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Asymmetric Polymerization

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I. Introduction

The synthesis and application of optically active polymers are topics currently attracting much attention. This may arise mainly from their chiral structure which is common to naturally occurring polymers. Most of the naturally occurring polymers are optically active and some of them show characteristic functionalities such as molecular recognition ability and catalytic activity, owing to their specific chiral structure as represented by genes and proteins. In synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems that will be as effective as those in living systems, and the optically active synthetic polymers have today become of great interest and importance in this respect.

Asymmetric polymerization, in which chirality is introduced to a polymer chain via polymerization reaction, is one of the ways available for synthesizing optically active polymers. The interest in asymmetric polymerization is not only because it is an effective way of synthesis but also because it provides an insight to the polymerization mechanism.

With regard to reaction process and structure of the obtained polymers, asymmetric polymerization can be classified into the following three major categories: (1) asymmetric synthesis polymerization, (2) helix-sense-selective polymerization, and (3) enantiomer-selective (also referred to as enantioselective, stereoelective, asymmetric-selective, or enantioasymmetric) polymerization. The polymerizations of categories 1 and 2 are distinguished from the polymerization of category 3, because they include an asymmetric synthesis process generating a chiral center (configuration) or conformation.

In asymmetric synthesis polymerization, an optically inactive prochiral monomer or a prochiral monomer with optically active auxiliary is polymerized to give a polymer with configurational main-chain chirality. In the polymerization reaction, the growing species (radical or ion) attacks a monomer selectively on one enantioface. This type of polymerization has been reported for various types of olefinic compounds, although the degree of asymmetric induction is unclear in most cases.

The synthesis and analysis of stereoregular polymers have been extensively studied since the discovery of Ziegler–Natta catalyst[1] and the development of NMR spectroscopy,[2,3] and the relation between optical activity of a polymer and its chain configuration has been discussed by several researchers.[3-8] the polymers of dienes and cyclic olefins can be optically active when the chiral centers in the main chain have preferentially one of the two possible configurations (*R* or *S*), since the chiral centers can be true asymmetric centers. However, as for those of vinyl monomers ($CH_2{=}CHX$ and $CH_2{=}CXY$, 1-substituted and 1,1-disubstituted olefins), the iso- and syndiotactic polymers cannot be optically active even if a significant asymmetric induction occurs at the chiral centers in the main chain, because the whole polymer chain has a mirror plane, ignoring the end groups, i.e., the chiral center in the main chain is pseudoasymmetric. This was first pointed out by Frisch, Schuerch, and Szwarc.[9] Therefore, in order to obtain an optically active vinyl polymer, some higher-order stereoregularities are necessary. The possibility of asymmetric synthesis polymerization of a vinyl monomer was recently surveyed by Wulff[8,10] and realized by his group.

In helix-sense-selective polymerization, optically active polymers whose chirality is based on a helical conformation with an excess of single-screw sense are produced. Because the right- and left-handed helices are mirror images (atropisomers), if one of the two is preferentially synthesized for a polymer chain, the polymer can be optically active.[8,12]

Although many stereoregular polymers have a helical conformation in the solid state,[13,14] most of them cannot maintain a helical conformation in solution, except for some polymers having an optically active side group like polyolefins,[6] because the dynamics of the polymer

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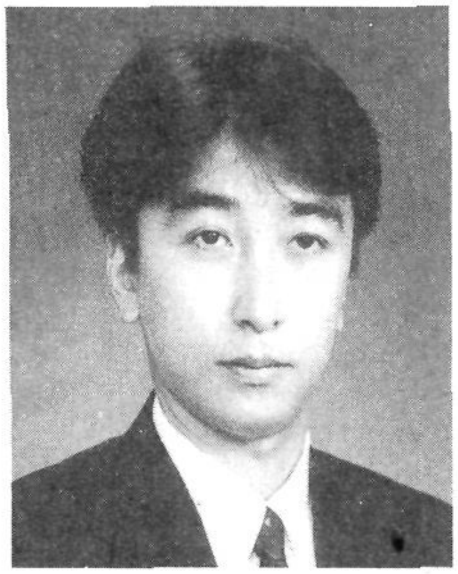


Tamaki Nakano was born in Shizuoka, Japan, on August 24, 1962. He received his B.S. degree in 1986, M.S. degree in 1988 and Ph.D. in 1991 from Osaka University. The Ph.D. thesis work on asymmetric polymerization of methacrylates was conducted under the direction of Y. Okamoto and K. Hatada. In 1990, he accepted a position as research associate at Nagoya University, where he currently resides with Y. Okamoto. He intends to begin his postdoctoral work with D. Y. Sogah at Cornell University in 1993. His current research concerns asymmetric polymerization producing optically active polymers and application of the polymers for molecular recognition and also liquid crystalline polymers.

chain is extremely fast in solution. Therefore, isotactic polystyrene[15,16] and polypropylene[17] prepared with an optically active catalyst do not show optical activity due to a helical conformation. However, it is possible to obtain optically active polymers whose chirality is based on the helical structure of single-screw sense by helix-sense-selective polymerization when rigidity of the polymer backbone or sterical repulsion of the side groups prevents random conformation. Clear atropogenic polymerizations have been attained for bulky methacrylates, isocyanides, chloral (trichloroacetaldehyde), and isocynates. The screw sense of the helix is produced by the chirality of the initiator (catalyst) or monomer. In these examples, polyisocyanates are different than other polymers. In the asymmetric synthesis of helical bulky polymethacrylates, polychloral, and bulky polyisocynides, the helical conformation is formed under kinetic rather than thermodynamic control (i.e., as the monomer inserts into the chain end, it adopts its helical conformation). Once formed, these conformations are locked in by the high helix inversion barriers of these polymers. In contrast, polyisocyanates have very low helix inversion barriers and as a result, the helical conformation of these polymers is under thermodynamic control [i.e., these helical polymers undergo rapid racemization (helical inversion) at normal temperatures]. When an asymmetric initiator is used in the polymerization it becomes the endgroup of the polymer. Due to new asymmetric center, the two forms of the helix are now diastereomers of one another and one form dominates due to thermodynamic reasons. The one-handed helical polymethacrylates show excellent chiral recognition ability when used as a chiral stationary phase for high-performance liquid chromatography (HPLC).[18,19]

In enantiomer-selective polymerization, one antipode of a racemic chiral monomer is preferentially polymerized to give an optically active polymer. In this process, kinetic optical resolution of the racemic monomer is attained. The first clear enantiomer-selective polymerization was reported for propylene oxide by Inoue and co-workers.[11] Thereafter, various examples were reported for other monomers such as α-olefins, propylene sulfide, lactones, and methacrylates. Enantiomer-selective polymerization is also known for α-amino acid *N*-carboxy anhydrides. In connection with enantiomer-selective polymerization, stereoselective polymerization must be referred to, although this method does not produce an optically active polymer. In stereoselective polymerization, a racemic chiral monomer is polymerized to give a mixture of a polymer preferentially consisting of one antipode and that consisting of the opposite enantiomer. Review articles are available mainly concerning these types of polymerizations.[12,20]

Several comprehensive reviews have appeared that discuss the important topics of optically active polymers.[3,5–8,10,12,20,21] In the present review article, we survey asymmetric polymerization and structure of the obtained polymers in accordance with the above classification of the polymerization process with emphasis on those of the polymers with a helical conformation. We also describe the chiral recognition ability of the optically active polymers.

II. Asymmetric Synthesis Polymerization

A. Vinyl Monomers (1-Substituted and 1,1-Disubstituted Olefins)

As mentioned in the Introduction, isotactic and syndiotactic vinyl polymers cannot be chiral because they possess a mirror plane, and they do not show optical activity except for that due to the asymmetric centers in the vicinity of the chain ends. Several negative examples have been shown such as those for the polymers of styrene,[15,16] propylene,[17] methacrylates,[22,23] and acrylonitrile.[22]

However, it is possible to obtain an optically active vinyl polymer with main-chain configurational chirality if some higher order tacticities are realized with

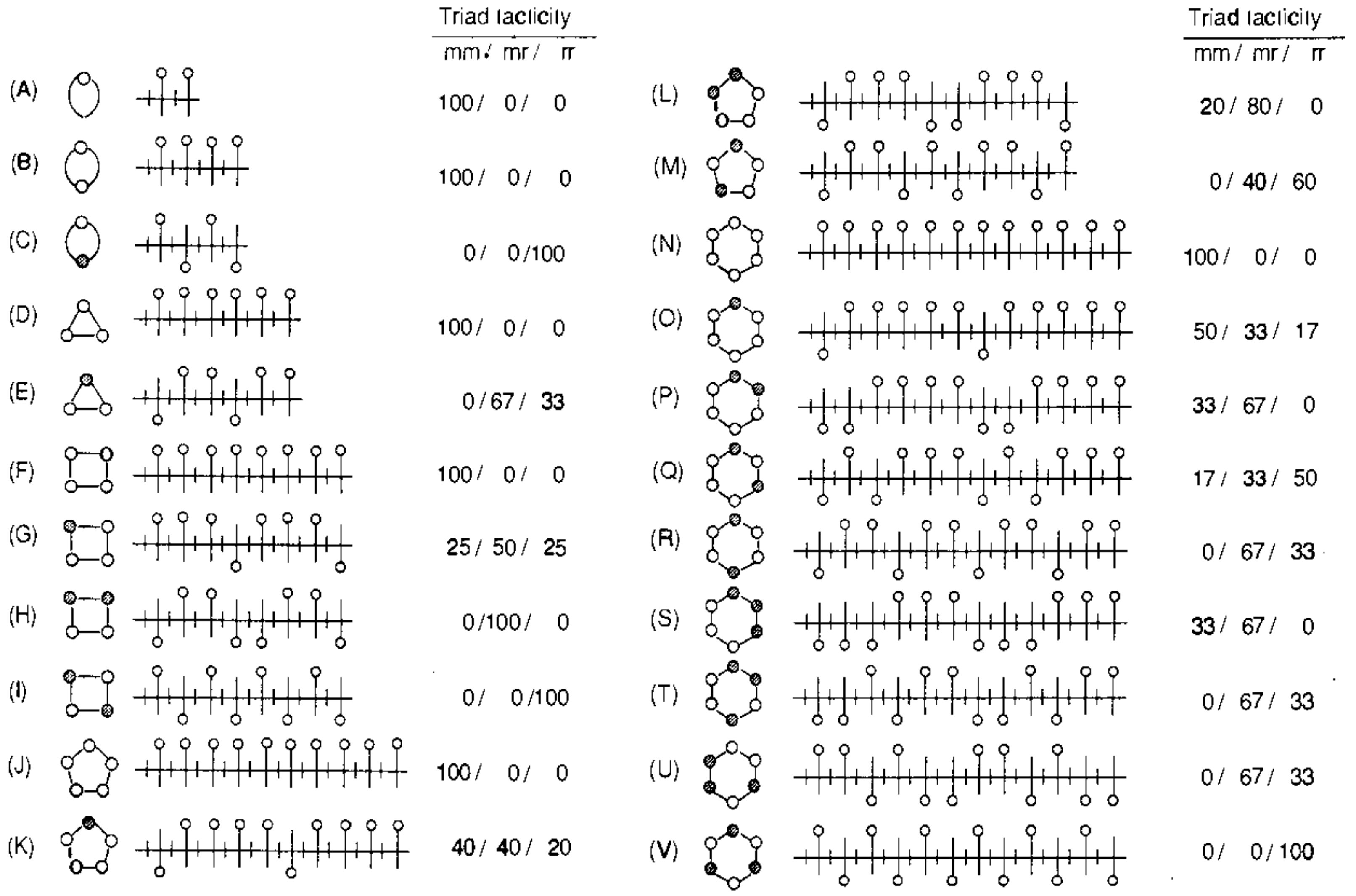


Figure 1. Cyclic (left of each) and infinite chain (right of each) models of stereoregular vinyl polymers and their tacticity. In the cyclic models, the open and filled circles represent chiral centers with opposite configuration, methylene groups being neglected.

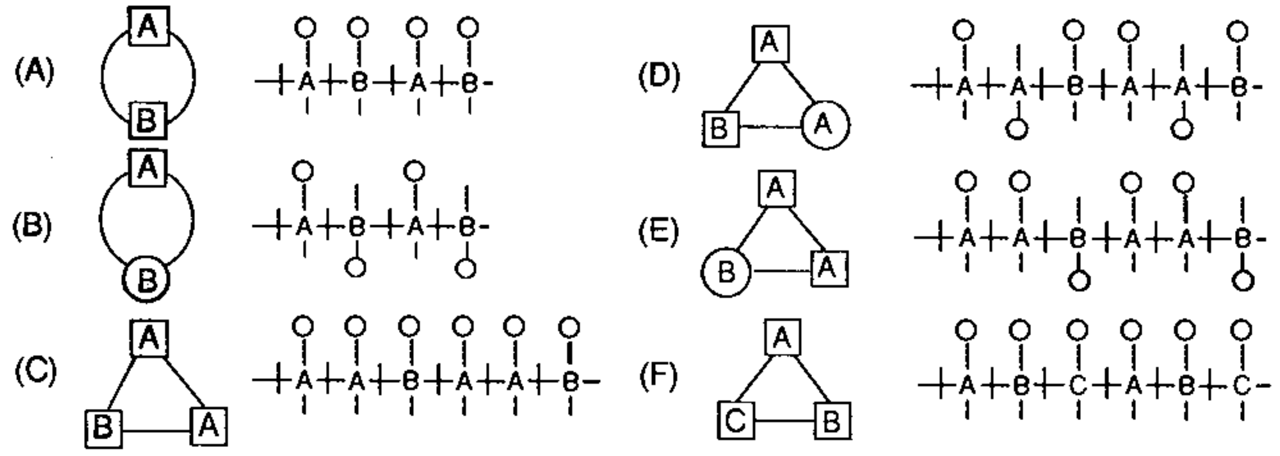
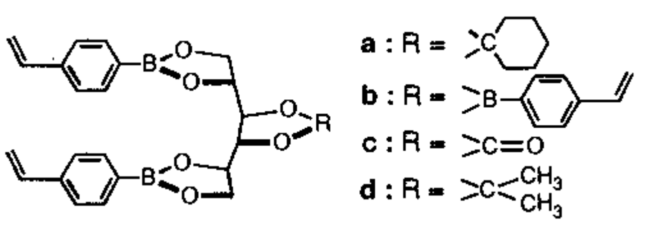


Figure 2. Cyclic (left of each) and infinite chain (right of each) models of vinyl copolymers. In the cyclic modes, the square and the circle represent chiral centers with opposite configuration, methylene groups being neglected.

asymmetric induction for the main chain. Chirality of a polymer chain with a given tacticity can be conveniently tested by representing a stereotactic infinite chain as a cyclic compound and considering symmetry of the compound (Figure 1 and 2).[3,7,8] As for a homopolymer, no stereotactic sequences of diad, triad, tetrad, and pentad are chiral, and one hexad sequence having the triad tacticity mm:mr:rr = 0:67:33 is chiral (Figure 1, parts T and U). The number of chiral sequences increases with increasing length of the stereosequence. The same consideration can be applied to copolymer sequences: for instance one of the three possible triad sequences A–A–B in a copolymer is chiral (Figure 2, part D). Chirality of the polymers of 1,2-disubstituted olefins (CHX=CHX or CHX=CHY) (e.g. fumarates and crotonates) can be considered in the same way.

