Synthetic Helical Polymers: Conformation and Function

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I. Introduction

The high functionalities of naturally occurring macromolecules such as proteins and genes arise from their precisely ordered stereostructures.[1] In such systems, the helix is often found among the most fundamental structures of the polymer chain and plays important roles in realizing biological activities. On the other hand, the helix also attracts the particular interest of synthetic polymer scientists, because broad applications and characteristic features are expected for synthetic helical polymers. The potential applications include molecular recognition (separation, catalysis, sensory functions), a molecular scaffold function for controlled special alignment of functional groups or chromophores, and ordered molecular alignment in the solid phase such as that in liquid crystalline materials.

The history of helical macromolecules is traced back to the finding of the conformation for some natural polymers. The progress in this field is summarized in Chart 1 with selected topics. The helical structure of α-amylose was proposed by Hanes in 1937[2a] and was extended by Freudenberg.[2b] Pauling proposed the α-helical structure for natural polypeptides,[3] and then Watson and Crick found the double-helical structure for DNA[4] in the early 1950s. These two findings were major breakthroughs in the field of molecular biology. Regarding the helix of polypeptides, in 1956, Doty demonstrated helix formation for poly(γ-benzyl-L-glutamate) arising from the polymerization of the *N*-carboxyanhydride of the corresponding α-amino acid, where a random-coil conformation changes into an α-helix as the chain grows.[5] As a family of amino acid polymers, the conformation of poly(β-amino acid)s was investigated.[6–8] Although β-structures were proposed for poly[(*S*)-β-aminobutyric acid] by Schmidt in 1970[6a] and by Goodman in 1974[6b] and for poly(α-isobutyl L-aspartate) by Yuki in 1978,[7] experimental results suggesting a helical conformation for poly(α-isobutyl L-aspartate) were obtained by Subirana in 1984.[8] Later, in 1996, Seebach[9] and Gellman[10] independently proved that β-peptide oligomers take a helical conformation that is different from the α-helical structure of the α-peptide polymers. In 1955, Natta found that stereoregular isotactic polypropylene has a helical structure in the solid state.[11] This was the beginning of the field of synthetic helical macromolecules, leading to the wide variety of helical polymers available today.

A helical structure for vinyl polymers with an excess helicity in solution was realized for isotactic poly(3-methyl-1-pentene) by Pino in 1960.[12] Although the chiral side groups affect the helical conformation in the polyolefin, the single-handed helix of poly-

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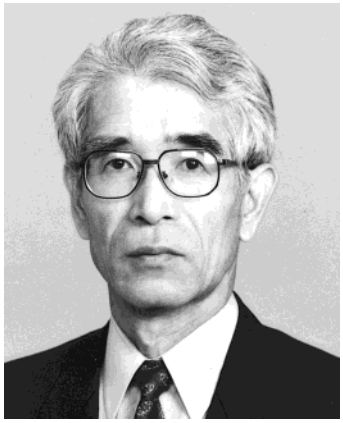
Tamaki Nakano was born in Shizuoka, Japan, on Aug 24, 1962. He received his B.S. degree in 1986, M.S. degree in 1988, and Ph.D. degree in 1991 from Osaka University. At Osaka University, he worked with Professors Yoshio Okamoto and Koichi Hatada on helix-sense-selective polymerization of bulky methacrylates. He joined the faculty at Nagoya University as Assistant Professor in the Department of Applied Chemistry, Graduate School of Engineering, in 1990 and was promoted to Associate Professor in 1998. At Nagoya University, he worked on the asymmetric polymerization systems and also on the stereoregulation of free-radical polymerization of vinyl monomers with Professor Yoshio Okamoto. He was a visiting scientist with Professor Dotsevi Y. Sogah at Cornell University (1993–1994), where he studied group-transfer polymerization (GTP) of methacrylates and synthesis of novel peptide-based polymers. In 1999, he moved to NAIST as Associate Professor. His current research interest is in the areas of chiral polymers, stereocontrol of polymerization, and photophysics of polymers. A research topic of his group on the synthesis and photophysics of *π-stacked polymers* has been a Precursory Research for Embryonic Science and Technology (PRESTO) project (2000–2003) supported by Japan Science and Technology Corp. (JST). He lives with his wife and daughter in the city of Nara.



Yoshio Okamoto was born in Osaka, Japan, in 1941. He received his bachelor (1964), master (1966), and doctorate (1969) degrees from Osaka University, Faculty of Science. He joined Osaka University, Faculty of Engineering Science, as an assistant in 1969, and spent two years (1970–1972) at the University of Michigan as a postdoctoral fellow with Professor C. G. Overberger. In 1983, he was promoted to Associate Professor, and in 1990 moved to Nagoya University as a professor. His research interest includes stereocontrol in polymerization, asymmetric polymerization, optically active polymers, and enantiomer separation by HPLC. He received the Award of the Society of Polymer Science, Japan, in 1982, the Chemical Society of Japan Award for Technical Development in 1991, the Award of The Chemical Society of Japan (1999), and the Chirality Medal (2001), among others.

(triphenylmethyl methacrylate) synthesized by Okamoto and Yuki in 1979 did not require chiral side chains.[13] This was the first vinyl polymer prepared from an achiral (prochiral) monomer having a single-handed helical structure stable even in solution. In addition, the polymer exhibits high chiral recognition and has been successfully commercialized, clearly demonstrating the practical use of synthetic helical structures.[14−16]

Chart 1. Historical Aspect of Helical Polymers

1937 α-Amylose (Hanes [Freudenberg 1939])
1951 Polypeptide (α-Helix) (Pauling)
1953 DNA (Watson, Crick)
1955 Isotactic polypropylene (Natta)
1956 Poly(γ-benzyl-L-glutamate) (Doty)
1960 Isotactic poly(3-methyl-1-pentene) (Pino)
1969 Poly((+)-1-phenylethyl isocyanide) (Millich)
1970 Poly(isocyanate) (Goodman)
1974 Poly(*t*-butyl isocyanide) (Drenth, Nolte)
1974 Polyactetylene derivatives (Ciardelli [Sinionescu, Percec 1977; Grubbs 1991; Yashima, Okamoto 1995])
1979 Poly(triphenylmethyl methacrylate) (Okamoto, Yuki)
1980 Polychloral (Vogl [Ute, Hatada, Vogl 1991])
1984 Poly(α-isobutyl L-aspartate) (Subirana [Yuki 1978])
1987 Helicates (Lehn)
1988 Poly(alkyl isocyanate) with isotopic chirality (the uniform chiral field concept) (Green)
1994 Polysilane (Fujiki, Möller [Matyjaszewski 1992])
1995 Induced helix of poly(phenylactetylene) derivatives (Yashima, Okamoto)
1995 Oligoarylene (Lehn)
1996 β-Peptide oligomers (Seebach, Gellman)
1997 Oligoaryleneethynylene (Moore)

The helical conformation of polyisocyanides having bulky side-chain groups was first postulated by Millich[17] in 1969 and confirmed by Drenth and Nolte in 1974.[18] This aspect was later studied by Green,[19] Hoffman,[20] and Salvadori.[21] Goodman synthesized helical polyisocyanates having chiral side groups in 1970.[22] Green further studied the helix of polyisocyanates with chirality only by virtue of a deuterium substitution and in other ways introduced extreme amplification of chirality that can be associated with helical structures in 1988.[23]

