymerization

Optically active polymers are definitely important in a variety of applications, including the polymeric catalysts in asymmetric synthesis and separation of racemic mixtures. Many naturally occurring polymers are optically active. Synthetic chiral polymers can also be prepared by several methods. Polymerization of optically active monomers simply produces chiral polymers. The main-chain chiral polymers discussed in Section 1.2.2 obviously belong to this category. Another way to prepare optically active polymers is asymmetric polymerization. Prochiral monomers are polymerized with a chiral catalyst to produce the optically active polymers (Scheme 1.11). A typical example is helical polymer synthesis by means of asymmetric polymerization.

Basically, many asymmetric reactions can be applied to synthesize optically active polymers [68]. An asymmetric reaction between monomers should produce corresponding polymers that have chiral centers in the main chain of the polymer. For example, an asymmetric aldol reaction has been vigorously developed in the field of organic synthesis. Optically active polymers were prepared by means of a repeated asymmetric aldol reaction [106, 107]. Asymmetric allylation polymerization [108, 109] and asymmetric Diels–Alder polymerization [110, 111] were also developed.

Asymmetric polymeization of propyrene and CO has been successfully performed in the presence of the chiral phosphinephosphite Pd complex [112]. Chiral 1,4-polyketones bearing asymmetric carbons in the main chain have been prepared in an asymmetric manner initiated by optically active transition metal complexes. Chapter 14 covers the synthesis of optically active polyketones.

REFERENCES

[1] (a) In *Handbook of Asymmetric Heterogeneous Catalysis* (Ding, K. ; Uozumi, Y., Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany (2008). (b) In *Recoverable and Recyclable Catalysts* (Benaglia, M., Ed.) Wiley, New York (**2009**).

[2] (a) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (b) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039–4070. (c) Fujiki, M. *Macromol. Rapid Comm.* **2001**, *22*, 539–563. (d) Yashima, E.; Maeda, K. In *Foldamers: Structure, Properties, and Applications* (Hecht, S.; Huc, I., Eds.), Wiley-VCH: Weinheim, Germany, ch. 11 (2007).

[3] Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039–4070.

[4] Yashima, E.; Maeda, T.; Nishimura, T. *Chem. Eur. J.* **2004**, *10*, 42–51.

[5] Okamoto, Y.; Suzuki, K.; Ohta, K.; Harada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763–4765.

[6] Lifson, S.; Felder, C. E.; Green, M. M. *Macromolecules*, **1992**, 25, 4142–4148.

[7] Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *Polymer J.* **1993**, *25*, 391–396.

[8] Suginome, M.; Ito, Y. *Adv. Polymer Sci.* **2004**, *171*, 77–136.

[9] Maeda, K.; Mochizuki, H.; Watanabe, M.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 7639–7650.

[10] Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446–6447.

[11] Ito, Y.; Miyake, T.; Hatano, S.; Shima, R.; Ohara, T.; Suginome, M. *J. Am. Chem. Soc.* **1998**, *120*, 11880–11893.

[12] Schlitzer, D. S.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 2196–2197.

[13] Bergbreiter, D. E. In *Chiral Catalyst Immobilization and Recycling* (De Vos, D. E.; Vankelecom, I. F. J.; Jacobs, P. A.Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany, pp. 43–80 (2000).

[14] Clapham, B.; Reger, T. S.; Janda, K. D., *Tetrahedron* **2001**, *57*, 4637–4662.

[15] Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217–3273.

[16] McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275–3299.

[17] Brase, S.; Lauterwasser, F.; Ziegert, R. E. *Adv. Synth. Catal.* **2003**, *345*, 869–929.

[18] El-Shehawy, A. A.; Itsuno, S. *Curr. Top. Polymer Res.* **2005**, 1–69.

[19] Dioos, B. M. L.; Vankelecom, I. F. J.; Jacobs, P. A. *Adv. Synth. Catal.* **2006**, *348*, 1413–1446.

[20] Itsuno, S.; Haraguchi, N. In *Handbook of Asymmetric Heterogeneous Catalysis* (Ding, K. ; Uozumi, Y. Eds.), Wiley-VCH Verlag GmbH, Weinheim, Germany, pp. 73–129 (2008).