Wulff and co-workers have realized the synthesis of optically active homo- and copolymers using styrene derivatives **1a-d** with optically active, removable template groups.[8,24-29] They carried out radical copolymerization of the monomer **1a** with styrene and converted the copolymer into polystyrene by removal of the template and deboronation (Figure 3).[27] The resulting polystyrene showed optical activity ($[\alpha]^{30}_{365}$ -0.5 to $-3.5°$), which was attributed to the existence of chiral monomeric diads separated by atactic sequences. The monomer **1a** undergoes cyclopolymerization, in which chiral diad with (*S*,*S*) configuration is formed by the stereoeffect of the template moiety.[25] They also succeeded in synthesizing optically active copolymers of styrene and other monomers in a similar way:[24-26,28,29]



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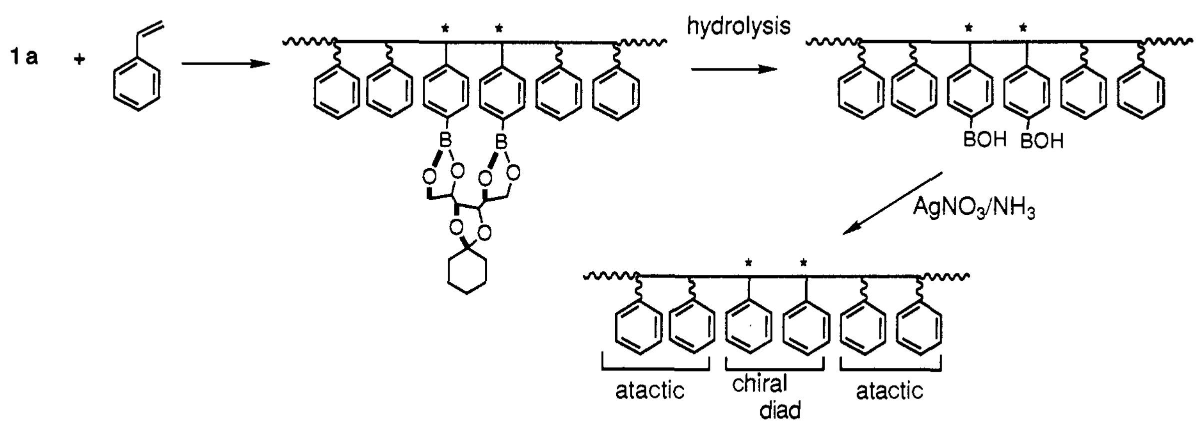
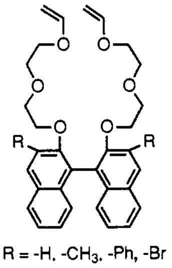


Figure 3. Preparation of optically active homopolymer of styrene by using chiral template.

the optical activity of the polymers can be attributed to the chiral triad of A–A–B shown in Figure 2, part D. (An A monomeric unit corresponds to a styrene unit in this case.) The polymerization method with a chiral template developed in this series of work may be one practical solution in constructing the chiral stereosequences of a vinyl polymer, because it seems to be of significant difficulty to obtain such sequences by polymerization with conventional catalysts or initiators.

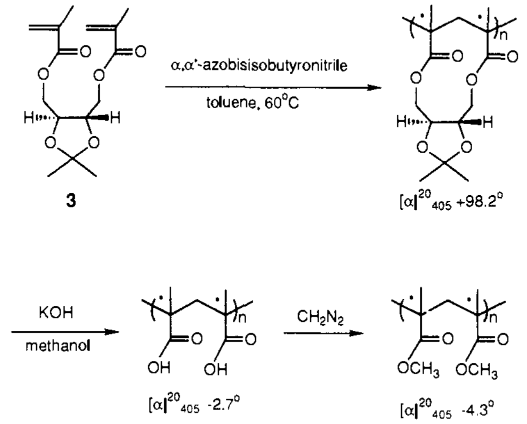
Two more examples of template-mediated asymmetric synthesis polymerization are known. One is the cyclopolymerization of divinyl monomers with an optically active moiety such as **2** and **3** by Kakuchi, Yokota, and co-workers.[30–32] The optical activity and



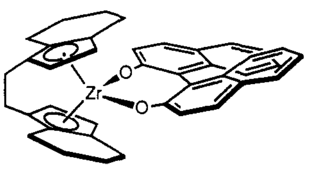
2

^{1}H NMR spectral pattern of the obtained polymer varied depending on the reaction conditions in the polymerization of **2**, and this was ascribed to the varying content of chiral (*S*,*S*)-diad in the main chain, which was induced by perturbation of the optically active binaphthyl moiety.[30] Chemical modification of the radical polymerization product of **3** gave optically active poly(methacrylic acid) ($[\alpha]^{20}_{405}$ −2.7°) and poly(methyl methacrylate) [poly(MMA)] ($[\alpha]^{20}_{405}$ −4.3°) with a tacticity (mm:mr:rr = 12:49:39) which is different from that of poly(MMA) prepared by conventional radical polymerization (Scheme 1).[31,32] The other is the radical polymerization of methacrylic acid in the presence of chitosan as an optically active matrix.[33,34] The Poly(MMA) derived from the obtained poly(methacrylic acid) showed clear optical activity ($[\alpha]^{21}_{D}$ +16°) and the tacticity of the polymer (mm:mr:rr = 29:19:52) differed from that in conventional radical polymerization also in this case.

Scheme 1



Detailed investigations of the asymmetric synthesis process in vinyl oligomerization are known. Pino and co-workers performed a detailed stereochemical analyses of oligomers of propylene,[35,36] 1-pentene,[36] and 4-methyl-1-pentene[36] prepared with optically active zirconocenes **4** and **5**with MAO in the presence of H_2 (D_2), and they showed that the stereoregulation of polymerization in these systems arose from the asymmetric addition of monomers to the propagating chain. Asymmetric synthesis radical oligomerization (telomerization) was recently reported by Porter and co-workers; acryl amides with optically active auxiliary **6a-d** gave oligomers with preferentially one-handed chirality of the main chain.[37–39] This work was extended to stereoregular radical polymerization of **6b-d** affording isotactic polymers (mm ~92%).[40] Hogen-Esch and co-workers have demonstrated the asymmetric oligomerization of vinyl phenyl sulfoxide.[41]



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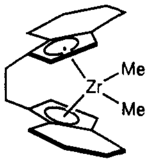

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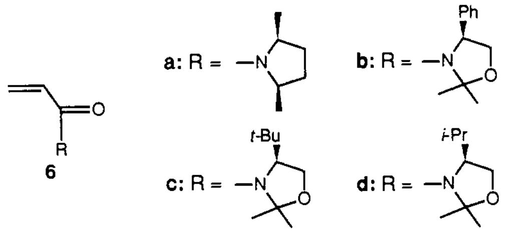
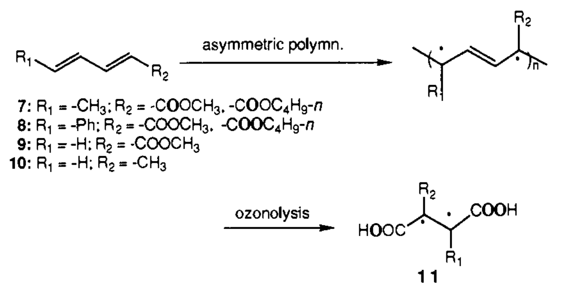


Scheme 2



7: R_1 = $-CH_3$; R_2 = $-COOCH_3$, $-COOC_4H_9$-*n*
8: R_1 = -Ph; R_2 = $-COOCH_3$, $-COOC_4H_9$-*n*
9: R_1 = -H; R_2 = $-COOCH_3$
10: R_1 = -H; R_2 = $-CH_3$

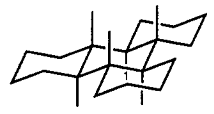
11

Apart from the stereotactic polymers, Green and Garetz presented a unique consideration of the chirality of an atactic polymer produced under achiral conditions.[42] They showed that an atactic polymer sample cannot be a racemic mixture when the degree of polymerization (DP) is 70 or larger. This is because the number of possible diastereomers is far larger than that of the polymer chains and the existence of both antipodes of the enantiomer is impossible. However, optical activity is actually not observed by compensation of optical activities of different diastereomers.

B. Dienes

Natta, Farina, and co-workers presented the first successful examples of asymmetric polymerization of conjugated 1,3-diene monomers (Scheme 2).[6,43–47] They polymerized sorbates (**7**), β-styrylacrylates (**8**), and methyl 1,3-butadiene-1-carboxylate (**9**) by ((+)-2-methylbutyl)lithium and butyllithium/(−)-menthyl ethyl ether initiator systems,[43–45] and 1,3-pentadiene (**10**) in the presence of $AlEt_3/Ti((-)\text{-menthoxy})_4$, $Ti(OC_4H_9)_4/Al((+)\text{-2-methylbutyl})_3$, and $VCl_3/Al((+)\text{-2-methylbutyl})_3-Et_2O$ catalysts[46,47] to obtain optically active polymers. They demonstrated that the polymer's optical activity is based on main-chain chirality by ozonolyzing the polymers to give an optically active diacid, **11**; optical purity of the resulting acid obtained from the polymers of **7** and **8** is reported to be 0.4–6% (Scheme 2).[6] Afterward, the relationship between the structure of the catalyst consisting of titanium and aluminum used for 1,3-pentadiene polymerization and asymmetric inductivity was reexamined by Zambelli and co-workers.[48] This type of polymerization of achiral 1,3-diene monomers has also been done by other researchers.[49–51] Asymmetric induction to main-chain chiral centers has also been observed in the radical polymerization of sorbates having an optically active ester group[52,53] and 1,3-butadiene-1-carboxylic acid complexed with optically active amines.[54–56]

Asymmetric synthesis polymerization of 1,3-dienes with solid matrices has been reported.[57,58] This was first attained by Farina and co-workers: they obtained an optically active polymer with isotactic *trans*-**10** by γ-ray irradiation polymerization of *trans*-1,3-pentadiene included in an optically active (*R*)-(−)-*trans-anti-trans-anti-trans*-perhydrotriphenylene (**12**) matrix.[59,60] Deoxyapocholic[61,62] and apocholic[63,64] acids (**13** and **14**) are also effective as an optically active matrix. The matrix crystals possess a chiral channel inside, and polymerization of the monomer included in the channel occurs in the chiral spatial environment. These inclusion polymerizations produced polymers with rather higher optical purity than the catalytic and radical



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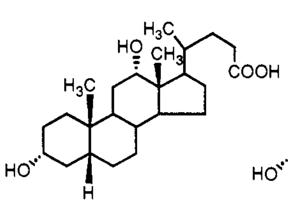
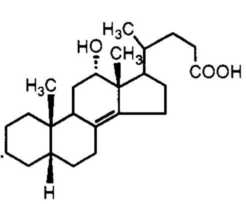


13

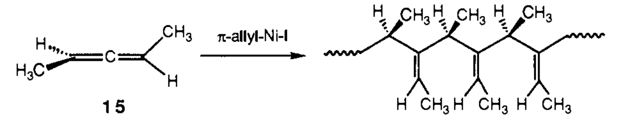


14

polymerization described above; the highest value of optical purity so far reported is 36% for the polymerization of (*Z*)-2-methyl-1,3-butadiene with **14** as a matrix.[64]

Asymmetric synthesis polymerization is known also for an allene monomer. (*R*)-2,3-Pentadiene (**15**) gives an optically active polymer with a unique structure (Scheme 3).[65] The polymer is obtained by polymerization with π-allylnickel iodide, and four triad sequences are possible for the polymer, among which only one **16** is chiral.

Scheme 3

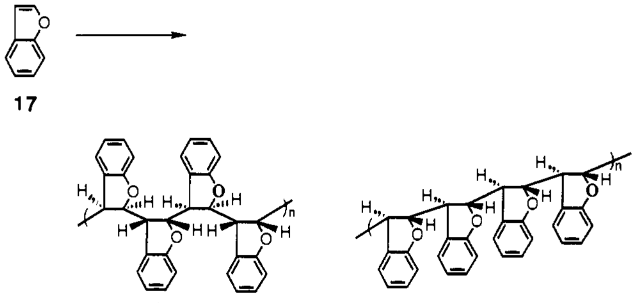


15 **16**

C. Cyclic Olefins

The first asymmetric synthesis homopolymerization of a cyclic olefin was realized for benzofuran (**17**) by Natta, Farina, and co-workers (Scheme 4).[6,66–68] The polymerization was carried out with $AlEtCl_2$ or $AlCl_3$ in the presence of optically active cocatalysts such as β-phenylalanine and 10-camphorsulfonic acid; the polymer is considered to possess the chiral erythro- or threodiisotactic structure (**18a** or **18b**).[67,68] Fueno, Furukawa, and co-workers also obtained optically active poly-**17** with a binary initiator system of $AlCl_3$/(−)-menthoxytriethyltin, -germanium, or -silicon.[69,70]

Scheme 4



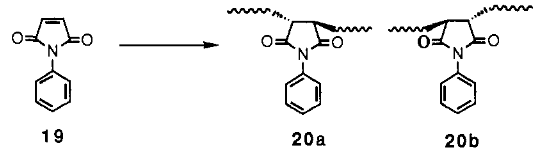
17

erythrodiisotactic
18a

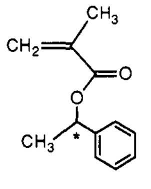
threodiisotactic
18b

N-Phenylmaleimide (**19**), a monomer with a C_2 axis of symmetry, also gave an optically active homopolymer.[71,72] In contrast to the polymer from a monomer without a C_2 axis of symmetry such as **17**, in which all the asymmetric centers in the main chain are true chiral centers, poly-**19** can be optically active only if the main chain has in excess one of two enantiomeric *trans* structures, **20a** and **20b** (Scheme 5).

Scheme 5



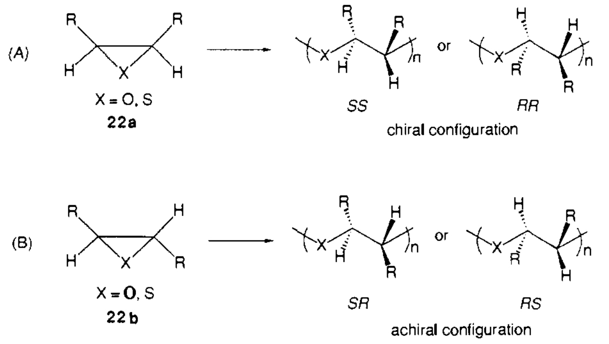
Various types of copolymers of cyclic olefins and other monomers have been prepared by asymmetric synthesis polymerizations using monomers with optically active side groups,[73-79] optically active additives,[80-83] catalysts,[84,85] or solvents.[86-88] Among those, the synthesis of a copolymer of maleic anhydride and (*S*)-(−)-α-methylbenzyl methacrylate (MBMA, **21**)by Beredjick and Schuerch is the first example of preparation of an optically active polymer consisting of a C–C backbone with chiral induction to the main chain.[73]



MBMA, 21

Cyclic monomers with the structure **22a** give optically active polymers by ring-opening polymerization with optically active chiral initiators (Scheme 6, part A).