The helical conformation of polyacetylene derivatives bearing chiral side chains was first pointed out by Ciardelli in 1974[24] and later extended and more clearly demonstrated by Grubbs in 1991[25] and by Yashima and Okamoto in 1994.[26a] For poly(phenylacetylene) derivatives bearing no chiral side groups, Yashima and Okamoto showed that a helical conformation can be induced by interaction with added chiral small molecules.[26b] Apart from optical activity, a helical conformation of cis-cisoidal poly(phenylacetylene) in the solid state was pointed out by Simionescu and Percec.[27]

The helical structure of polychloral was proposed by Vogl in 1980[28] and was demonstrated by Ute, Hatada, and Vogl via a detailed conformational analysis of chloral oligomers.[29] As an example of a helical polymer with an inorganic backbone, polysilanes bearing a chiral side chain were synthesized and their conformational aspects were studied. A helical conformation with an excess screw sense for this class of polymers in solution was found in 1994 independently by Fujiki[30a] and by Möller.[30b] Matyjaszewski had pointed out such a conformation for chiral polysilanes in the solid state in 1992.[30c]

In addition to these examples, and as notable progress in this field, helical conformations were found for "helicates (helical complexes of oligomeric ligands and metals)" by Lehn in 1987,[31] oligoarylenes by Lehn in 1995,[32] and oligo(aryleneethynylene)s by Moore in 1997,[33] although these helices may be

regarded as only oligomers by synthetic polymer scientists.

A helix is a chiral structure; that is, right- and left-handed helices are nonidentical mirror images. Hence, if one of the two helices is selectively synthesized or induced for a polymer, the polymer may be optically active even if it contains no configurationally chiral group in the side chain or the main chain.

There are basically two types of helical structures. One is a rigid helix having a stable existence at room temperature, while the other is a dynamic helix in which helix reversals can readily move along a polymer chain at room temperature. The average length of a one-handed helical sequence can be very long for some polymers. In the former case, one may expect to obtain an optically active polymer with an excess of a screw sense through the polymerization process using a chiral initiator or catalyst. This kind of polymerization is interesting and important in the field of polymer synthesis and has been called helix-sense-selective polymerization. The first helix-sense-selective polymerization was achieved from the monomer triphenylmethyl methacrylate, leading to a nearly 100% one-handed helical polymer during polymerization with a chiral anionic initiator.[13]

We published a review paper in this journal entitled "Asymmetric Polymerization" in 1994 which encompassed this aspect of helical polymer synthesis in addition to the other types of polymerization in which chirality is introduced during the polymerization process.[34] There have been several other review papers on asymmetric polymerization and chiral polymers.[35−40] On the other hand, if the energy barrier is low enough to allow rapid helix inversion at room temperature, one cannot expect to obtain a stable one-handed helical polymer but may expect to induce a prevailing helical sense with a small amount of chiral residue or stimulant. The existence of this type of polymer was most clearly demonstrated with poly(alkyl isocyanate)s.[23,41]

In the present paper, in addition to the helical polymers with a screw-sense excess, those in a completely racemic form will also be discussed. Following up on the types of polymers discussed in our last review, newer publications that appeared since 1994 will be mainly reviewed here. Moreover, in addition to the "classical" helical polymers consisting of monomeric units connected to each other through covalent bonds, polymeric aggregates having a helical form in which their constituent units interact through weaker forces have been reported lately. This type of aggregate will also be covered. Furthermore, although a helical conformation stable in solution was the theme of our last review, some newer polymers and aggregates whose helical structures were proposed in the solid phase (liquid crystals, suspensions) are also included this time.

The method and accuracy of proving the presence of a helical structure varies depending on the type of study and the structure of the polymer. Structural questions can be addressed by (1) various methods based on computer calculations or observations of molecular models, (2) achiral spectroscopic evidence (NMR spectra, absorption spectra, X-ray diffraction), (3) viscosity or light scattering data giving information on the shape and size of an entire molecule, (4) chiroptical properties [optical activity, circular dichroism (CD)] when the helix has an excess screw sense, (5) X-ray diffraction data for fiber samples of polymers, (6) microscopic observation, or (7) single-crystal X-ray analysis.

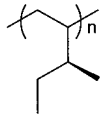
Although the last method generally gives the surest information on molecular conformation, it has limitations in that it is only applicable to oligomers and polymers uniform in terms of molecular weight including proteins but not to polydisperse real polymers and that it reveals only the structure in the solid state. In most cases, one or more of these methods (1−7) have been chosen to support the presence of helical structures. Hence, the structural proof in the studies reviewed in this paper may not be necessarily perfect in establishing helical structures. In the following sections, the topics are classified in terms of the chemical structure of the polymers.

II. Helical Polymers

A. Polyolefins

The isotactic polyolefins prepared using a Ziegler−Natta catalyst form a helical conformation in the solid state (crystalline regions).[11,38,42] This helical structure persists in solution, but because of fast conformational dynamics, only short segments of the helix exist among disordered conformations. When an isotactic polyolefin is prepared from an optically active monomer having a chiral side group, the polymer shows the characteristic chiroptical properties which can be ascribed to a helical conformation with an excess helicity.[12,43−46] The chiroptical properties arise in this case predominantly from the helical conformation of the backbone.

Because polyolefins do not absorb light in the accessible UV range, CD spectroscopy, which is a powerful tool for studying the chiral structure of polymers, could not be used for these vinyl-derived polymers. Hence, the chiral structures were elucidated in terms of optical rotatory dispersion. For example, isotactic poly[(*S*)-3-methyl-1-pentene] (**1**)



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shows a larger specific rotation than the corresponding monomer.[12,43−46] The optical activity of the polymer increased with its decreasing solubility and increasing melting point, which are related to the isotacticity of the polymer, but decreased as the temperature of the measurement increased (Table 1).[44] This relation between isotacticity and optical rotation means that the helical conformation may become imperfect when configurational disorders take place in the main chain. In addition, in the conformation of the polyolefin, right- and left-handed helical segments are considered to be separated

Table 1. Physical Properties of Poly[(*S*)-3-methyl-1-pentene] Fractions Having Different Steroregularities[n]

	sample A,[i] catalyst Al(*i*-C_4H_9)$_3$/$TiCl_4$					sample B,[l] catalyst Al(*i*-C_4H_9)$_3$/$TiCl_3$				
fraction	%	$[\eta]^{25}{}_D$[a,b] (deg)	$[\eta]$[b] (dL/g)	mp (°C)	$\Delta[\eta]_D$[a]/ΔT	%	$[\eta]^{25}{}_D$[c,h] (deg)	$[\eta]$[b] (dL/g)	mp (°C)	$\Delta[\eta]_D$[c]/ΔT
acetone-soluble	6.3	+29.4	d	nd	−0.08	2.4	+75.8	nd	nd	nd
acetone-insoluble, diethyl ether-soluble	2.6	+96.4	0.08	65−75[e]	−0.23	4.8	+127	0.13	93−96[f]	nd
diethyl ether-insoluble, benzene-soluble	0.9	+120	0.10	135−140[e]	−0.26	1.5	+146	0.13	187−193[f]	−0.31
isooctane-insoluble, benzene-soluble	0.4	+158	0.11	175−180[e]	−0.34	0.5	+157	nd	200−210[e]	−0.39
benzene-insoluble, decalin-soluble	2.0	+161[m]	0.50	228−232[e]	−0.36	1.7	+158[m]	0.60	200−210[e]	−0.40
residue	87.8	nd	nd	271−273[g]	nd	89.1	nd	nd	265−275[e]	nd

[a] In tetralin solution. [b] Determined in tetralin at 120 °C. [c] In toluene solution. [d] Molecular weight determined by cryoscopy in benzene 1200 ± 100. [e] Determined by a Kofler melting point apparatus. [f] Determined by the X-ray method. [g] Determined by the capillary method. [h] Referred to one monomeric unit. [i] Monomer optical purity 91%. [l] Monomer optical purity 89%. [m] ±10%. [n] Reprinted with permission from ref 44. Copyright 1963 Wiley-VCH.