[21] Cozzi, F. *Adv. Synth. Catal.* **2006**, *348*, 1367–1390.

[22] Degni, S.; Wilen, C. E.; Leino, R. *Tetrahedron: Asymmetry* **2004**, *15*, 231–237.

[23] Bruguete, M. I.; Verdugo, E. G.; Vincent, M. J.; Luis,S. V.; Pennemann, H.; Keyserling, N. G.; Martens, J. *Org. Lett.* **2002**, *4*, 3947–3950.

[24] Svec, F.; Frechet, J. M. J. *Science* **1996**, *273*, 205–211.

[25] Zarka, M. T.; Nuyken, O.; Weberskirch, R. *Chem. Eur. J.* **2003**, *9*, 3228–3234.

[26] Sanda, F.; Araki, H.; Masuda, T. *Chem. Lett.* **2005**, *34*, 1642–1643.

[27] Wang, X.; Yin, L.; Yang, T.; Wang, Y. *Tetrahedron: Asymmetry* **2007**, *18*, 108–114.

[28] Sekiguti, T.; Iizuka, Y.; Takizawa, S.; Jayaprakash, D.; Arai, T.; Sasai, H. *Org. Lett.* **2003**, *5*, 2647–2650.

[29] Arakawa, Y.; Chiba, A.; Haraguchi, N.; Itsuno, S. *Adv. Synth. Catal.* **2008**, *350*, 2295–2304.

[30] Arai, T.; Sekiguchi, T.; Otsuki, K.; Takizawa, S.; Sasai, H. *Angew. Chem. Int. Ed.* **2003**, *115*, 2194–2197.

[31] Akabori, S.; Sakurai, S.; Izumi, Y.; Fujii, Y. *Nature* **1956**, *178*, 323–324.

[32] Juliá, S.; Masana, J.; Vega, J. C. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 929–931.

[33] Itsuno, S.; Sakakura, M.; Ito, K. *J. Org. Chem.* **1990**, *55*, 6047–6049.

[34] Canali, L.; Karjalainen, J. K.; Sherrington, D. C.; Hormi, O. *Chem. Comm.* **1997**, 123–124.

[35] Johannsen, M.; Jorgensen, K. A.; Zheng, X. -F.; Hu, Q. -S.; Pu, L. *J. Org. Chem.* **1999**, *64*, 299–301.

[36] Cozzi, P. G. *Angew. Chem. Int. Ed.* **2003**, *42*, 2895–2898.

[37] Pathak, K.; Bhatt, A. P.; Abdi, S. H. R.; Kureshy, R. I.; Khan, N. -U. H.; Ahmad, I.; Jasra, R.V. *Chirality* **2007**, *19*, 82–88.

[38] Kureshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Singh, S.; Ahmed, I.; Jasra, R. V. *J. Mol. Catal. Chem.* **2004**, *218*, 141–146.

[39] Ooi, T.; Maruoka, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 4222–4266.

[40] Hashimoto, T.; Maruoka, K. *Chem. Rev.* **2007**, *107*, 5656–5682.

[41] Casson, D.; Rembaum, A. *Macromolecules* **1972**, *5*, 75.

[42] Noguchi, H.; Rembaum, A. *Macromolecules* **1972**, *5*, 253.

[43] Rembaum, A.; Noguchi, H. *Macromolecules* **1972**, *5*, 261.

[44] Yu, Q.; Frömmel, J.; Wolff, T.; Stepanek, M.; Procházka, K. *Langmuir* **2005**, *21*, 6797.

[45] Itsuno, S.; Paul, D. K.; Ishimoto, M.; Haraguchi, N. *Chem. Lett.* **2010**, *39*, 86–87.

[46] Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*, Wiley, Chichester, U.K. (2002).

[47] Fan, Q.; Deng, G.; Feng, Y.; He, Y. In *Handbook of Asymmetric Heterogeneous Catalysis*, (Ding, K.; Uozumi, Y., Eds.), Wiley-VCH, Weinheim, Germany, p. 131 (2008).

[48] Seebach, D.; Beck, A. K.; Heckel, A. *Angew. Chem. Int. Ed.*, **2001**, *40*, 92–138.