Scheme 6

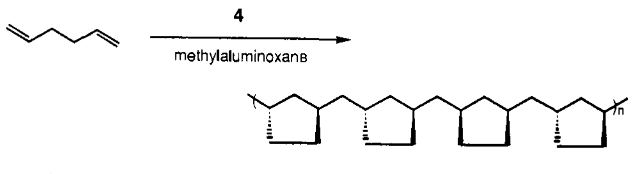


Because inversion of one of the asymmetric centers occurs during the ring-opening process, the obtained polymer possesses the monomeric units of chiral *RR* or *SS* configuration. Asymmetric polymerization of *cis*-2-butene oxide and sulfide, and cyclohexene oxide and sulfide with chiral initiators based on $ZnEt_2$ or $CdEt_2$ has been reported by Spassky and co-workers; the sulfide monomers generally gave polymers with higher optical activity.[89] In contrast, chiral monomers with *trans* structure **22b** give polymers with monomeric units of *RS* or *SR* configuration which are achiral (Scheme 6, part B). As an example, polymerization of *trans*-2-butene sulfide with $ZnEt_2$/(*R*)-(−)-$(CH_3)_3CCH(OH)$-CH_2OH as an initiator afforded an optically inactive polymer, although this polymerization process was enantiomer selective where the unreacted monomer was rich in one antipode.[90]

D. Cyclopolymerization

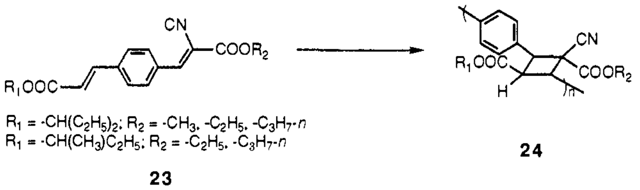
Recently, Coates and Waymouth reported a novel asymmetric synthesis cyclopolymerization of 1,5-pentadiene with an optically active metalocene catalyst (Scheme 7).[91] The polymer obtained by (*S*)-ethylenebis(tetrahydroindenyl)zirconium (*S*)-binaphtholate ($[\alpha]^{28}_{435}$ + 1848°) (**4**) in the presence of methylaluminoxane (MAO) showed molecular rotation $[\phi]^{28}_{405}$ −49.3°, and ^{13}C NMR analysis showed that the polymer had ca. 68% *trans* structure.

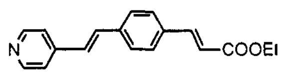
Scheme 7



Addadi, Lahav, and co-workers succeeded in asymmetric photopolymerization of the prochiral monomers **23** in the crystalline state (Scheme 8).[92-96] The monomers form enantiomorphic crystals. One of the enantiomorphic crystals can be preferentially formed by recrystallization with a trace amount of optically active compounds; photoirradiation of the obtained crystal allows asymmetric synthesis polymerization affording polymers with cyclobutane moiety in the backbone (**24**). A similar polymerization of a cinnamic acid derivative **25** has been reported.[97]

Scheme 8





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III. Helix-Sense-Selective Polymerization

A. Methacrylates

We have been investigating the atropogenic polymerization of methacrylates and found that several bulky methacrylates afford highly isotactic, optically active polymers with one-handed helical conformation by asymmetric anionic polymerization and that some of the obtained polymers undergo stereomutation. The one-handed helical conformation of the polymers is maintained by sterical repulsion between the bulky ester groups. The stereochemistry of polymerization, the stereostructure of the obtained polymer, and the conformational transition sensitively depend on the structure of the ester group.

1. Triphenylmethyl Methacrylates and Its Analogues

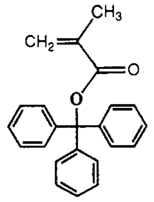
Triphenylmethyl methacrylate (TrMA, **26**) gives a highly isotactic, optically active polymer with one-

Table 1. Asymmetric Polymerization of TrMA with (–)-Sp-, (+)-DDB, (+)-PMP-FlLi Complexes in Toluene at –78 °C (Reprinted from Ref 102. Copyright 1992 American Chemical Society)[a]

			B/H[b]-insoluble part						
initiator	time (h)	yield[c] (%)	yield (%)	$[\alpha]^{25}_{D}$[d] (deg)	$[\theta]$[e] $\times 10^{-4}$ (235 nm)	$[\theta]$[e] $\times 10^{-5}$ (210 nm)	DP[f]	M_w/M_n[f]	tacticity[g] (%) mm
(i)-Sp-FlLi	24	99	82	+383	+9.42	+2.32	60	1.31	>99[h]
(+)-DDB-FlLi	24	100	93	+344	+8.45	+1.86	47	1.10	>99[h]
(+)-PMP-FlLi	3	100	94	+334	+7.78	+1.76	39	1.12	>99[h]

[a] Conditions: TrMA 1.0 g; toluene 20 mL/; [TrMA]/[Li] = 20. [b] A mixture of benzene and hexane (1/1, v/v). [c] CH_3OH = insoluble part. [d] $c = 0.5$ (tetrahydrofuran). [e] CD spectrum was measured in tetrahydrofuran at ca. 25 °C. Units: $cm^2\ dmol^{-1}$. [f] Determined by GPC of poly(MMA) derived from poly(TrMA). [g] Determined by ^1H NMR of poly(MMA) derived from poly(TrMA). [h] The signals due to the racemo sequence were found only in the termination end.

handed helical structure by anionic polymerization with optically active initiators at low temperature.[98-106] This



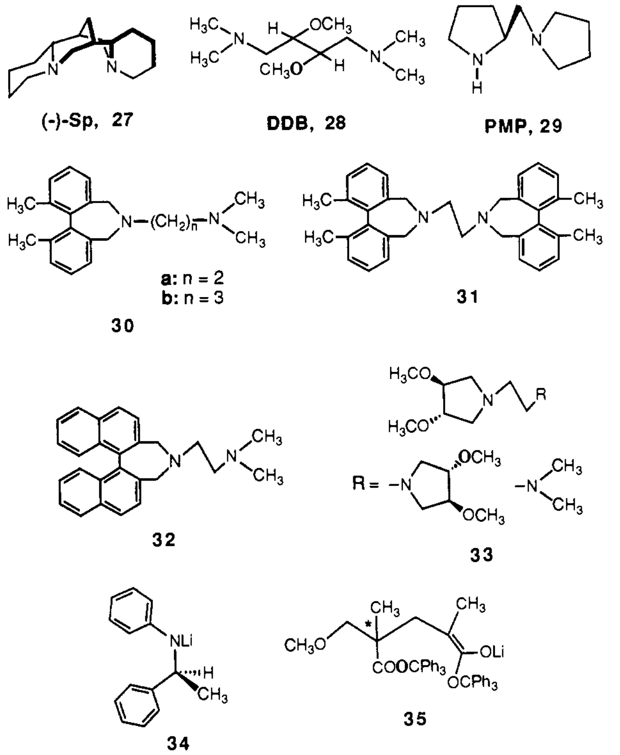
TrMA, 26

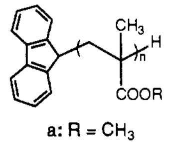
polymer is the first example of an optically active vinyl polymer whose chirality arises exclusively from its helical conformation of the main chain. The optical activity is lost when the polymer is converted into the methyl ester, indicating that the helical conformation is maintained by sterical repulsion of bulky trityl groups.

The polymer is obtainable by polymerization with the complexes of achiral organolithiums with optically active ligands or optically active organolithiums. (–)-Sparteine ((–)-Sp, **27**),[98,99,101,1,02,106] (*S*,*S*)-(+)- and (*R*,*R*)-(–)-2,3-dimethoxy-1,4-bis(dimethylamino)butanes ((+)- and (-)-DDB, **28**),[100,102] (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine ((+)-PMP, **29**),[102] and the ligands bearing a biphenyl or binaphthyl moiety **30a**,**b** and **31**–**33**[103-105] (Chart 1) are effective for the complexes with achiral organolithiums, and a lithium amide **34**[98,99] and a lithium enolate having the structure of a TrMA-dimer anion (**35**)[107] can directly afford optically active poly(TrMA) without a chiral ligand. Table 1 shows the results of polymerizations with the complexes of 9-fluorenyllithium (FlLi) with (–)-Sp, (+)-DDB, and (+)-PMP.[102] In all cases, the obtained polymers showed high optical activity and they possessed almost perfectly isotactic configuration of the main chain, indicating that these polymers have a one-handed helical structure. Optical activity seems to increase with DP. Chromatographic optical resolution of mixture of right- and left-handed helical poly(TrMA)s ($[\alpha]^{25}_{D}$ –82°) prepared with **34** in tetrahydrofuran gave a fraction of high optical activity ($[\alpha]^{25}_{D}$ –365°) which is considered to contain pure one-handed helical polymer.[108] One-handed helical poly(TrMA) shows high optical activity also in the solid state.[109] Copolymerization of TrMA with (*S*)-(–)-MBMA also gives an optically active polymer which contains isotactic TrMA sequences with helical conformation.[110,111]

We have investigated the stereochemical mechanism of TrMA polymerization in detail.[101,102] In the asymmetric polymerization of TrMA, a small amount of oligomers with low optical activity is produced in addition to the highly optically active polymer. It had been assumed that oligomer anions with certain specific stereostructure might predominantly add monomers to give a polymer and the others might remain as oligomers until the completion of polymerization.[99] In order to obtain information on this point, we carried out the asymmetric oligomerization of TrMA with the complexes of FlLi with (–)-Sp, (+)-DDB, and (+)-PMP and made a detailed analysis mainly on oligo(MMA)s (**36a**) derived from the original oligo(TrMA) (**36b**) obtained by the reaction. The polymers obtained with

Chart 1





a: R = CH_3
b: R = $-CPh_3$
36

these initiators seem to possess the helical conformation of the same screw sense, because they show the optical rotation and circular dichroism absorption of the same positive sign (Table 1). Figures 4–6 show the GPC curves of oligo(MMA)s derived from oligo(TrMA)s obtained from the oligomerizations at several [TrMA]/[Li] ratios with methanol as a terminating reagent. The

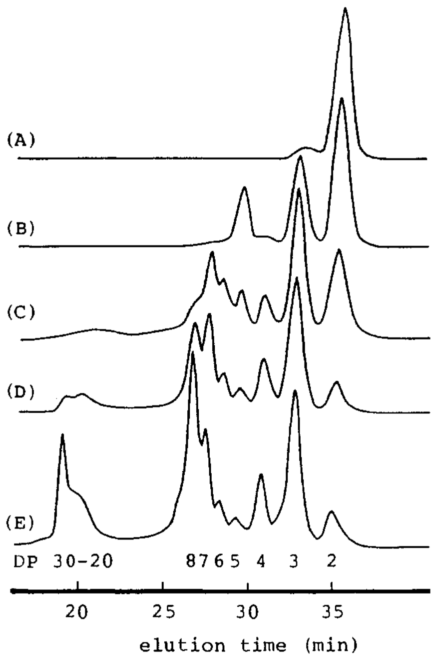


Figure 4. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with (–)-Sp-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E) in toluene at –78 °C. (Reprinted from ref 102. Copyright 1992 American Chemical Society.)

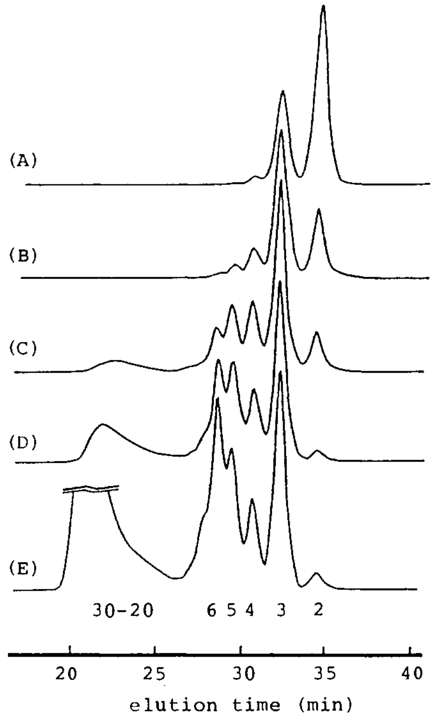


Figure 5. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with (+)-DDB-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E) in toluene at –78 °C. (Reprinted from ref 102. Copyright 1992 American Chemical Society.)

curves show some characteristic features: (1) almost no unimer (DP = 1) is observed in all cases (this was the case even in the equimolar reaction of TrMA and (–)-Sp-FlLi), (2) a small amount of polymer exists in addition to the oligomers of DP = 2–8 in the (–)-Sp system and DP = 2–6 in the other two systems, and the content of the intermediate oligomers is unnaturally low at [TrMA]/[Li] ≥ 5, and (3) the distributions of the oligomers of DP = 2–8 in the (–)-Sp system and

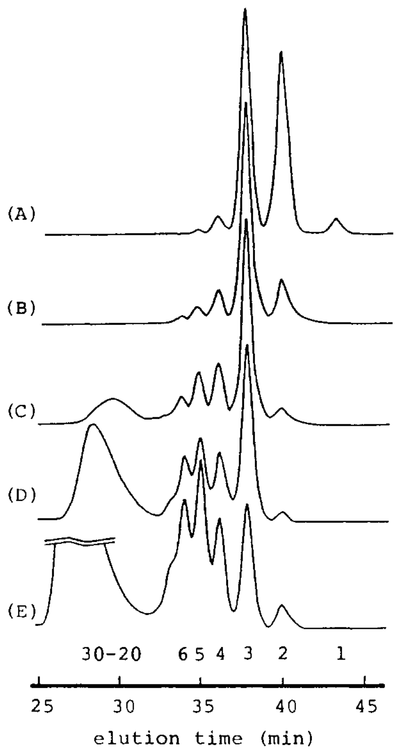


Figure 6. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with (+)-PMP-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E) in toluene at –78 °C. (Reprinted from ref 102; copyright 1992 American Chemical Society.)

those of the oligomers of DP = 2–6 in the other two systems are apparently irregular (e.g., a relatively low content of tetramer in the reactions at higher [TrMA]/[Li] ratios). From these observations, we concluded the following: (1) the unimer anion is much more active than the initiator complex and dimer anion; (2) a stable helix starts at DP ≈ 9 in the (–)-Sp system and at DP ≈ 7 in the other systems and acceleration of the reaction occurs at these DPs; and (3) one turn of helix is formed with three or four monomeric units. The last is supported by the results of the molecular mechanics calculation of conformation for isotactic poly(TrMA) by Vacatello and co-workers.[112] Wulff and co-workers also obtained similar results for the (–)-Sp–1,1-diphenylhexyllithium initiator system.[106]

The oligomers of DP = 2–8 obtained in the (–)-Sp system and those of DP = 2–6 in the other two systems were separated into diastereomers by HPLC (Figure 7) and the structure was assigned by NMR and X-ray crystal structure analyses.[113] In all systems, the oligomers of DP ≥ 5 contained mainly isotactic isomers, indicating that the predominantly propagating oligomers are isotactic. The diastereomers were further separated into enantiomers by HPLC optical resolution in order to obtain further information on propagation stereochemistry. The absolute configuration of the dimer was determined by synthesizing an optically active MMA dimer **37** from (*R*,*R*)-(–)-2,4-dimethylglutaric acid (**38**, Scheme 9) and that of the higher oligomers was reasonably deduced. The content of isomers in the dimer and trimer remarkably changed depending on the [TrMA]/[Li] ratio in some cases, or it remained almost unchanged with a slight deviation in other cases, and the isotactic oligomers of DP ≥ 5 consisted of almost pure antipodes of enantiomers, in most cases, whose

Table 2. Ratios of Optical Isomers of Isotactic Oligo(MMA)s Derived from Oligo(TrMA)s Obtained with (−)-Sp-, (+)-DDB-, and (+)-PMP-FlLi (Reprinted from Ref 102. Copyright 1992 American Chemical Society)[a]

		pentamer		hexamer		heptamer		octamer	
initiator	[TrMA]/[Li]	mmmm *RRRRR*/*SSSSS*	mmmr *RRRRS*/*SSSSR*	mmmmm *RRRRRR*/*SSSSSS*	mmmmr *RRRRRS*/*SSSSSR*	mmmmmm *RRRRRRR*/*SSSSSSS*	mmmmmr *RRRRRRS*/*SSSSSSR*	mmmmmmm *RRRRRRRR*/*SSSSSSSS*	mmmmmmr *RRRRRRRS*/*SSSSSSSR*
(−)-Sp-FlLi	3	~100/~0	~100/~0	~100/~0	98/2	~100/~0	~100/~0	*b*	*b*
	5	95/5	85/15	97/3	54/46	~100/~0	97/3	~100/~0	~100/~0
(+)-DDB-FlLi	3	2/98	2/98	3/97	1/99	10/90	9/91	*b*	*b*
	5	3/79	7/93	1/99	2/98	1/99	~0/~100	*b*	*b*
(+)-PMP-FlLi	3	~0/~100	18/82	~0/~100	13/87	*b*	*b*	*b*	*b*
	5	~0/~100	10/90	~0/~100	5/95	*b*	*b*	*b*	*b*

[a] Determined by HPLC optical resolution of the diastereomers with UV detection at 254 nm. [b] Not obviously detected in the separation of diastereomers (see Figure 7).