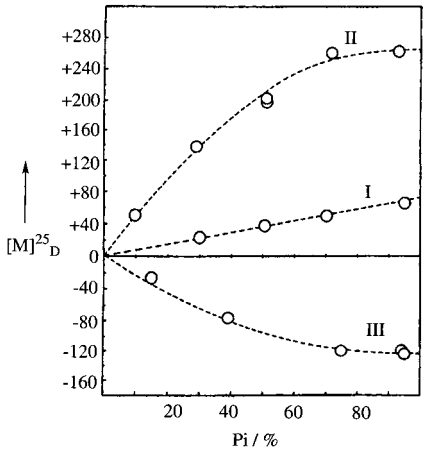
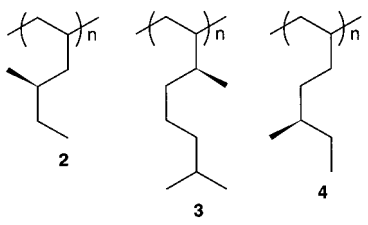


Figure 1. Relation between molecular rotation in a hydrocarbon solvent (referred to the monomeric unit) of the unfractionated methanol-insoluble **4** (I), **2** (II), and **3** (III) samples and the optical purity of the monomers used for polymerization. (Reprinted with permission from ref 47. Copyright 1967 Wiley.)

dynamically by helical reversals. This model is consistent with the temperature dependence of the optical activity of the polymer in which an increase in temperature increased the population of the helical reversals.

In these isotactic polymers, the optical purity of the monomer affected the optical activity via the relationship to the excess helical sense of the polymer (Figure 1).[47] In the case of isotactic poly[(*S*)-4-methyl-1-hexene] (**2**) and poly[(*R*)-3,7-dimethyl-1-octene] (**3**), an increase in the optical purity of the monomers resulted in an increase in the optical activity of the polymers in a nonlinear fashion: the optical activity of the polymers leveled off when the optical purity of the monomer reached ca. 80%. In contrast, in the case of isotactic poly[(*S*)-5-methyl-1-heptene] (**4**), the



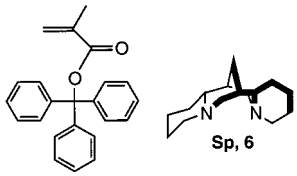
relation was linear. These findings imply that the side-chain chiral centers of poly[(*S*)-5-methyl-1-heptene], which are separated from the main chain by three covalent bonds, may be too far from the main chain to affect the helical conformation.

Helical conformations were also proposed for the isotactic copolymer derived from (*R*)-3,7-dimethyl-1-octene and styrene.[48,49] The copolymer showed intense CD bands based on the styrene units incorporated into the polymer chain. The CD intensity was much larger than that of a model compound of an adduct of the chiral olefin and styrene. The helical structure of polyolefins has also been supported by force field calculations.[50] The relationship of these considerations to isotactic vinyl polymers and more recent studies have recently been reviewed.[41]

B. Polymethacrylate and Related Polymers

1. Poly(triphenylmethyl methacrylate)

Vinyl polymers with a stable helical conformation are obtained from methacrylates with a bulky side group by isotactic specific anionic or radical polymerization.[13,34] This type of polymer was first synthesized by asymmetric anionic polymerization (helix-sense-selective polymerization) of triphenylmethyl methacrylate (TrMA, **5**) using a complex of *n*-BuLi with (−)-sparteine (Sp, **6**).[13] Although, as discussed



in the preceding section, a chiral side group was necessary in realizing a helical conformation with an excess helical sense in solution for stereoregular polyolefins, helical poly(TrMA) is prepared from the achiral (prochiral) vinyl monomer. The poly(TrMA) possesses a nearly completely isotactic configuration and a single-handed helical conformation of the main chain, which is stabilized by steric repulsion of the bulky side groups, and shows high optical activity based on the conformation.[13,51−53] The helical conformation is lost when the triphenylmethyl group is removed from the polymer chain. Thus, the PMMA derived from the poly(TrMA) shows only a small optical activity based on the configurational chirality

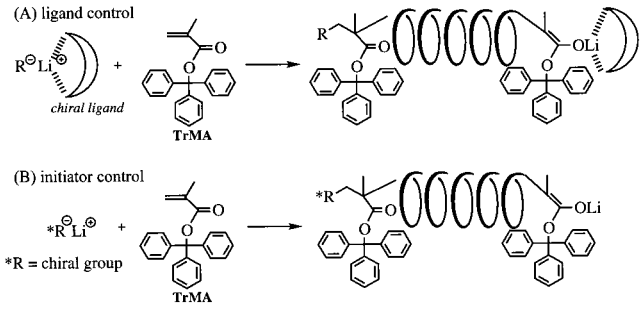


Figure 2. Helix-sense-selective anionic polymerization of TrMA: ligand (A) and initiator (B) control.

Table 2. Optical Activity of Poly(TrMA) in the Polymerization at −78 °C[a]

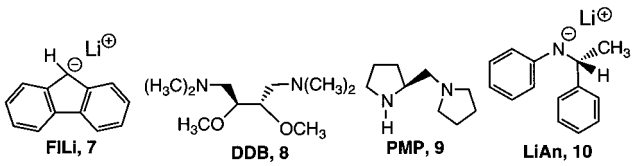
control method	initiator	solvent	yield (%)	$[\alpha]_D$ (deg)
ligand control	FlLi−(−)-Sp	toluene	99	+383
ligand control	FlLi−(+)-DDB	toulene	100	+344
ligand control	FlLi−(+)-PMP	toulene	100	+334
ligand control	*n*-BuLi−(−)-Sp	THF	100	+7
initiator control	LiAn	toulene	73	−70
initiator control	LiAn	THF	93	−82

[a] Conditions: [monomer]/[intiator] = 20. Data cited from refs 13 and 52.

of the stereogenic centers in the vicinity of the chain terminals.[53]

The helical-sense excess in polymethacrylates is estimated, in principle, by comparing their optical activity and CD band intensity with those of the corresponding single-handed helical specimen having the same side group. A polymer is expected to have a single-handed helical structure if it has a completely isotactic configuration, except for minor configurational errors in the vicinity of the chain terminals, and has no clear dependence of optical activity on molecular weight. In the case of poly(TrMA), a nearly completely isotactic sample which is a mixture of right- and left-handed helices was resolved into several fractions showing different specific rotations with different helical-sense excesses by chiral chromatography.[54] The polymer contained in the fraction showing the highest optical activity obtained through resolution was taken as a single-handed one.