[49] Slagt, M. Q.; Stiriba, S. E.; Holger Kautz, H.; Gebbink, R. J. M. K.; Holger Frey, H.; Koten, G. *Organometallics* **2004**, *23*, 1525–1532.

[50] Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349–372.

[51] Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866.

[52] Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038.

[53] Hasegawa, T.; Goto, H.; Furusho, Y.; Katagiri, H.; Yashima, E. *Angew. Chem. Int. Ed.* **2007**, *46*, 5885–5888.

[54] Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187–2209.

[55] Arai, T.; Sekiguti, T.; Otsuki, K.; Takizawa, S.; Sasai, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 2144–2147.

[56] Jayaprakash, D.; Takizawa, S.; Arai T.; Sasai, H. *J. Exp. Nanosci.* **2006**, *1*, 477–510.

[57] Mak, X. Y.; Laurino, P.; Seeberger, P. H. *Beilstein J. Org. Chem.* **2009**. *5*, 1–11.

[58] Itsuno, S.; Ito, K.; Maruyama, T.; Kanda, N.; Hirao, A.; Nakahama, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3329–3331.

[59] Bonfils, F.; Cazaux, I.; Hodge, P.; Caze, C. *Org. Biomol. Chem.* **2006**, *4*, 439–497.

[60] Hodge, P.; Sung, D. W. L.; Stratford, P. W. *J. Chem. Soc., Perkin. Trans.* **1999**, *1*, 2335–2342.

[61] Pericas, M. A.; Herrerias, C. I.; Sola, L. *Adv. Synth. Catal.* **2008**, *350*, 927–932.

[62] Mandoli, A.; Orlandi, S.; Pini, D.; Salvadori, P. *Tetrahedron: Asymmetry* **2004**, *15*, 3233–3244.

[63] France, S.; Bernstein, D.; Weatherwax, A.; Lectka, T. *Org. Lett.* **2005**, *7*, 3009–3012.

[64] Burguete, M. I.; Cornejo, A.; García-Verdugo, E.; García, J.; Gil, M. J.; Luis, S. V.; Martínez-Merino, V.; Mayoral, J. A.; Sokolova, M. *Green Chem.* **2007**, *9*, 1091–1096.

[65] Coates, G. W. In *Comprehensive Asymmetric Catalysis*, vol. III (Jacobsen, E. N.; Pfalts, A.; Yamamoto, H. Eds.). Springer, Berlin, Germany, pp. 1329–1349. (1999).

[66] Pu, L. *Acta Polym.* **1997**, *48*, 116–141.

[67] Nozaki, K.; Hiyama. T. *J. Organomet. Chem.* **1999**, *576*, 248–253.

[68] Itsuno, S. *Prog. Polymer. Sci.* **2005**, *30*, 540–558.

[69] Morton, D.; Leach, S.; Cordier, C.; Warriner, S.; Nelson, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 104–109.

[70] Spandl, R. J.; Bender, A. *Org. Biomol. Chem.* **2008**, *6*, 1149–1158.

[71] Stavenger, R. A.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2001**, *40*, 3417–3421.

[72] Doi, T.; Takahashi, T. In *Combinatorial Synthesis of Natural Product-Based Libraries*, (Boldi, A. M., Ed.), CRC Press, Boca Raton, Fl, pp. 227–245 (2006).

[73] Green, M.; Andrea, C.; Reidy, N. *J. Am. Chem. Soc.* **1988**, *110*, 4063–4065.

[74] Fujiki, M. *Macromol. Rapid Comm.* **2001**, *22*, 539–563.

[75] Okamoto, Y.; Matsuda, M.; Yashima, E. *J. Polymer Sci.: Part A* **1994**, *32*, 309–315.

[76] (a) Kamer, P.; Nolte, R.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818–6825. (b) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818–6825.

[77] Ute, K.; Hirose, K.; Hatada, K. *J. Am. Chem. Soc.* **1991**, *113*, 6305–6306.

[78] Fujiki, M.; Koe, J. R.; Terao, K.; Sato, T.; Teramoto, A.; Watanabe, J. *Polymer J.* **2003**, *35*, 297–344.

[79] Nakano, H.; Nomura, R.; Masuda, T. *Macromolecules* **1999**, *32*, 2861–2864.

[80] Yashima, E.; Huang, S.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184–4193.