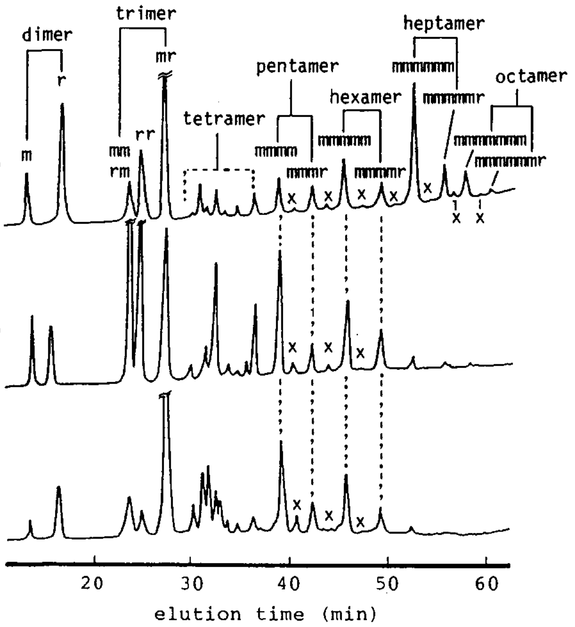
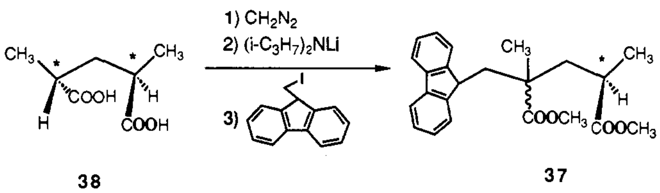


Figure 7. Chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with (−)-Sp-FlLi (A), (+)-DDB-FlLi (B), and (+)-PMP-FlLi (C) at [TrMA]/[Li] = 5 in toluene at −78 °C (ref 102); m and r mean meso and racemo diad sequences, respectively. (Reprinted from ref 102. Copyright 1992 American Chemical Society.)

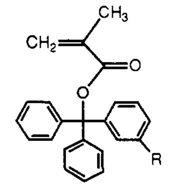
Scheme 9



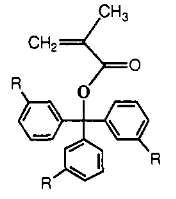
absolute configuration was *R* in the (−)-Sp system and *S* in the other two systems (Table 2). On the basis of these findings, it was concluded that oligomer anions with an *R* main-chain configuration in the (−)-Sp system and those with *S* configuration in the systems with (+)-DDB and (+)-PMP predominantly propagate to give optically active helical polymers respectively with -*RRR*- and -*SSS*- configuration, though the polymers possess the same screw sense. The prevailing helix sense is not governed by the main-chain configuration but mainly by the chirality of the ligands of initiator complexes during the polymerization process.

The side-group conformation (propeller structure) has been investigated in terms of Raman spectroscopy.[114] Thermal- and radiation-induced degradation[115] and hydrolysis of the ester group[116] of poly(TrMA) have been studied. The isotactic poly(MMA) with the uniform main-chain configuration obtained from optically active poly(TrMA) forms an optically active stereocomplex with syndiotactic poly(MMA).[117]

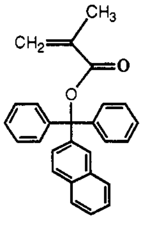
Chart 2



39 a: R = -F b: R = -Cl



40 a: R = -CH$_3$ b: R = -Cl



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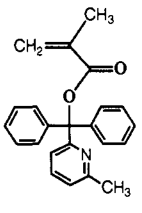

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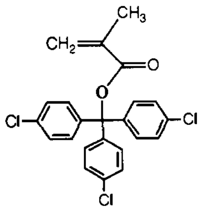

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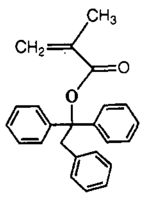

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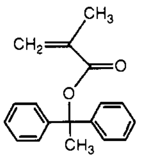

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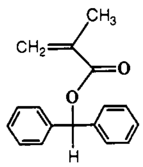

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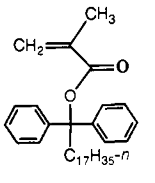

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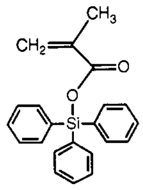
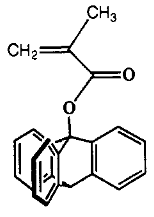


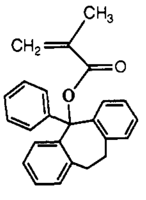
48

Optically active polymers with helical conformation have been obtained from the analogous methacrylates **39a,b**, **40a,b**,[118] **41**,[119] and **42**[120] although not from **43**,[118] **44**,[121] **45**,[12] **46**,[12] **47**,[121] and **48**[12] (Chart 2). **43** did not give a polymer under conditions similar to those applied for TrMA polymerization; the ester group of this monomer may be too bulky to give a high polymer. The ester groups of **45**–**47** do not seem to have enough bulkiness. In the case of **48**, the O–Si and C–Si bonds may be too long and the ester group is too flexible to form a rigid helix. This monomer gave a syndiotactic polymer. Polymerization of 9-triptycenyl methacrylate (**49**) was carried out by Matsuda and co-workers with (−)-Sp- and (+)-DDB-BuLi complexes but the obtained polymer showed only low optical activity ([α]D −5°).[122]



49

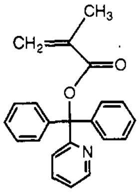
Recently, 1-phenyldibenzosuberyl methacrylate (**50**) was synthesized and polymerized. This monomer gave a one-handed helical, highly isotactic polymer by anionic polymerization with optically active initiators.[123] Noteworthy, **50** produced a highly isotactic polymer (mm > 98%) by radical polymerization in toluene at 40 °C.[124] Although TrMA also gives an isotactic polymer by radical polymerization, the degree of isotacticity is ca. 65%.[125] The high stereoregulation in the radical polymerization of **50** seems to be based on the rigid structure of the ester group.



PDBSMA, 50

2. Diphenyl-2- and -4-pyridylmethyl Methacrylates

Diphenyl-2-pyridylmethyl methacrylate (D2PyMA, **51**) also affords an optically active polymer.[126-131]



D2PyMA, 51

However, the polymers obtained by the (−)-Sp and DDB initiator systems showed much lower optical rotation ($[\alpha]^{25}_{365}$ −153° (initiator (−)-Sp-FlLi), +132° (initiator (+)-DDB-FlLi)) than one-handed helical poly(TrMA) ($[\alpha]^{25}_{D}$ 350°, $[\alpha]^{25}_{365}$ 1400°); the polymers were mixtures of right- and left-handed helices. Although the optically active ligands **52**–**70** have been synthesized and used for D2PyMA polymerization by our group, most of them were ineffective in obtaining a one-handed helical polymer. Table 3 shows the optical rotation of the polymers obtained with the complexes of **52**–**70** and (*N*,*N*′-diphenylethylenediamine)monolithium (DPEDA-Li, **71**) (Chart 3). The values of optical rotation of the polymer were rather low in all cases. Among the various chiral ligands, only PMP gave a highly isotactic (mm > 98%) polymer with a narrow molecular weight distribution showing high positive rotation (Table 4).[130,131] Figure 8 shows the GPC curves of the obtained poly(D2PyMA) (DP = 27, 45, 81). The curves by UV detection correspond well to those by polarimetric detection, indicating that the products consist uniformly of (+)-polymer of almost the same degree of optical activity. The polymodal curves for the polymers of DP = 45 and 81 in spite of the polymers' narrow molecular weight distributions have been attributed to the existence of aggregates of the polymers, which was confirmed by vapor-pressure osmometric measurement.[131] Interestingly, the results of polymerization with the **68** complex were quite in contrast to the those with (+)-PMP complexes. Although (+)-PMP and **68**

Table 3. Polymerization of D2PyMA with the Complexes of 52–70 with DPEDA-Li in Toluene at −78 °C[a]

ligand	yield (%)	$[\alpha]^{25}_{365}$ (deg)	ligand	yield (%)	$[\alpha]^{25}_{365}$ (deg)
52	100	−661	**62**	100	−100
53	99	−457	**63**	96	−100
54	100	−1108	**64**	99	+53
55	100	−1170	**65**	86	+228
56	100	−32	**66**	95	−657
57	100	+202	**67**	98	−221
58	99	−105	**68**	100	−212
59	100	−21	**69**[b]	3.5	+14
60	100	473	**70**	96	−324
61	93	+1012			

[a] Conditions: D2PyMA 1.0 g, toluene 20 mL, [D2PyMA]/[Li] = 20. Data from ref 131. [b] Used as *O*-lithiated form.

Table 4. Asymmetric Polymerization of D2PyMA with the Complexes of (+)-PMP with DPEDA-Li and FlLi in Toluene at −78 °C[a]

RLi	[D2PyMA]/[Li]	$[\alpha]^{25}_{365}$[b] (deg)	DP[c]	M_w/M_n[c]
DPEDA-Li	15	+1325	27	1.04
DPEDA-Li	20	+1406	30	1.08
DPEDA-Li	30	+1651	45	1.13
DPEDA-Li	50	+1675[d]	81	1.12
FlLi	15	+1530	30	1.14
FlLi	30	+1641	60	1.10

[a] Conditions: D2PyMA 1.0 g; toluene 20 mL. The polymer yield was almost quantitative in all cases. Data from ref 131. [b] Measured in a mixture of $CHCl_3$ and 2,2,2-trifluoroethanol (9/1, v/v). [c] Determined by GPC of poly(MMA) derived from poly(D2PyMA). [d] $[\alpha]^{25}_{D}$ + 414°.

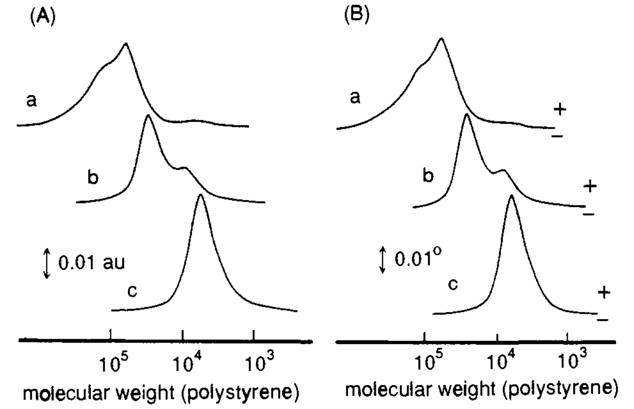
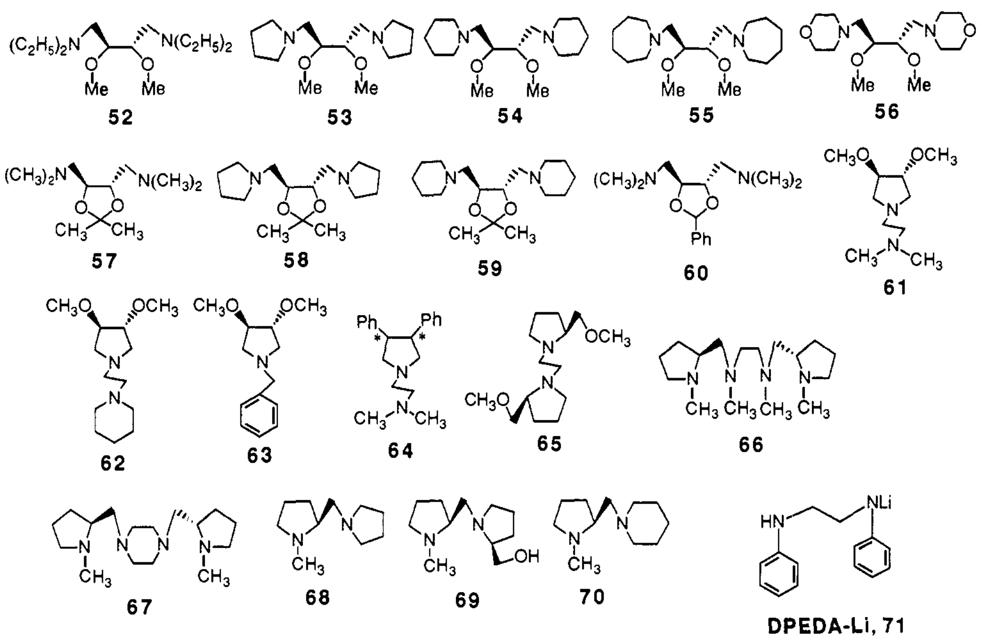
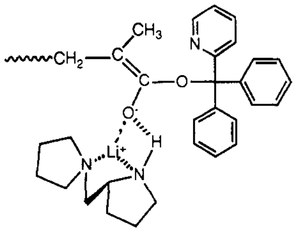


Figure 8. GPC curves measured by a UV (254 nm) detector (A) and a polarimetric (Hg) detector (B) of poly(D2PyMA) prepared with (+)-PMP-DPEDA-Li in toluene at −78 °C: DP = 81 (a), 45 (b), and 30 (c). Data from ref 131.