Asymmetric anionic polymerization is carried out using a complex of an organolithium with a chiral ligand or using a chiral organolithium (Figure 2).[13,51,52] The helix-sense selection takes place on the basis of the chirality of the ligand or the initiator. The chiral ligand is assumed to coordinate to the countercation (Li^+) at the living growing end and to create a chiral reaction environment (path A), while the chiral initiator will affect the initial stages of helix formation (path B). Table 2 shows the results of polymerization using the complexes of 9-fluorenyllithium (FlLi, **7**) or *n*-BuLi with (−)-Sp, (+)- and (−)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB, **8**), and (+)-(1-pyrrolidinylmethyl)pyrrolidine (PMP, **9**) as chiral ligands and lithium (*R*)-*N*-(1-phenylethyl)-anilide (LiAn, **10**), a chiral initiator, to compare the effectiveness of the two methods. Ligand control has been shown to lead to a higher helix-sense excess, i.e., higher optical activity of the product, in the polymerization in toluene than in THF. This is



because the coordination of the ligand is inhibited by the coordination of the solvent in THF, removing the chiral ligand from the chain end and therefore reducing its influence. The initiator control gives relatively low selectivity independent of the solvent polarity.

In the asymmetric polymerization of TrMA using a complex of an organolithium and a chiral ligand, the chiral ligand controls the main-chain configuration in addition to the conformation. (−)-Sp, (+)-PMP, and (+)-DDB convert TrMA into the (+)-polymers having the same helical sense; however, the one synthesized using Sp has an ---*RRR*--- configuration, while those prepared using the other two ligands have an ---*SSS*--- configuration.[52]

Helical block copolymers of TrMA with other monomers have been prepared, and their properties have been studied.[55−57]

Poly(TrMA) exhibits chiral recognition ability toward various types of racemic compounds when used as a chiral stationary phase for high-performance liquid chromatography (HPLC).[14−16]

Helical poly(TrMA) and its analogues can be used as chiral template molecules in molecular-imprint synthesis of a chiral cross-linked gel.[58] The chirality of the helical polymer may be transferred to the cross-linked material.

2. Poly(triphenylmethyl methacrylate) Analogues: Anionic Polymerization

Since the finding of the helix-sense-selective polymerization of TrMA, various other bulky monomers have been designed to find parallels to this behavior. The examples that appeared after our last review[34] are discussed in this section.

Some monomers having a pyridyl group in the side chain including diphenyl-3-pyridylmethyl methacrylate (D3PyMA, **11**),[59] phenylbis(2-pyridyl)methyl methacrylate (PB2PyMA, **12**),[60] 1-(2-pyridyl)dibenzosuberyl methacrylate (2PyDBSMA, **13**),[61] and 1-(3-pyridyl)dibenzosuberyl methacrylate (3PyDBSMA, **14**)[62] were prepared and polymerized. These mono-

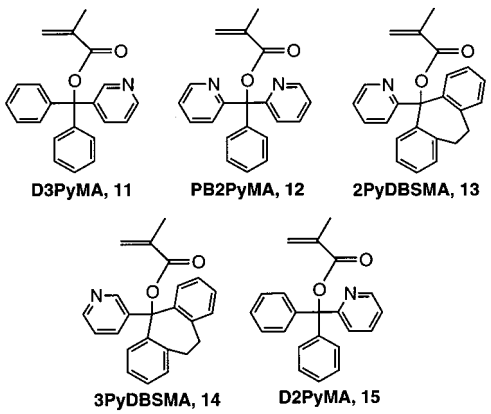


Table 3. Methanolysis of Bulky Methacrylates[a]

monomer	k^b (h^{-1})	half-life (min)	monomer	k^b (h^{-1})	half-life (min)
TrMA	2.86	14.5	PB2PyMA	1.24×10^{-5}	335×10^4
D2PyMA	0.0256	1620	2PyDBSMA	0.0165	2520
D3PyMA	0.0291	1439	3PyDBSMA	0.0444	936

[a] Measured by monitoring the monomer decompostion (methanolysis) in a $CDCl_3/CD_3OD$ (1/1) mixture at 35 °C by means of ^1H NMR spectroscopy. Data cited from refs 60 and 61. [b] Pseudo-first-order rate constant.

mers were designed so that their ester linkage is more durable toward methanolysis than that of poly(TrMA). This design had been introduced for diphenyl-2-pyridylmethyl methacrylate (D2PyMA, **15**).[63−65] The durability of the ester linkage is an important feature of the helical polymethacrylates when they are used as chiral packing materials for HPLC. Poly(TrMA) is known to slowly decompose and lose its helical structure by reaction with methanol, which is a good solvent for a chiral separation experiment.[14−16] The methanolysis rates of these monomers are shown in Table 3 with the data for TrMA. The results indicate that the pyridyl-group-containing monomers are more durable than TrMA, suggesting that the monomers will afford helical polymers more resistant to methanolysis than poly(TrMA).

Stereoregulation in the anionic polymerization of D3PyMA and PB2PyMA using organolithium−chiral ligand complexes was more difficult than that of TrMA reasonably because the coordination of the pyridyl group to Li^+ cation competes with the effective complexation of a chiral ligand to Li^+ cation. Sp and DDB that are effective in controlling the TrMA polymerization[13,52] resulted in rather low specific rotation values, and only PMP led to the polymers showing a relatively high optical activity [poly(D3PyMA),[59] $[\alpha]_{365}$ +708°; poly(PB2PyMA),[60] $[\alpha]_{365}$ +1355°]. However, in contrast, the polymerization of 2PyDBSMA[61] and 3PyDBSMA[62] was much more readily controlled using Sp, DDB, and PMP as ligands. The bulky and rigid fused ring systems in these monomers may prevent the side-chain−Li^+ coordination.

The polymers obtained from D3PyMA and P2BPyMA have a less stable helix than that of poly(TrMA).[59,60] Their helical conformation undergoes helix−helix transition, leading to a decrease in the screw-sense excess as observed for the single-handed helical poly(D2PyMA).[66]

Helical copolymers of some of the monomers discussed in this section with TrMA have been synthesized.[67]

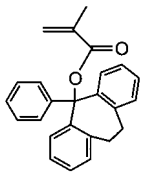
The optically active polymers obtained from D3PyMA, PB2PyMA, 2PyDBSMA, and 3PyDBSMA show chiral recognition ability toward some racemic compounds in chiral HPLC or chiral adsorption experiments, though the ability was generally lower than that of poly(TrMA).[16,59−62]

Quaternary salt formation with alkyl iodides was studied using the optically active poly(D3PyMA) and poly(3PyDBSMA).[68] The polymers were found to form a quaternary salt by reaction with CH_3I in $CHCl_3$. Upon salt formation, poly(D3PyMA) lost its helical conformation and optical activity probably due to electrostatic repulsion between the charged side groups, whereas poly(3PyDBSMA) maintained the helical conformation, with the polymer still exhibiting optical activity in the salt form. Poly(3PyDBSMA) also formed a salt with *n*-butyl iodide.

3. Poly(triphenylmethyl methacrylate) Analogues: Free-Radical Polymerization

As discussed so far in this section, the helical polymethacrylates are synthesized predominantly using anionic polymerization techniques. However, recently, more versatile, inexpensive, and experimentally simple free-radical polymerization has been proved to be an alternative, effective way to prepare helical polymethacrylates from some monomers. Although the stereochemical control of radical polymerization is generally more difficult compared with that in other types of polymerization,[69] an efficient method would make it possible to synthesize helical, optically active polymers having functional side chains by direct radical polymerization without using protective groups. In the radical polymerization of bulky methacrylates, helix-sense selection is governed by the chirality of a monomer itself or an additive.