[81] Langeveld-Voss, B.; Meijer, E. *J. Am. Chem. Soc.* **1996**, *118*, 4908–4909.

[82] Tian, G.; Lu, Y.; Novak, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4082–4083.

[83] Tang, H. Z.; Lu, Y.; Tian, G.; Capracotta, M. D.; Novak, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 3722–3723.

[84] Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449–451.

[85] Hase, Y.; Ishikawa, M.; Muraki, R.; Maeda, K.; Yashima, E. *Macromolecules* **2006**, *39*, 6003–6008.

[86] Hase, Y.; Mitsutsuji, Y.; Ishikawa, M.; Maeda, K.; Okoshi, K.; Yashima, E. *Chem. Asian J.* **2007**, *2*, 755–763.

[87] Hasegawa, T.; Morino, K.; Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Macromolecules* **2006**, *39*, 482–488.

[88] Miyagawa, T.; Furuko, A.; Maeda, K.; Katagiri, K.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2005**, *127*, 5018–5019.

[89] Maeda, K.; Morino, K.; Okamoto, Y.; Sato, T.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 4329–4342.

[90] Nomura, R.; Tabei, J.; Masuda, T. *J. Am. Chem. Soc.* **2001**, *123*, 8430–8431.

[91] Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346–6347.

[92] Kaneko, T.; Umeda, Y.; Jia, H.; Hadano, S.; Teraguchi, M.; Aoki, T. *Macromolecules* **2007**, *40*, 7098–7102.

[93] Oishi, T.; Isobe, Y.; Onimura, K.; Tsutsumi, H. *Polymer J.* **2003**, *35*, 245–254.

[94] Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1554–1556.

[95] Suginome, M.; Collet, S.; Ito, Y. *Org. Lett.* **2002**, *4*, 351.

[96] Ito, Y.; Ohara, T.; Shima R.; Suginome, M. *J. Am. Chem. Soc.* **1996**, *118*, 9188–9189.

[97] Yamamoto, T.; Yamada, T.; Nagata, Y.; Suginome, M. *J. Am. Chem. Soc.* **2010**, *132*, 7899–7901.

[98] Kawakami, Y.; Takeyama, T.; Komuro, K.; Ooi, O. *Macromolecules* **1998**, *31*, 551–553.

[99] Kakihana, Y.; Uenishi, K.; Imae, I.; Kawakami, Y. *Macromolecules* **2005**, *38*, 6321–6326.

[100] Oishi, M.; Kawakami, Y. *Org. Lett.*, **1999**, *1*, 549–552.

[101] Zhou, D.; Kawakami, Y. *Macromolecules* **2005**, *38*, 6902–6908.

[102] Morisaki, Y.; Saito, K.; Imoto, H.; Suzuki, K.; Ouchi, Y.; Chujo, Y. *Polymer Sci. Ser. A* **2009**, *51*, 1218–1228.

[103] Ouchi, Y.; Morisaki, Y.; Ogoshi, T.; Chujo, Y. *Chem. Asian J.* **2007**, *2*, 397–402.

[104] Morisaki, Y.; Ouchi, Y.; Tsurui, K.; Chujo, Y. *J. Polymer Sci. Part A: Polymer Chem.* **2007**, *45*, 866–872.

[105] Morisaki, Y.; Ouchi Y.; Tsurui, K.; Chujo Y. *Polymer Bull.* **2007**, *58*, 665–671.

[106] Komura, K.; Itsuno, S.; Ito, K. *Chem. Comm.* **1999**, 35–36.

[107] Itsuno, S.; Komura, K. *Tetrahedron* **2002**, *58*, 8237–8246.

[108] Itsuno, S.; Kumagai, T. *Helv. Chim. Acta* **2002**, *85*, 3185–3196.

[109] Kumagai, T.; Itsuno, S. *Macromolecules* **2002**, *35*, 5323–5325.

[110] Itsuno, S.; Tada, S.; Ito, K. *Chem. Comm.* **1997**, 933–934.

[111] Kamahori, K.; Tada, S.; Ito, K.; Itsuno, S. *Macromolecules* **1999**, *32*, 541–547.

[112] Nozaki, K. *J. Polymer Sci., Part A: Polymer Chem.* **2004**, *42*, 215–221.