Chart 3



Scheme 10



with the same absolute-configuration differ only in the substituent on the nitrogen atom, FlLi and DPEDA-Li complexes with **68** gave a polymer of lower negative optical activity ($[\alpha]_{365}$ −677 and −212°, respectively). The smaller substituent (hydrogen) on the nitrogen atom of (+)-PMP may make the ligand coordination to Li cation tighter, and the closer coordination may result in strict control of polymerization stereochemistry (Scheme 10). The complexes of (*S*)-**30a** also gave an almost one-handed helical poly(D2PyMA) ($[\alpha]^{25}_{D}$ +340°).[105]

The one-handed helical poly(D2PyMA) obtained with PMP complexes showed remarkable mutarotation due to the conformational change (helix–helix transition).[132] Figure 9 shows the change in optical activity of the polymers of DP = 27–81 in chloroform solution; the optical activity of the polymers decreased with time and the final values depended on DP. The polymer of DP = 30 which had undergone the mutarotation was chromatographically separated into fractions showing high positive and negative rotations (Figure 10: fraction a $[\alpha]^{25}_{365}$ −532°, c $[\alpha]^{25}_{365}$ +1138°), and the CD spectral patterns of these fractions were similar to those of poly(D2PyMA)s of high optical rotation. In addition, the ^{1}H NMR spectral pattern of the polymer did not show a clear change during the mutarotation. These results indicate that the decrease in the optical rotation shown in Figure 9 is not ascribed to helix–coil transition (distortion of the helix) but to helix–helix transition of the main chain changing the one-handed helix to a mixture of right- and left-handed helices. This is the first example of such a transition of a vinyl polymer. The right- and left-handed helices are not complete enantiomers because of the chiral centers in the vicinity of chain ends. This seems to result in an unbalance of the contents of the helices. The rather higher conformational stability of the polymers of DP = 45 and 81 (Figure 9) may be ascribed to the formation of aggregates of the polymer chain.

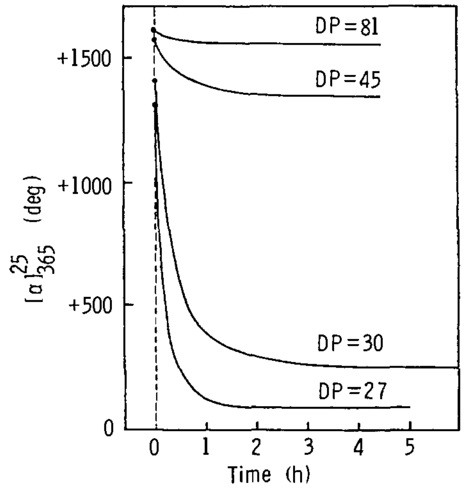
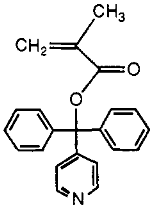


Figure 9. Change of optical rotation of poly(D2PyMA)s of DP = 27, 30, 45, and 81 in $CHCl_3$ at 60 °C. (Reprinted from ref 132. Copyright 1989 American Chemical Society.)

Diphenyl-4-pyridylmethyl methacrylate (D4PyMA, **72**) affords highly isotactic, optically active polymers



D4PyMA, 72

by polymerization with (−)-Sp-BuLi and (+)-DDB-

Table 5. Enantiomer-Selective Polymerization of Racemic PPyoTMA with Preformed Living Poly- and Oligo[(+)-PPyoTMA] Anions in Toluene at −78 °C

poly[(+)-PPyoTMA] anion					
initiator	DP[b]	time (h)	conversion of (±)-PPyoTMA (%)	ee of polymer (%)	ee of unreacted monomer (%) (α)[c]
(+)-DDB-FlLi	30	5.0	12.8	100	14.7 (−)
(+)-DDB-FlLi	30	5.0	16.6	100	20.0 (−)
(+)-DDB-FlLi	30	16.5	59.2	42.8	62.3 (−)
(+)-DDB-FlLi	1–5	1.5	30.1	37.8	16.3 (−)
TMEDA-BzLi	40	8.5	24.9	40.0	13.3 (−)
TMEDA-BzLi	40	26	9.5	31.7	46.6 (−)

[a] Conditions: monomer/toluene = 1/20 gmL^{-1}; [(±)-PPyoTMA]/[Li] = 40. Data from ref 134. [b] Determined by GPC of poly(MMA) derived from a part of the poly [(+)-PPyoTMA]. [c] Sign of optical rotation of unreacted monomer.

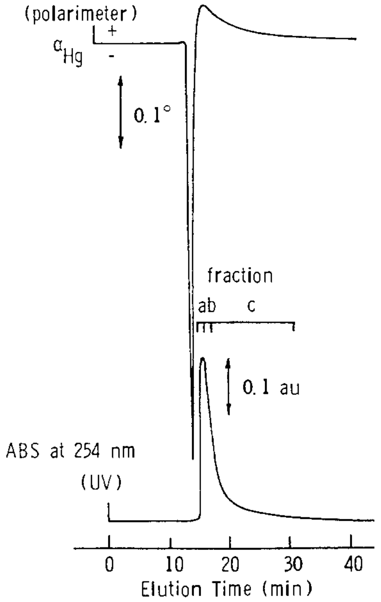
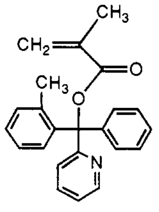


Figure 10. Chromatograms of optical resolution of poly(D2PyMA) (DP = 30, $[\alpha]^{25}_{365}$ +389°) on a (+)-poly(TrMA) column. UV (1.0-mm cell) and polarimetric (5 × 0.2 (i.d.) cm cell) detectors were connected in series (column, 50 × 0.72 (i.d.) cm; eluent $CHCl_3$; flow rate, 1.0 mL min^{-1}; temperature, 15 °C; amount of sample, 4 mg). (Reprinted from ref 132. Copyright 1989 American Chemical Society.)

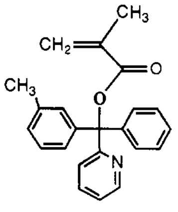
DPEDA-Li complexes.[126,128] Although the optical activity of the polymers was rather low ($[\alpha]^{25}_{546}$ −40° ((−)-Sp-BuLi system), +14° ((+)-DDB-DPEDA-Li system)), the contents of the prevailing helix in these polymers seem to be similar to that of optically active poly(TrMA), because the intensity of the CD spectra of the polymers was comparable to that of one-handed helical poly(TrMA).

3. Phenyl-2-pyridyl-o- and -m-tolylmethyl Methacrylates

In the polymerization of phenyl-2-pyridyl-*o*- and -*m*-tolylmethyl methacrylate (PPyoTMA, **73** and PPymTMA, **74**) having a chiral ester group, enantiomer selectivity as well as helix-sense selectivity is of interest.



PPyoTMA, 73



PPymTMA, 74

Racemic (±)-PPyoTMA gives highly optically active, one-handed helical polymers by polymerization with (−)-DDB-FlLi complex, and a high enantiomer selectivity was observed in the polymerization.[133] The enantiomer selectivity was rather low in the initial stage of polymerization and increased as polymerization proceeded, because the enantiomer selection is governed by the helical structure of the growing polymer anion. this was evidenced by the enantiomer-selective polymerization of the racemic monomer with preformed polymer and oligomer anions of (+)-PPyoTMA (Table 5).[134] In the reaction initiated by the polymer anion of DP = 30 having helical conformation prepared with (+)-DDB-FlLi, the ee of the monomer incorporated into the polymer was 100% at 12.8% and 16.8% conversions, while in the reaction with the oligomer anion of DP = 1–5, whose main chain is not long enough to take helical conformation, the enantiomer selectivity was much lower. Furthermore, enantimer-selective polymerization was also achieved when a polymer anion prepared with achiral *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)-*n*-BuLi complex.

In the polymerization of optically active (+)-PPyoTMA, the polymerization systems at −78 °C showed high positive rotation, and this slowly changed into a large negative one at −20 °C or a higher temperature regardless of the chirality of initiator.[135] Although this mutarotation has been ascribed to a conformational change in the side group, the helix–helix transition of the main chain similar to that observed for poly(D2PyMA) can possibly result in such a change in optical rotation.

The results of polymerization of PPymTMA are shown in Table 6. In the polymerization of (±)-PPymTMA[136] with (+)-PMP-DPEDA-Li, one-handed helical polymers were obtained; the optical activities were comparable to those of helical poly(TrMA) and poly(D2PyMA) with single-screw sense. However, almost no enantiomer selectivity was observed in this polymerization.[136] The optically active poly[(±)-PPymTMA] underwent a helix–helix transition similarly to poly(D2PyMA) and its optical activity decreased in solution.[136] The optically active (±)-PPmyTMA also gave optically active polymers by polymerizations with (+)-PMP-FlLi, (+)- and (−)-DDB-DPEDA-Li, and TMEDA-DPEDA-Li complexes, and the optical activity of the polymers depended on the initiator in contrast to the polymerization of PPyoTMA.[137] This indicates that the helix sense is controlled by the chirality of the ligand during the polymerization

Table 6. Polymerization of (±)- and (+)-PPymTMA in Toluene at -78 °C[a]

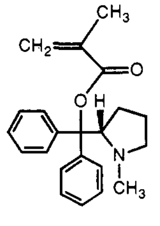
monomer	initiator	[PPymTMA]/[Li]	DP[b]	$[\alpha]^{25}_{365}$ (deg)		ref
				c	d	
(±)-PPymTMA	(+)-PMP-DPEDA-Li	20	39	+1417	+214	136
(±)-PPymTMA	(+)-DPEDA-Li	30	60	+1629	+1124	136
(+)-PPymTMA	(+)-PMP-FlLi	15	24	+1456	+1450	137
(+)-PPymTMA	(+)-DDB-DPEDA-Li	20	55	+1125	+1646	137
(+)-PPymTMA	TMEDA-DPEDA-Li	20	30	+262	+1370	137
(+)-PPymTMA	(-)-DDB-DPEDAhLi	20	49	-845	+1481	137

[a] Conditions: monomer/toluene 1/20 gmL^{-1}; time 3-21 h. The polymer yield was almost quantitative in all cases. [b] Determined by GPC of poly(MMA) derived from poly(PPymTMA). [c] Specific rotation of polymers immediately after being dissolved in $CHCl_3$. [d] Specific rotation of polymers after heat treatment at 60 °C.

reaction. The optical activity of poly[(+)-PPymTMA]s obtained with (+)- and (−)-DDB and TMEDA moved in a positive direction while that of the polymer obtained with (+)-PMP-DPEDA-Li did not show a significant change. The final values in the changes were comparable with that of the polymer obtained with (+)-PMP. The helicity of these polymers seems to have changed into the same one showing positive rotation by the influence of the chirality of the ester group through a helix–helix transition.

4. (S)-Diphenyl(1-methylpyrrolidin-2-yl)methyl Methacrylate

The optically active, helical polymer obtained from (*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate (DMPMA, 75) shows reversible helix–helix transition depending on the properties of the solvent.[138]



DMPMA, 75

The highly isotactic poly(DMPMA)s obtained by polymerization with the complexes of DPEDA-Li with (+)- and (−)-DDB, (+)-PMP, and TMEDA showed high positive rotation ($[\alpha]^{25}_{365}$ + 786 to +939°) in methanol–20% (v/v) CH_3SO_3H regardless of the chirality of ligands, indicating that the screw sense of the polymer is governed by the chirality of the monomer. The polymers were insoluble in common organic solvents such as chloroform and tetrahydrofuran but soluble in polar solvents such as methanol and water containing acid. The optical activity of the polymers changed slightly in the positive direction and reached a positive constant value in methanol–20% CH_3SO_3H, while it changed in the negative direction in solution containing a much smaller amount of acid. Figure 11 shows the change in optical activity of poly(DMPMA) of DP = 37 (tacticity mm ~99%) in methanol containing CH_3SO_3H. The polymer showed positive rotation ($[\alpha]^{25}_{365}$ +780°) immediately after being dissolved in methanol–0.01% CH_3SO_3H which changed gradually to a negative value ($[\alpha]^{25}_{365}$ -410°) (curve A). Addition of CH_3SO_3H to the solution induced a reverse change from negative to positive and the rotation reached $[\alpha]^{25}_{365}$ +779° (curve B). The CD spectra of the solution also showed a reversible change between a large positive absorption and a large negative one whose intensity was almost proportional to the optical activity. Such conformational transition had been known only for polypeptides and polynucleotides; this is the first example of a reversible helix–helix transition of a vinyl polymer.

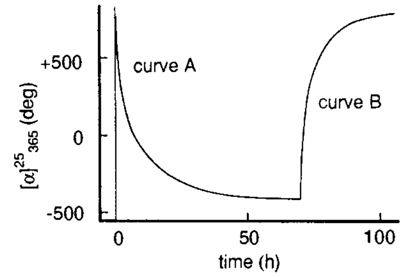
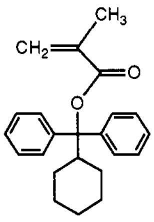


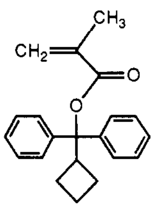
Figure 11. Reversible change of optical rotation of poly(DMPMA) of DP = 37 in methanol containing CH_3SO_3H; change in methanol-0.01% CH_3SO_3H (curve A) and that after addition of CH_3SO_3H (in methanol-13% CH_3SO_3H) (curve B). Data from ref 134.

5. Cycloalkyldiphenylmethyl Methacrylates

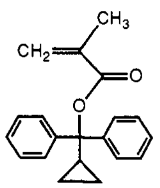
Information on the critical bulkiness (stereostructure) of an ester group suitable to afford a helical polymethacrylate has been obtained from the results of asymmetric polymerization of cyclohexyl-, cyclobutyl-, and cyclopropyldiphenylmethyl methacrylates [CHDPMA (76), CBDPMA (77), and DPDPMA (78)]. The results of polymerization of CHDPMA and CPDPMA are shown in Table 7.[139] The poly(CHDPMA)s obtained by polymerization with the optically active DPEDA-Li complexes were highly isotactic and optically active, indicating that these polymers possess the one-handed helical conformation. In contrast, CPDPMA afforded atactic, almost optically inactive polymers under the same reaction conditions. On the other hand, the polymers obtained from CBDPMA, having an ester group of intermediate bulkiness, with the DPEDA-Li complexes did not show significant optical activity at 25 °C, although the polymers were isotactic.[140] However, the polymerization systems with (+)-DDB- and (+)-PMP-DPEDA-Li complexes at -78 °C showed large



CHDPMA, 76



CBDPMA, 77



CPDPMA, 78

Table 7. Asymmetric Polymerization of CHDPMA and CPDPMA with DPEDA-Li Complexes in Toluene at −78 °C for 24 h[a]

monomer	chiral ligand	yield (%)	DP[b]	M_w/M_n[b]	tacticity (%)[c] mm/mr/rr	$[\alpha]^{25}_{365}$[d] (deg)
CHDPMA	(+)-PMP	99	34	1.10	98/2/~0	+758
CHDPMA	(+)-DDB	95	65	1.40	98/1/1	+589
CPDPMA	(+)-PMP	99	34	1.10	28/31/41	−1
CPDPMA	(+)-DDB	97	36	3.71	44/32/42	−4

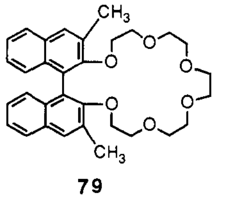
[a] Conditions: monomer/toluene = 1/20 gmL^{-1}; [monomer]/[Li] = 20. Data from ref 139. [b] Determined by GPC of poly(MMA) derived from original polymer. [c] Determined by ^{1}H NMR of poly(MMA) derived from original polymer. [d] Specific rotation immediately after being dissolved in $CHCl_3$.

positive rotation ($[\alpha]^{-78}_{435}$ ~+670°, +360°), and the optical activity decreased to the values around zero at −40 °C or higher temperature. It seems that the poly(CBDPMA) possesses the helical conformation with prevailing helical sense at −78 °C, and it changes into a random coil conformation at higher temperature because of its low stability. The results described here suggest that cyclobutyldiphenylmethyl is of critical bulkiness in the formation of one-handed helical polymethacrylate and its maintenance in solution.