Although most of the bulky methacrylates described so far give isotactic polymers by radical polymerization as well as by anionic polymerization at low temperatures, the isotactic specificity of the radical polymerization is generally lower than that in the anionic polymerization.[70] However, 1-phenyldibenzosuberyl methacrylate (PDBSMA, **16**)[71−73]



PDBSMA, 16

and its derivatives, 2PyDBSMA[61] and 3PyDBSMA,[62] afford nearly completely isotactic polymers by radical polymerization regardless of the reaction conditions. A possible polymer structure of isotactic poly(PDBSMA) is shown in Figure 3 in which the polymer has an approximately 7/2-helical conformation. The high isotactic specificity implies that the obtained polymer is an equimolar mixture of completely right- and left-handed helical molecules, suggesting that introduction of a nonracemic chiral influence to the polymerization reaction could result in the production of a single-handed helical, optically active polymer with an almost complete isotactic structure.

This concept was realized in the radical polymerization of PDBSMA using optically active initiators DMP (**17**) and CMBP (**18**), chain-transfer agents NMT (**19**) and MT (**20**), and solvents including

Table 4. Radical Polymerization of PDBSMA[a]

initiator	chain-transfer agent or solvent	$[M]_o$ (M)	$[I]_o$ (M)	yield[c] (%)	THF-soluble part[b] yield (%)	THF-soluble part[b] $[\alpha]_{365}$[d] (deg)	THF-soluble part[b] DP
(−)-DMP	none	0.16	0.16	75	3	+40	44
(*i*-PrOCOO)$_2$	(+)-NMT (0.032 M)	0.16	0.003	71	5	−140	42
(*i*-PrOCOO)$_2$	(−)-menthol (4.6 M)/toluene	0.05	0.0017	45	1	+180	50

[a] Data cited from ref 72. Polymerization in toluene at 40 or 50 °C. [b] Washed with a benzene/hexane (1/1) mixture. [c] Hexane-insoluble products. [d] In THF.

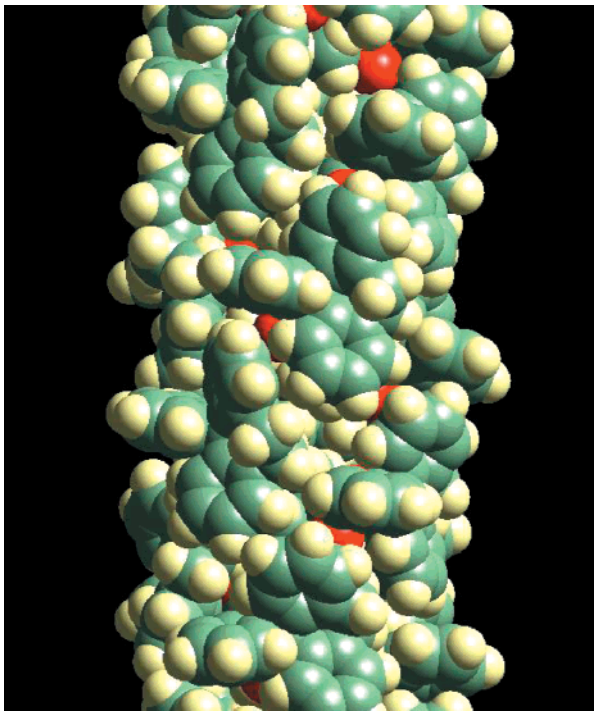
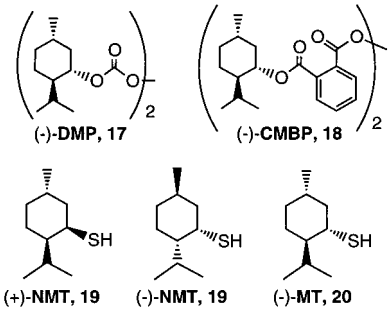


Figure 3. A possible 7/2 helix of isotactic poly(PDBSMA).

menthol (Table 4).[72,73] The reaction using DMP as chiral initiator gave an optically active polymer



whose chirality appeared to be based on excess single-handed helicity, while CMBP failed in the helix-sense selection. Helix-sense selection was also possible by polymerization in the presence of the chiral thiols NMT and MT. The optical activity of the products obtained using the chiral initiator or the chiral chain-transfer agents depended on the molecular weight as revealed by an SEC experiment with simultaneous UV (concentration) and polarimetric (optical activity) detections. For example, the polymer prepared with (+)-NMT (Table 4, third row) consisted of levorotatory fractions of higher molecular weight and dextrorotatory fractions of lower molecular weight. These results strongly suggest that helix-sense selection

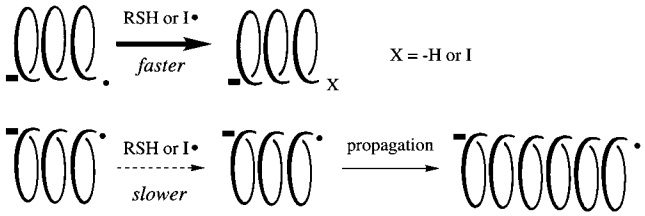
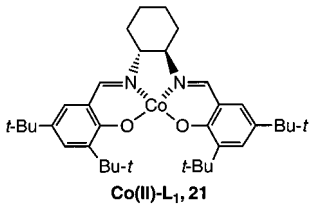


Figure 4. Helix-sense-selective radical polymerization using optically active thiol as a chain-transfer agent or initiator.

took place at the step of the termination reaction, that is, primary radical termination in the polymerization using DMP and hydrogen abstraction from the thiol by a growing radical in the polymerization using NMT or MT (Figure 4). The highest specific rotation of the poly(PDBSMA) prepared using (+)-NMT was $[\alpha]_{365}$ −750° after SEC fractionation. This specific rotation corresponds to a ratio of enantiomeric helices of 3/7 as estimated by comparison with the optical activity of the anionically synthesized, single-handed helical poly(PDBSMA) ($[\alpha]_{365}$ +1780°). The polymerization in a mixture of toluene and menthol was also effective in synthesizing optically active poly(PDBSMA)s. The mechanism of helix-sense selection in this case seemed to be the same as that for the polymerization using the thiols.

Helix-sense-selective radical polymerization of PDBSMA was also performed using a chiral Co(II) complex, Co(II)−L_1 (**21**).[74] Complex Co(II)−L_1 can possibly interact with the growing radical in the



polymerization system because Co(II)−L_1 is a d^7 species. Regarding the interaction of a Co(II) species with a growing radical, several examples of catalytic chain transfer in methacrylate polymerization by the use of Co(II) have been published.[75,76] The polymerization was carried out in the presence of Co(II)−L_1 in a $CHCl_3$/pyridine mixture at 60 °C. Although the polymer yield and the molecular weight of the products became lower by the effect of Co(II)−L_1, the polymerization led to optically active polymers whose specific rotation was $[\alpha]_{365}$ +160° to +550° depending on the reaction conditions (Table 5). The CD spectrum of the polymer showing $[\alpha]_{365}$ +550° had a pattern very similar to that of the spectrum of a single-handed helical polymer synthesized by anionic

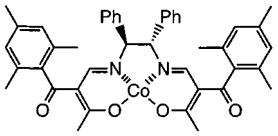
Table 5. Free-Radical Polymerization of PDBSMA with AIBN in the Presence of Co(II)−L_1 in a Chloroform/Pyridine Mixture at 60 °C for 24 h[a]

			THF-soluble part			
$[CO(II)-L_1]_o$ (M)	$[pyridine]_o$ (M)	yield[b] (%)	yield (%)	DP[c]	M_w/M_n[c]	$[\alpha]_{365}$[d] (deg)
0	0	74[e]	4	22	1.24	
0	0.51	86[f]	3	19	1.27	+270
0.011	0.54	59	2	19	1.20	+550
0.039	0.50	39[g]	3	19[h]	1.18	+160
0.057	0.54	16	4	19	1.19	

[a] Data cited from ref 74. Conditions: monomer 0.5 g, $[monomer]_o = 0.44-0.45$ M, $[AIBN]_o = 0.029-0.031$ M. [b] MeOH-insoluble part of the products. [c] Determined by GPC of poly(PDBSMA). [d] Estimated on the basis of GPC curves obtained by UV and polarimetric detections (see the text). [e] DP = 155 (M_w/M_n = 3.72) as determined by GPC of PMMA. [f] DP = 170 (M_w/M_n = 2.78) as determined by GPC of PMMA. [g] DP = 78 (M_w/M_n = 1.60) as determined by GPC of PMMA. [h] DP = 20 (M_w/M_n = 1.14) as determined by GPC of PMMA.

polymerization, indicating that the chiroptical properties of the radically obtained polymer arise from an excess of one helical sense. The SEC separation of the polymer revealed that the higher-molecular-weight fractions had higher optical activity. SEC fractionation of the high-molecular-weight part of the THF-soluble product gave ca. 8 wt % polymer: this fraction was found to have a completely single-handed helical structure (total yield 0.24%). Thus, the Co(II)−L_1-mediated method was demonstrated to be effective for helix-sense selection though the yield of the single-handed helical polymer was low.

Through a search for a better Co(II) complex, Co(II)−L_2 (**22**)[77] was recently found to be more effective than Co(II)−L_1 in the PDBSMA polymerization.[78] The polymerization in the presence of Co(II)−L_2 afforded a polymer showing $[\alpha]_{365}$ +1379° before GPC separation in a higher yield compared with the reaction using Co(II)−L_1.



Co(II)-L_2, 22

The mechanism of the helix-sense selection most probably involves the interaction of the Co(II) species with the growing polymer radical. It is assumed that the polymerization of PDBSMA proceeds only through the right- and left-handed helical radicals and that the two chiral radicals have different interactions with the chiral Co(II) species or different constants of binding with the chiral Co(II) species (Figure 5), leading to a difference in the apparent propagation rate of the two radicals, giving different molecular weights of the products derived therefrom. The dependence of optical activity on the degree of polymerization (DP) is indicative of a mechanism in which both helical senses are formed at a low DP of the growing species and one of the two has stronger interaction with the chiral Co(II) species, resulting in a lower apparent propagation rate.

In addition to PDBSMA, two novel monomers, DMPAMA (**23**) and DBPAMA (**24**), give highly isotactic polymers by radical polymerization as well as anionic polymerization.[79,80] This means that a fused ring system may be important in realizing a high stereospecifity in radical polymerization, though it should be noted that PFMA (**25**) leads to a relatively

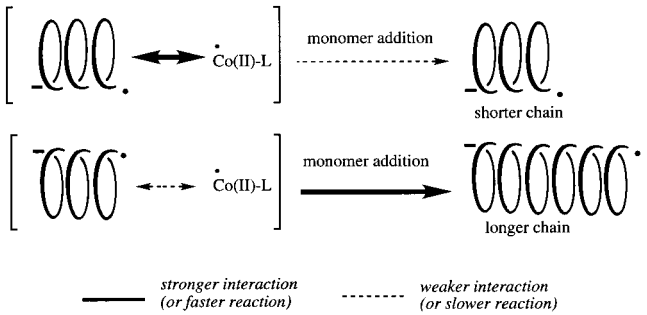
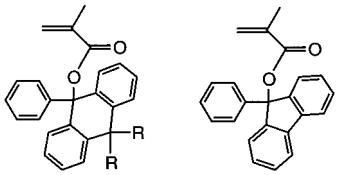


Figure 5. Helix-sense-selective radical polymerization using an optically active Co(II) complex.



DMPAMA, 23: R = -CH_3
DBPAMA, 24: R = -$C_4H_9{}^n$

PFMA, 25

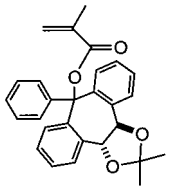
low isotactic specificity by radical and anionic polymerization.[53] DMPAMA results in mm selectivity of >99%, whereas DBPAMA affords polymers with slightly lower mm contents (mm 91−99%). An important result was that the isotactic poly(DBPAMA)s with relatively high DPs (up to 974) obtained by the radical polymerization were completely soluble in THF and chloroform, suggesting that the two butyl groups per unit prevent aggregation of the helical molecules. This is interesting because helical polymethacrylates with high DPs generally have a tendency to form aggregates and become quite insoluble.[13,52,65,72] The good solubility of the poly(DBPAMA)s would make it possible to clarify the solution properties of the high-molecular-weight, helical vinyl polymers.

The two monomers gave nearly completely isotactic, single-handed helical polymers by the anionic polymerization using the complex of *N*,*N*′-diphenylethylenediamine monolithium amide (DPEDA−Li) with DDB or PMP.[79,80] The single-handed helical polymers showed much lower optical activity [poly(DMPAMA), $[\alpha]_{365}$ +125°; poly(DBPAMA), $[\alpha]_{365}$ +183°] than the single-handed helical poly(TrMA) ($[\alpha]_{365} \approx +1500°$). The relatively low specific rotation values for a single-handed helix suggest that the reported high optical activity of poly(TrMA) and its analogues is partly based on the single-handed propeller conformation[14,15,81,82] of the triarylmethyl group in the side chain in addition to the helical arrangement of the entire polymer chain. Such a propeller conformation would be difficult for poly(DMPAMA) and poly(DBPAMA) because the anthracene moiety in the side chain should have a planar structure.

Helix-sense selection was also realized during the radical polymerization of DBPAMA at 0 °C using

optically active NMT as the chain-transfer agent.[79,80] Optically active poly(DBPAMA) [[α]$_{365}$ +74° using (+)-NMT; [α]$_{365}$ −53° using (−)-NMT] was obtained. The specific rotation values suggest that the helical sense excess (ee) may be ca. 30−40%. In contrast to the asymmetric radical polymerization of PDBSMA, the optically active product was completely soluble in this case.

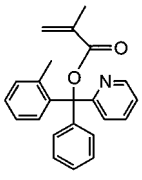
A chiral PDBSMA derivative, IDPDMA (**26**), was designed to form a single-handed helical polymer through radical polymerization due to the effect of the chirality in the side chain.[83] The anionic polym-



IDPDMA, 26

erization of (+)-IDPDMA with 100% ee ([α]$_{365}$ +548°) was performed using achiral DPEDA−Li in THF, resulting in an optically active polymer whose specific rotation ([α]$_{365}$ +1540°) was comparable to those of other single-handed helical polymethacrylates. Hence, the chiral side chain can induce an excess helicity in the anionic polymerization. The radical polymerization of (+)-IDPDMA led to polymers with an almost completely isotactic structure regardless of the ee of the monomers. The polymer obtained by the radical polymerization of the (+)-IDPDMA with 100% ee showed a CD spectrum with the features of both that of (+)-IDPDMA and that of the highly optically active poly[(+)-IDPDMA] obtained by the anionic polymerization. This suggests that the radically obtained poly[(+)-IDPDMA] has a prevailing helicity, though the helical sense in excess appeared to be lower than that of the anionically obtained polymer. In the radical polymerization of IDPDMA having various ee's, the ee of the monomeric units of the polymer was always higher than that of the starting monomer, indicating the enantiomer in excess was preferentially incorporated into the polymer chain (enantiomer-selective polymerization). The enantiomer selection may be governed by the excess helicity of the growing radical. The growing species consisting of an excess enantiomeric component of monomeric units probably takes a helical conformation with an excess helical sense which can choose one enantiomer of IDPDMA over the other.