The large positive optical rotation ($[\alpha]^{60}_{365}$ ~+770°) of the poly(CHDPMA) obtained with (+)-PMP-DPEDA-Li changed to a negative value ($[\alpha]^{60}_{365}$ ~−480°) in chloroform at 60 °C through a helix–helix transition of the main chain.[139] Because the right- and left-handed helices of the poly(CHDPMA) are considered to be diastereomeric taking into account the chiral centers in the vicinity of chain ends as already discussed for poly(D2PyMA), the helix–helix transition may be interpreted as the change from a less stable helix preferentially produced in polymerization at −78 °C into more stable one at 60 °C.

6. Other Methacrylates

Helix-sense-selective polymerization of less bulky methacrylates has been reported by Cram and Sogah.[141] They obtained isotactic polymers and oligomers (DP = 4–15) with large optical activity by polymerization of methyl, *tert*-butyl, and benzyl methacrylates with the complexes of chiral crown ethers **79** and **80** with *t*-BuOK and that of a chiral diamine **18** with *n*-BuLi in a mixture of toluene and tetrahydrofuran (95:5) at −78 °C. However, some results contrary to this report have been presented. Kanoh, Suda, and co-workers polymerized methyl and benzyl methacrylates with the complexes of *n*-BuLi and chiral biphenyl and binaphtyl derivatives [(*S*)-**30a**, (*S*,*S*)-**31**]; however, optically active product was not obtained.[104] In addition, we carried out oligomerization of methyl methacrylate with 1-naphthylmagnesium bromide, isolated isotactic oligomers (pentamer and octamer) immediately after termination reaction, and estimated the specific rotation of the optically pure antipodes of the oligomers by HPLC optical resolution with UV and polarimetric detections;[142] the values of rotation were $[\alpha]^{25}_{365}$ 26° for the pentamer and 23° for the octamer. On the basis of these and so far described results, we believe that methyl, *tert*-butyl, and benzyl ester groups are too small to form and maintain helical conformation of a polymethacrylate.



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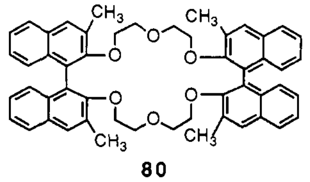

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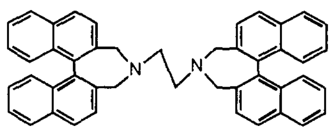

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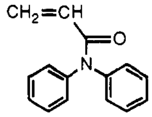
Table 8. Polymerization of Acrylamides 82–90 with the Complexes of (−)-Sp with *n*-BuLi and FlLi in Toluene[a]

acrylamide	RLi	time	temp (°C)	yield (%)	$[\alpha]^{25}_D$ (deg)
82	FlLi	7 s	−97	42	−101
83	*n*-BuLi	1 min	−78	64	+8.7
84	*n*-BuLi	1 min	−78	91	+81.7
85	FlLi	2 h	−97	54	−0.5
86	FlLi	5 h	−97	61	+8.2
87[b]	FlLi	2 h	−97	85	+57.4
88	FlLi	2 h	−97	55	−0.3
89	FlLi	5 h	−97	65	−23.7
90	*n*-BuLi	30 min	−78	45	−2.4

[a] Conditions: acrylamide/toluene = 1/20 gmL^{-1}, [acrylamide]/[Li] = 20. Data from ref 145. [b] [Acrylamide]/[Li] = 10.

B. Acrylamides

In contast to the poor polymerizability of *N*,*N*-disubstituted methacrylamides, *N*,*N*-disubstituted acrylamides afford polymers with high crystallinity by anionic polymerization.[143] *N*,*N*-Disubstituted acrylamides **82-90**having bulky substituents gave optically active polymers by polymerization with optically active anionic initiators.[144,145] The results of polymerization of these monomers with (−)-Sp complexes are shown in Table 8. The poly-**82** and poly-**84** showed rather large optical activity. In the GPC analysis with UV and polarimetric detections of the former polymer, the larger



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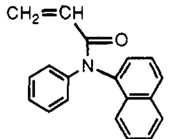

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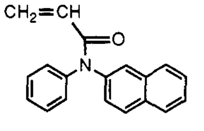

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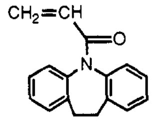

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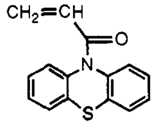

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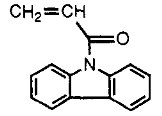

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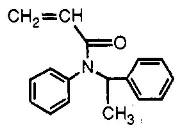

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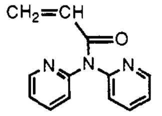

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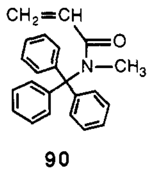

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Table 9. Asymmetric Polymerization of *tert*-Butyl Isocyanide (106) with Ni(CNR)$_4$(ClO$_4$)$_2$ and Optically Active Amine[a]

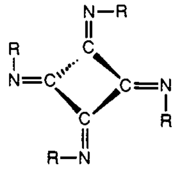
R (in catalyst)	amine	polymer $[\alpha]^{20}{}_D$[b] (deg)	polymer ee (%)	polymer screw sense of helix
t-Bu	(*S*)-(+)-$C_2H_5CH(CH_3)NH_2$	−3.5	7	*P*
t-Bu	(*S*)-(−)-$C_6H_5CH(CH_3)NH_2$	−28.7	61	*P*
t-Bu	(*R*)-(+)-$C_6H_5CH(CH_3)NH_2$	+29.0	62	*M*
t-Bu	(*S*)-(−)-c-$C_6H_{11}CH(CH_3)NH_2$	−23.2	50	*P*
2-(*t*-Bu)C_6H_4	(*S*)-(−)-$C_6H_5CH(CH_3)NH_2$	−37.7	83	*P*

[a] Conditions: catalyst 1 mol %, ambient temperature. Data from ref 151. [b] Measured in CHCl$_3$.

molecular weight fraction showed greater optical activity.[145] This fact suggests that the optical activity of the polyacrylamides can also be attributed to a helical conformation with prevailing screw sense and probably not to configurational chirality in the vicinity of the chain ends.

C. Isocyanides

Bulky isocyanides (R—N≡C) give a polymer of a unique structure (**91**) in which all main-chain carbons have a substituent by polymerization in the presence of Ni(II) salts. The polymer possesses 4/1 helical conformation.[146-148] an optically active polyisocyanide with only helical conformational chirality was first obtained by chromatographic optical resolution of poly(*tert*-butyl isocyanide) (**92**) using optically active poly((*S*)-*sec*-butyl isocyanide) (**93**)as a stationary phase by Nolte, Drenth, and co-workers;[149] it was assumed that the polymer showing positive rotation has *M*-helical conformation on the basis of CD spectra.[150] Optically active polyisocyanides with helical conformation of preferentially single-screw sense can also be obtained directly by polymerization of bulky achiral isocyanides with Ni(II) salts in the presence of optically active amines.[151] The results of asymmetric polymerization of **92** are shown in Table 9 where the degree of preference of single helix (*P* or *M*) is shown as ee (%) which was calculated by comparing the CD spectrum of the polymer with that of purely one-handed helical poly-**92**. The highest preference of single helix was 83% which corresponds to the ratio of *P*-helix to *M*-helix, 91.5 to 8.5.



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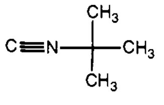

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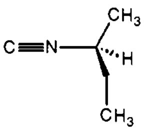

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The asymmetric polymerization mechanism of isocyanides is assumed as shown in Figure 12.[151] The polymerization reaction proceeds via a square–planar complex of Ni(II) with isocyanide monomers (A). An optically active amine (nucleophile) which coordinates to the Ni center attacks one of the monomers (monomer 1 in the figure), resulting in an adduct of the amine and an isocyanide (B). The adduct attacks the neighboring monomer and a new monomer (monomer 5) coordinates to the vacant site (C). The direction of attack (whether to monomer 2 or to monomer 4) of the initiating adduct is controlled by the chiral stereoeffect of the amine moiety: this determines the helix-sense of the polymer.

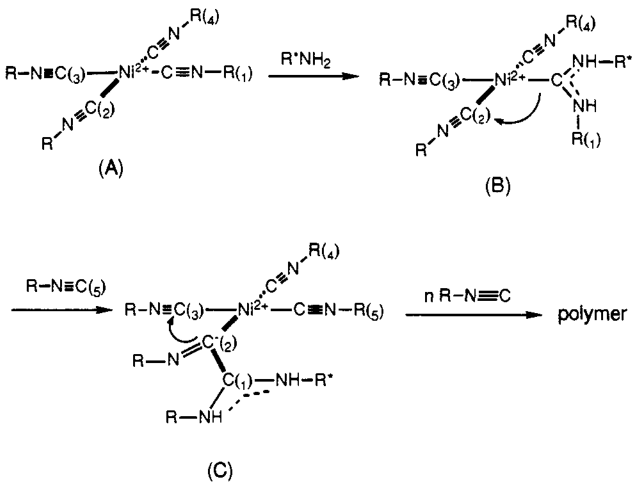
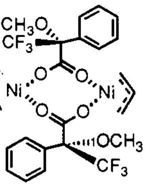


Figure 12. Asymmetric polymerization mechanism of isocyanides (ref 151).

Recently, Novak and co-workers reported on the helix-sense-selective polymerization of **92** with optically active Ni catalysts, **94** to **96** and obtained optically active polymers.[152]



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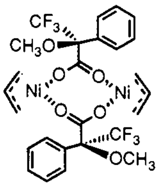

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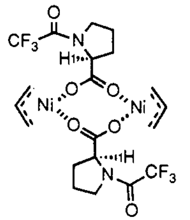

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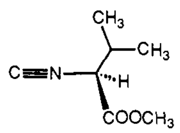
An interesting result has been reported for copolymerization of achiral and optically active isocyanides.[153] Copolymerization of achiral phenyl isocyanide and an optically active monomer (*S*)-**97** with NiCl$_2$ affords an optically active polymer with ca. 30% of optically active monomer incorporated into the chain. The prevailing helix sense of the copolymer was *P*, while that of homopolymer of (*S*)-**97** was *M*. This has been explained on the basis of polymerizability of the monomers. The polymerizability of the optically active monomer is much lower than that of the achiral monomer because of steric hindrance arising from the bulky side group. In the copolymerization, phenyl isocyanide preferentially polymerizes in the early stage to afford a mixture



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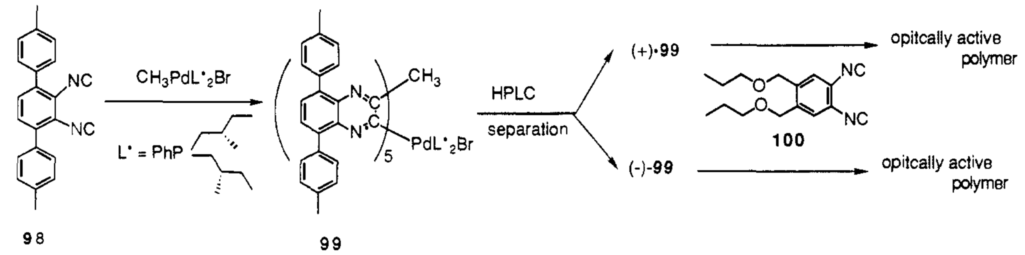
Scheme 11



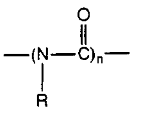
of *P*- and *M*-helical propagating chain, and the optically active monomer is incorporated preferentially into the *M*-helical growing chain. As a result, the propagation rate of the *M*-helical chain greatly decreases and the *P*-helix consisting mainly of phenyl isocyanide is the major component in the product.

The stereoregularity of optically active and inactive polyisocyanides, i.e., *syn-anti* isomerism with respect to C=N double bond, has been investigated with NMR spectroscopy by Green and co-workers: the regularity does not seem high.[154] They also pointed out that relaxing the steric hindrance allows the polymers to adopt a more random coillike conformation.

Diisocyanide compounds give helical polymers by polymerization with Pd[155] and Ni[156] complexes, and optically active polymers were obtained as shown in Scheme 11. 3,6-Di-*p*-tolyl-1,2-phenylene diisocyanide (**98**) was reacted with an optically active Pd complex to form diastereomeric helical pentamers **99**. The pentamers were separated by HPLC into (+)- and (−)-**99** and used as initators for polymerization of 3,6-dimethyl-4,5-bis[(propyloxy)methyl]-1,2-phenylene diisocyanides (**100**) which afforded one-handed helical polymers.[157]

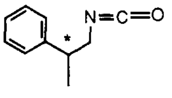
D. Isocyanates

Poly(*n*-alkyl isocyanate)s (**101**) possess a rigid helical conformation in solution[158] which was first obtained through anionic polymerization by Shashoua and co-workers.[159] Optically active polyisocyanates are obtainable by anionic polymerization of isocyanates with an optically active side group with NaCN. This was done by Goodman and Chen with (+)-2-phenylpropyl isocyanate (**102**) and (*S*)-(+)-2-methylbutyl isocyanate (**103**) for the first time.[160,161] The values of optical activity of the polymers [[α]$^{25}_{D}$ −469° (poly-**102**), +160° (poly-**103**)] were much larger than those of the monomer [[α]$^{25}_{D}$ +35° (**102**), +3° (**103**)] and were opposite in sign to those of model compounds **104** and **105** [[α]$^{25}_{D}$ +114° (**104**), −6° (**105**)]; this was attributed to a preferred helical conformation. Green and co-workers also reported on polymerization of optically active isocyanate monomers.[162–166] They prepared an optically active polymer from monomer **106** whose configurational chirality arises only from the difference between hydrogen and deuterium.[162] Although the optical activity of the (*R*)-**106** is very small ([α]$_D$ <1°), the homopolymer obtained with NaCN showed large optical activity ([α]$_D$ −367°). The CD spectrum of the polymer was similar to that of the optically active polymer obtained from monomer **107**, indicating that a significant excess of one of the two helices exists in the poly-**106**. Poly-**106** showed a remarkable dependence of optical activity on temperature. This has been ascribed to the situation in which a polymer chain has alternating right- and left-handed helical parts separated by the helix reversal points which can move along the chain quickly, and the equilibrium of the helix content changes depending on temperature.[165] Copolymers of hexyl isocyanate and a small mount of monomer **107** show optical activity larger than that expected from the content of the optically active monomeric unit [[α]$_D^{20}$ −75° (**107** content, 1%), −66° (0.5%)].[166] This is because only a small amount of an optically active side group originating from monomer **107** can cause an excess of one helical sense. The helical conformation has been studied by molecular mechanics calculation.[167]



$$-\left(\underset{R}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}\right)_n-$$

101



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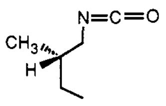

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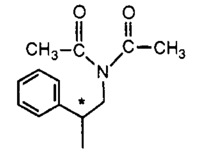

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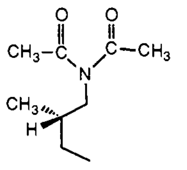

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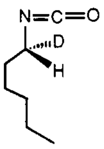

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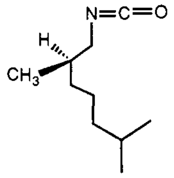
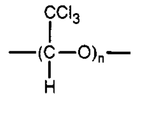


107

Recently, we found that optically active homopolymers are obtainable by anionic polymerization of achiral isocyanates with optically active lithium alkoxides and lithium amides.[168] In this case, the optically active group introduced at the chain end by initiation reaction forces the polymer chain to take the helical conformation of preferentially single-screw sense.