Phenyl-2-pyridyl-*o*-tolylmethyl methacrylate (PPyoTMA, **27**) having a chiral ester group is known to lead to highly enantiomer-selective and helix-sense-selective polymerization by anionic catalysis.[84−86] The selection was also found in the radical polymerization of optically active PPyoTMA having various ee's,



PPyoTMA, 27

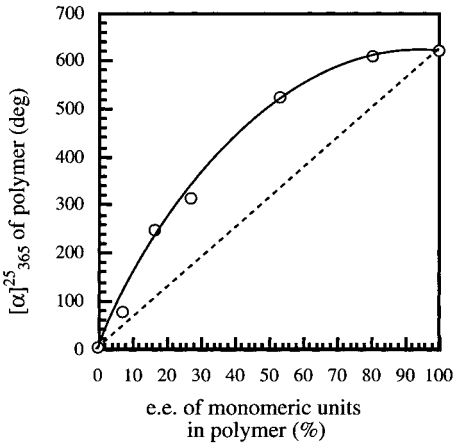
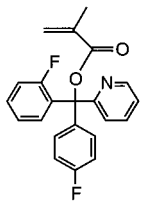


Figure 6. Relation between the optical activity of poly(PPyoTMA) obtained by radical polymerization and the optical purity of the monomeric units. (Reprinted with permission from ref 87. Copyright 1996 American Chemical Society.)

although the isotactic specificity in the radical polymerization was moderate (mm 72−75%) [polymerization in toluene at 40 °C using (*i*-PrOCOO)$_2$].[87] The polymer obtained from optically pure (+)-PPyoTMA ([α]$_{365}$ +190°) showed a large levorotation ([α]$_{365}$ −617°), suggesting that the polymer has a helical conformation with an excess helical sense. The anionic polymerization of the same monomer using *n*-BuLi at −78 °C produces a polymer with an mm content of 98% and a higher specific rotation ([α]$_{365}$ −1280°), which is comparable to the rotation values for the single-handed helical poly(TrMA). The radically obtained polymer may have a shorter single-handed helical sequence based on the lower isotacticity of the main chain.

In the polymerization of the (−)-monomers with various ee's, enantiomer selection was observed though the selectivity was lower compared with that of the polymerization of IDPDMA.[83,87] In this experiment, a nonlinear relation was observed between the ee of the monomer in the feed and the optical activity of the obtained polymer (Figure 6). This indicates that the optical activity of the polymer is not based only on the side chain chirality. Furthermore, the chirality of a one-handed helical part induced by a successive sequence of the (−)-monomeric units (monomeric units derived from a (−)-monomer) can overcome the opposite chiral induction by the sporadic (+)-monomeric units. In other words, once a one-handed helical radical comes under the influence of the (−)-monomeric units, an entering (+)-monomer becomes a part of the one-handed helix whose direction may be unfavorable to the chiral nature of the (+)-monomer.

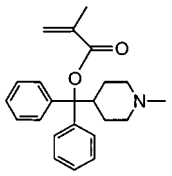
The stereochemistry of 2F4F2PyMA (**28**) polymerization was also investigated.[88,89] The optically pure



2F4F2PyMA, 28

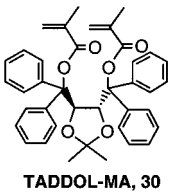
(+)-2F4F2PyMA ([α]$_{365}$ +28°) afforded polymers with a relatively low mm content and a low optical activity either by the anionic polymerization with DPEDA−Li in THF at −78 °C (mm/mr/rr = 70/30/~0, [α]$_{365}$ −82°) or by the radical polymerization in toluene using (*i*-PrOCOO)$_2$ at 40 °C (mm/mr/rr = 54/27/19, [α]$_{365}$ −2°).[89] The monomer design of 2F4F2PyMA was not as effective as that of PPyoTMA in controlling the polymerization stereochemistry.

(1-Methylpiperidin-4-yl)diphenylmethyl methacrylate (MP4DMA, **29**) has been revealed to afford highly isotactic, helical polymers by radical polymerization (mm 94−97%).[90] This is in contrast to the moderate mm specificity in the radical polymerization of cyclohexyldiphenylmethyl methacrylate.[91] MP4DMA was polymerized using a free-radical initiator in the presence of (−)-menthol to afford an optically active polymer with an excess helical sense. Because the *N*-substituent of the monomer can be replaced with other functional groups, the design of MP4DMA may be extended to the synthesis of a variety of helical polymers having functional groups attached to the side chain.

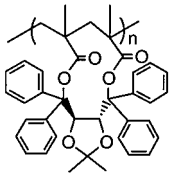


MD4PMA, 29

Free-radical and anionic polymerizations of TADDOL−MA (**30**) proceed exclusively via a cyclization mechanism, and the obtained polymer seems to have a helical conformation with an excess helicity.[92−94] The main chain structure of poly(TADDOL−MA) with cyclized units (poly-**30**) is different from that of all other polymethacrylates discussed here. Similar monomers have been synthesized and polymerized.[95]



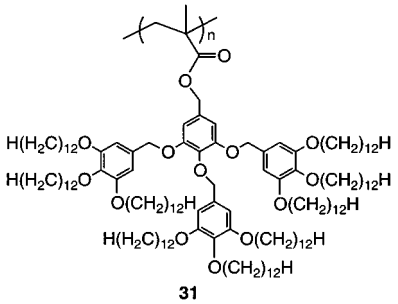
TADDOL-MA, 30



poly(TADDOL-MA), poly-30

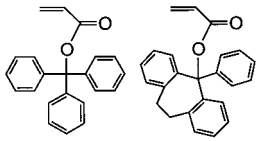
4. Polymers of Other Acrylic Monomers

There is a class of helical polymethacrylates whose conformation is induced by the assembly of their side groups.[96] The polymer **31**, having a dendritic side group, is an example. The helical conformation was first found in the solid state by the X-ray analysis of oriented fiber samples. The conformation was them confirmed visually by scanning force micrography. In contrast to the polymethacrylates discussed in the preceding section, the polymers are likely to form a helical conformation regardless of the main chain configuration. A similar conformational control has been realized also with polystyrene derivatives having a dendritic side group.