E. Chloral

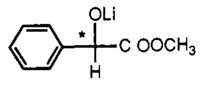
Vogl and co-workers anionically polymerized chloral (trichloroacetaldehyde) (CCl_3CHO) and obtained an isotactic polymer **108** which is insoluble in solvents.[169,170]



$-(\overset{CCl_3}{\underset{H}{C}}-O)_n-$

108

This polymer takes a 4/1 helical conformation in the solid state.[171,172] Polymerization with optically active lithium alkoxides such as **109**–**111** affords an optically active polymer and the polymer shows large optical activity ([α]$_D$ 4000°) in a film.[173-178] The optically active polymer is also obtainable by polymerization with the salts of carboxylic acids[173-175] and the other alkoxides.[176-178]



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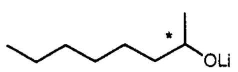

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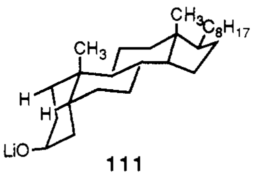
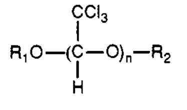


111

Although conformation of the optically active polymer in solution is unknown because of its insolubility, detailed structural analyses have been done on oligomers by means of molecular mechanics calculation[179,180] and crystallographic and NMR spectroscopic analyses of oligomers.[180-185] Hatada, Ute, and co-workers obtained oligomers **112** by anionic oligomerization and chromatographic separation of the products and clarified the following about the polymerization mechanism and the chiral structure of the oligomers.[180-185] As for **112a**, the trimer to hexamer portion isolated by GPC fractionation from the reaction products consisted almost completely of isotactic isomer, while the dimer consisted of meso and racemo isomers in the ratio of 3:1.[181-184] The isotactic oligomers had a 4/1 helical structure in the crystal and also in solution.[183,184] These results mean that the isotactic oligomer anions with a stable helical conformation predominantly propagate to become a helical polymer. The isotactic **112as** of n = 2–8 were resolved into the optically pure form by HPLC resolution.[185] Crystal structure analysis of the optically pure **112a** (−)-pentamer thus obtained showed that the pentamer had an *RRRRR* main-chain configuration and took a right-handed helical conformation.[185] The molecular mechanics calculation also supported this.[180a] The isotactic **112b** is a meso compound but can be chiral due to its stable helical conformation. The oligomers of n = 6–8 have been resolved by HPLC on a chiral stationary phase, (+)-poly-**26**.[180b] The isotactic **112bs** of n = 4–6 undergo a helix–helix transition which is detectable by means of NMR spectroscopy.[180a]



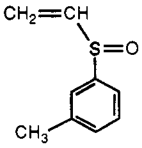
$R_1O-(\overset{CCl_3}{\underset{H}{C}}-O)_n-R_2$

a: R_1 = -Bu-*t*; R_2 = -COCH$_3$
b: R_1 = -CH$_3$; R_2 = -CH$_3$

112

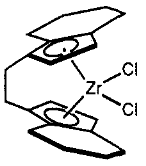
F. Other Monomers

Optically active (+)- or (−)-*m*-tolyl vinyl sulfoxide (**113**) ([α]$_D$ +486°, −486°) gives an optically active polymer ([α]$_D$ +274° to +311° from the (+)-monomer, −272° to 310° from the (−)-monomer) by polymerization with n-BuLi or (−)-Sp-n-BuLi complex. The poly(tolyl vinyl sulfone) with an achiral side group derived from the obtained polymers shows clear optical activity ([α]$_D$ +19 to +42° starting from the (+)-monomer, −16 to −41° starting from the (−)-monomer): this optical activity might be due to the prevailing helicity of the main chain.[186]



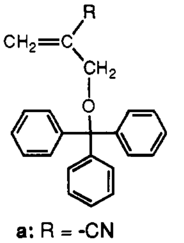
113

Kaminsky and co-workers have reported on the synthesis of optically active polypropylene and polybutene with an optically active metallocene catalyst (**114**).[187,188] The obtained isotactic polymers showed a large optical activity ([α]$_D$ −123°, −250° for polypropylene, +130° for polybutene) in suspension, but the optical activity was lost when the polymer was completely dissolved or heated. This optical activity has been attributed to a helical conformation or preferential screw sense.



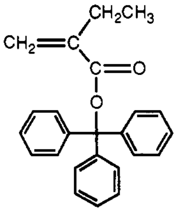
114

An acrylonitrile derivative **115a** whose structure is similar to TrMA gave an optically active polymer by polymerization under conditions similar to those applied to TrMA polymerization. The polymer was insoluble in solvent, and the optical activity was measured in suspension [e.g. [α]$^{20}_D$ +115° (initiator, (+)-DDB-FlLi)].[189] However, the monomers **115b**-**d**[190] and **116**[190,191] did not give a high polymer. These monomers do not seem to satisfy the spatial requirement for production of a helical polymer.



a: R = -CN
b: R = -COOCH$_3$
c: R = -COOC$_2$H$_5$
d: R = -C$_6$H$_5$

115



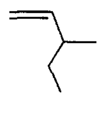
116

IV. Enantiomer-Selective Polymerization

A. α-Olefins and Vinyl Ethers

Enantiomer-selective and stereoselective polymerizations of α-olefins have been extensively been studied by Pino and co-workers.[6]

The polymerizations of racemic 3-methyl-1-pentene (**117**), 4-methyl-1-hexene (**118**), and 3,7-dimethyl-1-octene (**119**) with isotactic specific Ziegler–Natta catalysts are stereoselective,and a mixture of polymers consisting of preferentially (R)-enantiomer and (S)-enantiomer is formed.[192-195] This has been evidenced by the following findings: the crystalline structure of the above poly-(R,S)-**118** was identical to that of poly-(S)-**118**,[192] and the polymers obtained from the above three racemic monomers were separated into (+)- and (−)-fractions through chromatographic optical resolution with a chiral stationary phase.[193-195] The polymers were an optically active side group are considered to possess a helical conformation in solution.[196,197] The helical conformation is also assumed for syndiotactic poly-**118**.[198]



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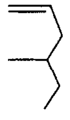

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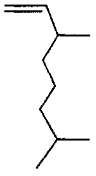
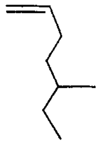


119

In the polymerization of the above racemic α-olefins with $TiCl_4/Zn[(S)\text{-}2\text{-}CH_2CH(CH_3)C_2H_5]_2$ catalyst, enantiomer selectivity has been observed, although it is rather low.[199-201] The selectivity decreased as the distance between double bond and the asymmetric carbon increased,[200,202] and no selectivity was observed for 5-methyl-1-heptene (**120**)whose asymmetric center is at the γ-position with respect to the double bond.[203] Enantiomer selectivity has also been observed in α-olefin polymerization with $MgCl_2$-supported catalysts modified with optically active Lewis bases[204] and in copolymerization of racemic α-olefins with optically active monomers.[205,206]



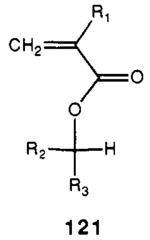
120

Enantiomer-selective polymerization of vinyl ethers is also known. Enantiomer selectivity was shown in copolymerization of racemic 1-methylpropyl vinyl ether with optically active 1-phenylethyl vinyl ether or menthyl vinyl ether using $Al(O\text{-}i\text{-}C_3H_7)/H_2SO_4$ initiator[207] and also in homopolymerization of *cis*- and *trans*-1-methylpropyl propenyl ethers with optically active aluminum initiators.[208]

B. Methacrylates

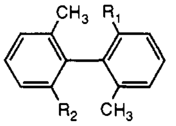
According to the results obtained in α-olefin polymerizations in which a racemic monomer having an asymmetric atom at the γ-position with respect to the double bond cannot be polymerized enantiomer selectively, enantiomer-selective polymerization of methacrylates would not be expected. Actually, almost no selectivity was shown in the polymerization of racemic menthyl methacrylate with (−)-amylmagnesium bromide,[209] that of racemic MBMA (**21**) with (+)-2-methylbutyllithium or a complex of butyllithium with lithium (−)-menthoxide,[210] and those of MBMA and racemic *sec*-butyl methacrylate with $AlEt_3$/(−)-Sp (**27**) complex.[211]

In contrast to these results, a highly enantiomer-selective polymerization of MBMA has been realized with Grignard reagent–(−)-Sp initiator systems.[212-216] For example, in the polymerization of MBMA with cyclohexylmagnesium bromide in toluene at −78 °C, where the (S)-monomer was preferentially polymerized over the (R)-monomer in an enantiomeric excess of 93%, the optical purity of the unreacted monomer was more than 90% at a polymer yield of 50–70%.[212] Moreover, the obtained polymer was highly isotactic, while the polymer obtained with the Grignard reagent alone was atactic, indicating that the initiator complex recognizes both the enantiomer and enantioface of a double bond. The Grignard reagent–(−)-Sp initiator systems were also effective for enantiomer-selective polymerization of α-methylbenzyl acrylate (**121a**),[217] α-methylbenzyl α-ethylacrylate (**121b**),[12] and several methacrylates, **121c**-**e**,[218] **f**,[219] and **g**.[220] The structure of initiator complexes[216,221] and conformation of some racemic methacrylates[220,222,223] have been investigated in detail in connection with enantiomer selectivity. These results have recently been surveyed in a review article.[12] Enantiomer-selective polymerization of MBMA has also been done with the reaction product of cyclohexylmagnesium bromide with axially chiral diamines **122a**-**c** and **123** as initiators;the selectivity was slightly lower than those with Sp initiator systems.[224,225] Recently, Inoue and co-workers realized the enantiomer-selective polymerization of MBMA using optically active aluminum compounds **124a**-**d** as catalysts and an aluminum porphyrin complex **125** as an initiator.[226] The highest electivity has been attained in the polymerization with **124a** as a catalyst, in which the ee of unreacted monomer was 40% at 75% conversion. The chiral aluminum compounds can preferentially activate one of MBMA's enantiomers.



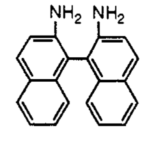
a: R_1 = -H; R_2 = -Ph; R_3 = $-CH_3$
b: R_1 = $-C_2H_5$; R_2 = -Ph; R_3 = $-CH_3$
c: R_1 = $-CH_3$; R_2 = -Ph; R_3 = $-C_2H_5$
d: R_1 = $-CH_3$; R_2 = -Ph; R_3 = $-C_3H_7\text{-}i$
e: R_1 = $-CH_3$; R_2 = -Ph; R_3 = $-C_4H_9\text{-}t$
f: R_1 = $-CH_3$; R_2 = -Ph; R_3 = $-CH_2Ph$
g: R_1 = $-CH_3$; R_2 = -Ph; R_3 = $-CPh_3$

121



122

a: $R_1 = R_2 = -NH_2$
b: $R_1 = R_2 = -NHCH_3$
c: $R_1 = -N(CH_3)_2$; $R_2 = -NH_2$

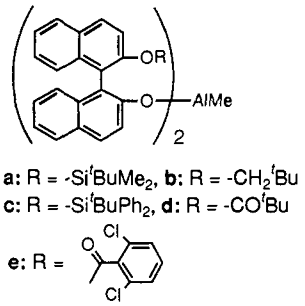


123

Phenyl-2-pyridyl-*o*-tolylmethyl methacrylate can also be enantiomer selectively polymerized and the selectivity is controlled by a rigid helical conformation of the growing polymer chain.[133,134] This has been described in the previous section.

C. Propylene Oxide, Propylene Sulfide, and Lactones

The first clear example of enantiomer-selective polymerization was demonstrated for propylene oxide



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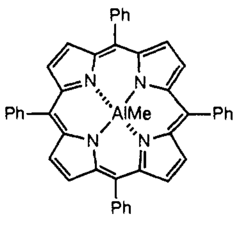
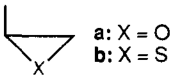


125

polymerization by Inoue and co-workers.[11] They polymerized racemic propylene oxide (**126a**) with $ZnEt_2$/(+)-borneol or $ZnEt_2$/(−)-menthol initiator system; the obtained polymer was optically active and the unreacted monomer was rich in the (*S*)-isomer. Various examples have been reported for enantiomer-selective polymerization[227-231] and copolymerization[232] of this monomer. For example, a chiral Schiff base complex (**127**) has recently been shown to be an effective catalyst.[231]



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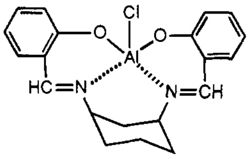
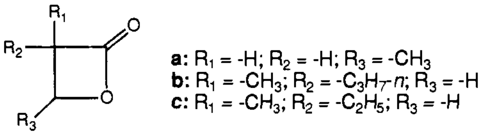


127

Propylene sulfide (**126b**) can also be polymerized enantiomer selectively with optically active initiators.[233-240] The enantiomer selectivity is generally higher than that in the polymerization of **126a**, and especially high selectivity has been reported for the polymerization with the $ZnEt_2$/(*S*)-(−)-2,2′-binaphthol initiator system:[238,239] the ratio of (*S*)-monomer consumption rate to (*R*)-monomer consumption rate (k_S/k_R) was 20 at room temperature.

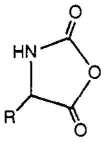
Enantiomer-selective polymerization is also known for lactones **128**.[231,236,241-245] The optically active polymer of β-butyrolactone (poly-**128a**) is an important material owing to its biodegradability.[246,247] For the polymerizations of α-methyl-α-propyl-β-propiolactone (**128b**) and α-ethyl-α-methyl-β-propiolactone (**128c**) with $ZnEt_2$/(*R*)-(−)-$(CH_3)_3CCH(OH)CH_2OH$, the k_R/k_S values were reported to be 1.25[242] and 1.02–1.07[243] at room temperature, respectively, by Spassky and coworkers. A higher value of electivity (k_R/k_S = 1.7)[245] was shown for the polymerization of **128a** with the same initiator system.



128

D. α-Amino Acid *N*-Carboxy Anhydride

Polymerization of α-amino acid *N*-carboxy anhydrides (NCA) such as **129** is important in synthesizing model compounds of proteins, and enantiomer-selective polymerization of α-amino acid NCA has been widely investigated. Lundberg and Doty first reported on enantiomer selectivity in the polymerization of γ-benzyl glutamate NCA; they found that a decrease in polymerization rate was observed in the polymerization of L-monomer by the addition of D-monomer and that the polymerization rate of L-monomer was larger than that of D-monomer in the polymerizations with preformed L-polymer as an initiator.[248-250] Tsuruta and co-workers also found enantiomer selectivity in the polymerizations of the same NCA and alanine NCA.[251-253] In addition, enantiomer selection has been observed in the polymerization of γ-benzyl glutamate NCA in the presence of a corresponding optically pure polymer[254] and in that with optically active amines[255,256] or a Ni catalyst.[257]



129

V. Chiral Recognition Ability of Optically Active Polymers

A. Helical Polymers

Various optically active polymers have been utilized for chiral catalysts and adsorbents;[258,259] most of those, however, are not the polymers prepared through asymmetric polymerization but chemically modified naturally occurring polymers and synthetic polymers derived from optically active monomers. The exceptions are one-handed helical polymers, especially polymethacrylates; they are used and commercialized as the chiral stationary phase in HPLC.[18,19]

The one-handed helical poly(TrMA),[260-264] its analogues (see section II.C.1.a),[188,265] and poly(D2PyMA)[266] prepared via helix-sense-selective polymerization show high optical resolving ability when used as a chiral stationary phase in HPLC. Many racemic compounds of stereochemical interest including drugs and their precursors have been resolved. In the first work, insoluble poly(TrMA) with high molecular weight (DP ≈ 220) was used.[260,261] The polymer was ground and sieved into small uniform particles and packed in an HPLC column. The column was effective for resolution of many racemic compounds; however, the durability and reproducibility were rather low because of the brittleness of the polymer. An improvement in this point was introduced using soluble poly(TrMA) supported on macroporous silica gel.[261,262] The soluble poly(TrMA) with lower molecular weight (DP ≈ 60) was adsorbed by 20 wt % on silica gel. The poly(TrMA)-coated silica gel showed higher resistance to compression and higher durability. Approximately 200 racemic compounds have been resolved on this stationary phase.[18,19] The structure of several compounds resolved on poly(TrMA) and the resolution chromatograms of 2,2′-dihydroxybinaphthyl are shown in Figures 13 and 14, respectively. In the resolution hydrophobic interaction between the polymer and racemic compounds seems to be important, because better separation was attained when a polar eluent such as methanol was used.

A stationary phase of poly(TrMA) chemically bonded to silica gel has also been made.[264] The optically active block copolymer of TrMA and 3-(trimethoxysilyl)propyl methacrylate was reacted with a silica gel surface to give the stationary phase. The advantage of this phase

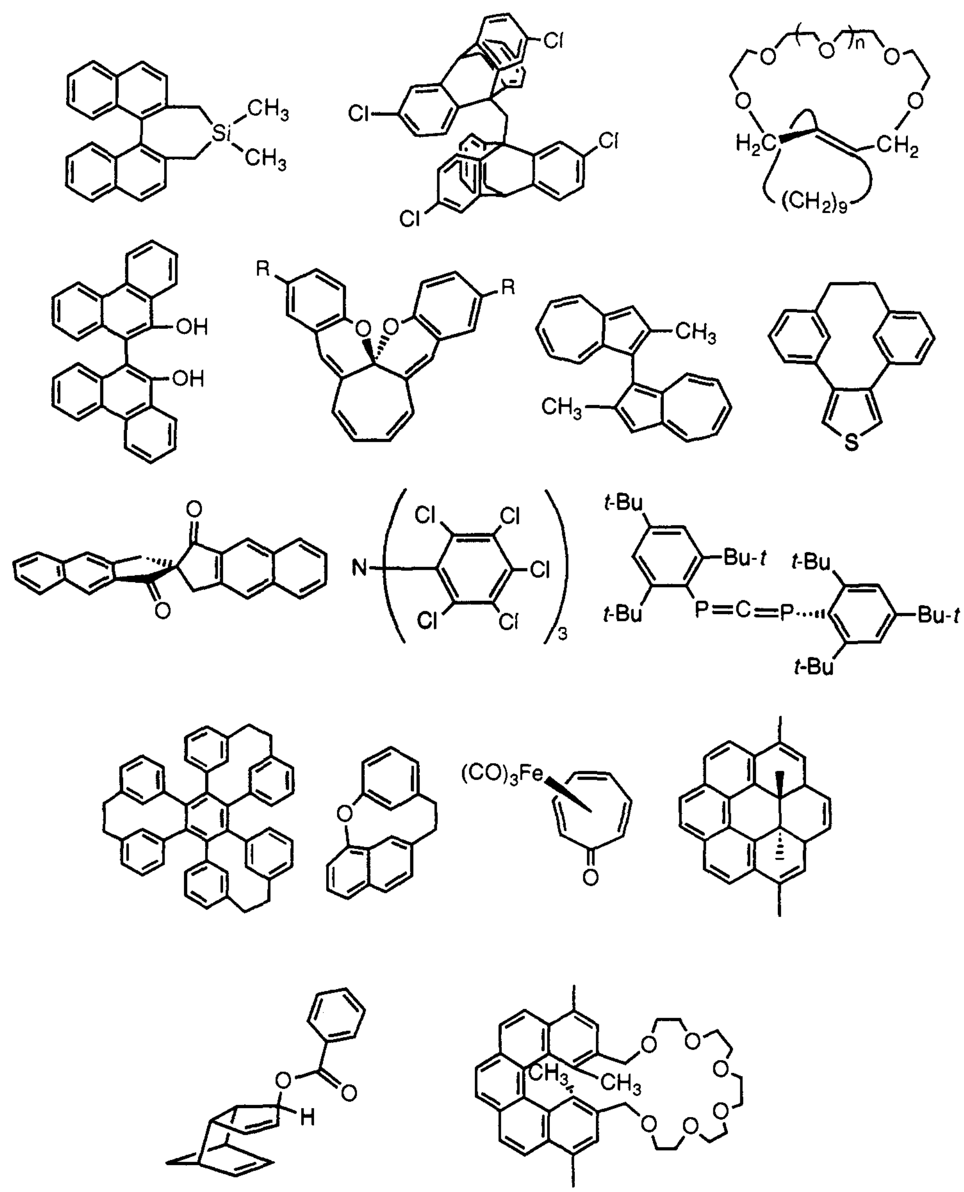


Figure 13. The structure of the chiral compounds resolved on poly(TrMA).

is the availability of eluents which dissolve poly(TrMA) such as chloroform and tetrahydrofuran. Polymethacrylates consisting of a mixture of right- and left-handed helices prepared with an achiral initiator[264] or obtained through a helix–helix transition of a one-handed helical polymer[132] were resolved into (+)- and (−)-fractions with chloroform as an eluent on this stationary phase.

Optically active poly(D2PyMA) also makes an efficient stationary phase.[266] This polymer shows higher durability against methanolysis of the ester linkage than poly(TrMA). Although, poly(D2PyMA)-coated silica gel showed slightly lower recognition ability with methanol as an eluent in comparison with poly(TrMA), some racemic alcohols were better resolved with nonpolar eluents. This suggests that polar interaction (hydrogen bonding) between the 2-pyridyl group and the alcohol may have an important role in the chiral recognition.

In contrast to the chiral recognition ability of the poly(TrMA) and poly(D2PyMA) described above, the isotactic, optically active polymers of MBMA (21) and 1,2-diphenylethyl methacrylate (130), which seem to possess random conformation, did not show chiral

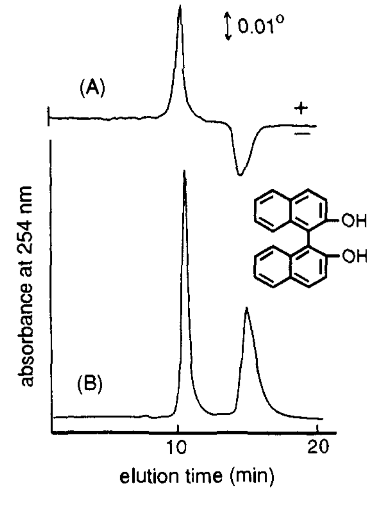
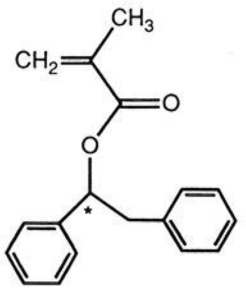


Figure 14. Chromatograms of optical resolution of 2,2′-dihydroxybinaphthyl on (+)-poly(TrMA)-coated silica gel measured by a polarimetric (Hg) (A) and a UV (254 nm) (B) detectors (column, 25 cm × 0.46 (i.d.); eluent, methanol; flow rate, 0.5 mL min^{-1}). (Reprinted from ref 18. Copyright 1987 American Chemical Society.)

recognition ability.[267] This indicates that the chiral recognition ability of poly(TrMA) and poly(D2PyMA) is based on their rigid helical conformation.



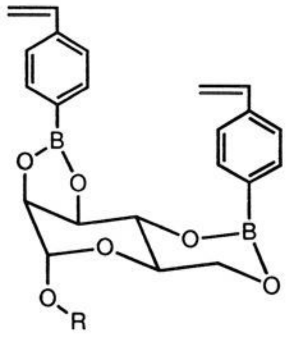
130

Optically active polychloral (**128**) also shows resolution ability for *trans*-stilbene oxide[268] and a mixture of poly[(*R*)-MBMA] and poly[(*S*)-MBMA].[269]

B. Optically Active Three-Dimensional Polymer Network (Cross-Linked Gel)

Optically active cross-linked polymer gels have been synthesized by a template polymerization technique, and the gels prepared with an optically active template show chiral recognition ability. The procedure includes polymerization of an achiral bifunctional monomer (cross-linking reagents) with a comonomer having a removable optically active auxiliary group or polymerization of a bifunctional monomer in the presence of a nonpolymerizable chiral additive followed by removal of the auxiliary group or the additive. The resulting polymer has a three-dimensional cross-linked structure with chiral cavities originating from the auxiliary or the additive, and the gel shows specific affinity for the template molecule; in other words, the gel has a memory of molecular shape of the chiral template. The idea of obtaining such a gel was first introduced by Dickey, although the template was not chiral. He showed that silica gel, which was synthesized in the presence of methyl orange, had stronger affinity for methyl orange than for ethyl, propyl, and butyl derivatives.[270]

As for the synthesis of organic polymers, the method of including a monomer having chiral auxiliary was first realized by Wulff and co-workers.[8,271–279] They synthesized various styrene derivatives having an optically active template moiety such as **131a–d**. The template moieties are based on sugars,[274,276–278] an α-amino acid,[275] and the other chiral compounds.[272,273] The monomers with the chiral template moiety were subjected to radical copolymerization with bifunctional monomers such as divinylbenzenes and ethylene dimethacrylate, and the optically active group was removed by hydrolysis from the obtained gel (Figure 15). The resulting gel processes a chiral cavity and showed chiral recognition ability for the racemic template compounds. Chirality of the gel seems to be based at least in part on a specific conformation of the polymer network because the gel did not show recognition ability after being heated in dioxane in which the gel strongly swells.[274] The chirality of the polymer also has been shown by optical activity measurement in suspension.[279]



a: R = $-C_6H_5$
b: R = $-C_6H_4-NO_2-p$
c: R = $-C_6H_4-NH_2-p$
d: R = $-CH_3$

131

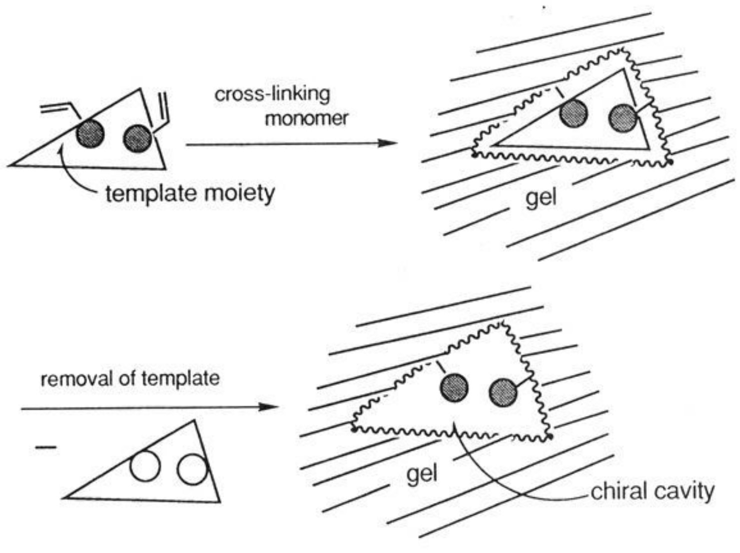
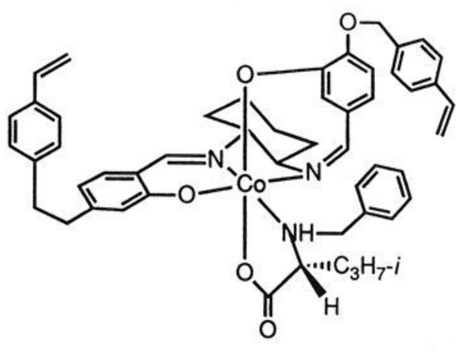


Figure 15. Synthesis of an optically active cross-linked gel by the template method.

Another simpler method including a nonpolymerizable chiral template molecule was applied in the studies by Mosbach and co-workers.[280–284] They chose *N*-protected amino acids as the template and synthesized gels from methacrylic acid or *p*-vinylbenzoic acid with cross-linking monomers. After washing out the template molecule with a solvent, the gel showed chiral recognition ability for some amino acid derivatives[281–283] and also for some drugs (β-blockers).[284] The electrostatic interaction between the acid moiety of the monomer and the template molecule seems to be important in the asymmetric induction process.

A chiral polymer gel containing a Co(II) Schiff base complex has also been prepared by Fujii and co-workers using monomer **132**, in which an amino acid derivative coordinates to the metal cation.[285]



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Similar approaches are known for the syntheses of chiral[286–288] and achiral[289–291] polymer gels.

IV. Summary

Asymmetric polymerizations of various monomers were surveyed, classifying them into four categories, and several examples of application were described.

Many studies have been reported on asymmetric synthesis polymerization. The problem in this topic is the difficulty in determination of the optical purity of the asymmetric centers; direct determination has been done only for 1,3-diene polymers. The template polymerization method, which is aimed at polymers with a chiral main-chain configuration, seems to be able to realize higher order stereoregulation than those in conventional catalytic polymerizations, although this type of polymerization has the same problem. The template method is also effective in preparation of chiral cross-linked polymers. This method is noteworthy not only as an effective synthetic way but also as a method of recording information on the molecular shape of the template into the structure of the polymer.

Optically active polymers with a helical structure have been produced from several types of monomers. Such polymers might be obtainable from other monomers by considering the spatial requirement for a specific conformation. The helical polymers are effectively applied for the HPLC stationary phase, and this is the only successful application of the polymers prepared by asymmetric polymerization. The helical polymers may possibly be utilized for other purposes such as asymmetric polymer catalysts and polymer liquid crystals, in which the specific chiral structure of the polymers may play a significant role.

In enantiomer-selective polymerization, a high selectivity was achieved in the polymerization of MBMA with Grignard reagent–(−)-Sp initiator systems. Such a drastic improvement is considered to be possible for other enantiomer-selective polymerization systems by devising appropriate catalysts.

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