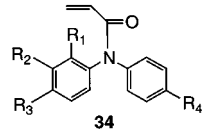


31

Helix-sense-selective anionic polymerization of acrylates TrA (**32**) and PDBSA (**33**)[97,98] and acrylamides including the series of *N*,*N*-diphenylacrylamides[99−104] (**34**) have been investigated using (+)-PMP, (−)-Sp, and (+)-DDB as chiral ligands. The stereocontrol in the polymerization of the acrylates and acrylamides was more difficult compared with that in the methacrylate polymerization. The specific rotations ([α]$^{25}_{365}$) of poly(TrA) and poly(PDBSA) obtained by the asymmetric polymerization were much smaller than those of the corresponding polymethacrylates prepared under similar conditions and were up to +102° (ligand PMP, diad isotacticity 70%) and −94° (ligand DDB, diad isotacticity 61%), respectively. The isotactic part of the polymers is considered to have a helical conformation with an excess helicity. For the polymerization of the bulky acrylamides, (−)-Sp has been mainly used as the chiral ligand. Sp was also a better ligand compared with DDB and PMP in the polymerization of **34d**. The highest isotacticity (mm 87%) and optical activity ([α]$^{25}_{365}$ −657°) in the asymmetric polymerization of acrylamides were achieved in the polymerization of **34h** using the (−)-Sp−FlLi complex as an initiator at −98 °C.[102] The stereostructure of poly-**34h** depended on the molecular weight, and the high-molecular-weight fractions separated by GPC fractionation exhibited large levorotation, [α]$^{25}_{365}$ −1122° (mm 94%), which is comparable to the optical activity of the single-handed helical polymethacrylates.[102]



TrA, 32 **PDBSA, 33**

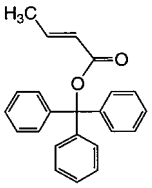


34

a: R_1 = -CH_3, R_2 = R_3 = R_4 = -H
b: R_1 = R_3 = R_4 =H, R_2 = -CH_3
c: R_1 = R_3 = R_4 =H, R_2 = -Cl
d: R_1 = R_3 = R_4 =H, R_2 = -OCH_3
e: R_1 = R_3 = R_4 =H, R_2 = -$OSi(CH_3)_2C(CH_3)_3$
f: R_1 = R_3 = R_4 =H, R_2 = -$OCO(CH_3)_3$
g: R_1 = R_3 = R_4 =H, R_2 = -$OCOCH(Ph)C_2H_5$
h: R_1 = R_2 = R_4 = -H, R_3 = -CH_3
i: R_1 = R_2 = R_4 = -H, R_3 = hexyl
j: R_1 = R_2 = -H, R_3 = R_4 = hexyl
k: R_1 = R_2 = -H, R_3 = R_4 = butyl

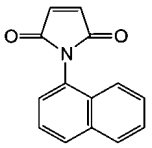
Helix-sense-selective polymerization has also been attempted for several bulky monomers including an acrylonitrile derivative[105] and α-substituted acrylates.[106,107] Triphenylmethyl crotonate (TrC, **35**) affords optically active, helical polymers by the polymerization using DDB−FlLi and PMP−FlLi complexes.[108,109] The polymers possess a nearly completely threo-diisotactic structure. Although the polymers indicate relatively small specific rotation ([α]$_D$ +5.6° and +7.4° for the samples with DP = 15 and

36, respectively), the optical activity is considered to be based on an excess helicity because the rotation was lost when the polymers were converted to the methyl esters.



TrC, 35

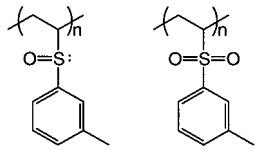
N-1-Naphthylmaleimide (NMI, **36**) affords an optically active polymer ($[\alpha]_{435}$ +152° to 296°) by polymerization using an Et_2Zn−Bnbox complex.[110] The obtained polymer resolves 1,1′-bi-2-naphthol when used as an HPLC packing material. Although the tacticity of the polymer is not clear, the polymer may have a helical conformation with an excess screw sense in this case.



NMI, 36

C. Miscellaneous Vinyl Polymers

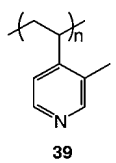
The anionic polymerization of optically active (+)- or (−)-*m*-tolyl vinyl sulfoxide ($[\alpha]_D$ +486°, −486°) using BuLi or BuLi−(−)-Sp leads to an optically active polymer, **37** [$[\alpha]_D$ +274° to +311° (from (+)-monomer); $[\alpha]_D$ −272° to −310° (from (−)-monomer)]. Oxidation of **37** afforded polymer **38** with an achiral



37 38

side group that was still optically active [$[\alpha]_D$ +19° to +42° starting from the (+)-monomer, −16° to ∠41°starting from the (−)-monomer]. Polymer **38** may have a helical conformation with a prevailing helicity of the main chain.[111]

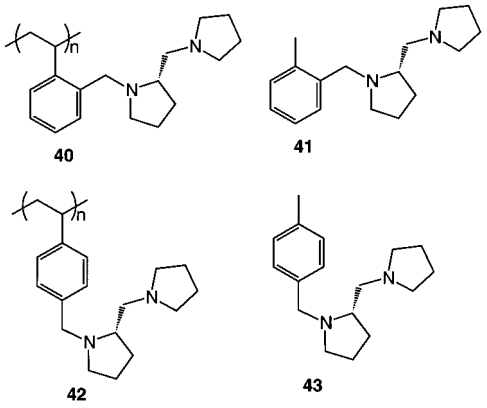
Optically active poly(3-methyl-4-vinylpyridine) ($[\alpha]^{-4}_{589}$ +14.2°) (**39**) has been prepared by anionic polymerization of the corresponding monomer using the (−)-DDB−DPEDA−Li complex in toluene at −78



39

°C.[112] The optical activity has been ascribed to a helical conformation, although the tacticity of the polymer is not yet clear. The optical activity was lost in solution at −4 °C within 30 min of dissolution. This is reasonably due to a conformational transition allowed only in solution.

An optically active polystyrene derivative, **40** ($[\alpha]^{25}_{365}$ −224° to −283°), was prepared by anionic and radical catalyses.[113] The one synthesized through the anionic polymerization of the corresponding styrene derivative using BuLi in toluene seemed to have a high stereoregularity and showed an intense CD spectrum whose pattern was different from those of the monomer and a model compound of monomeric unit **41**. In contrast, polymer **42** and a model compound, **43**,



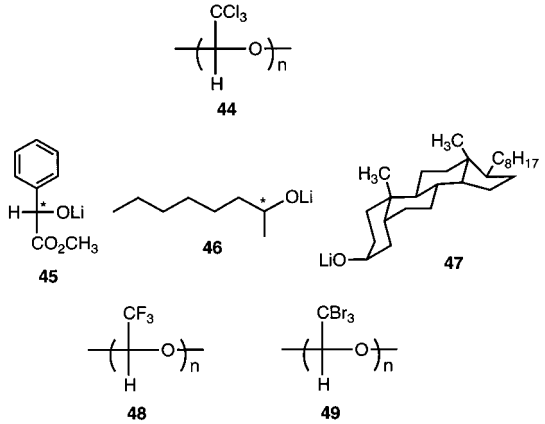
40 41 42 43

for the polymer indicated very similar CD spectra. These results suggest that polymer **40** may have a regular conformation, probably a helix, while the chiroptical properties of polymer **42** are mainly due to the chiral side-chain group. Together with the results on **40**, a substituent at the 2-position of the aromatic ring may be important in realizing a helical conformation for polystyrene derivatives and related polymers.

D. Polyaldehydes

1. Polychloral and Related Polymers

Asymmetric anionic polymerization can convert trichloroacetaldehyde (chloral) to a one-handed helical, isotactic polymer (**44**) having a 4/1-helical conformation with high optical activity ($[\alpha]_D$ +4000° in film).[28,114−118] Anionic initiators such as **45**,[115] **46**,[115] and **47**[117] and Li salts of optically active carboxylic acids or alcohols are used for the polymerization. Although the polymers are insoluble in solvents and their conformation in solution cannot be directly



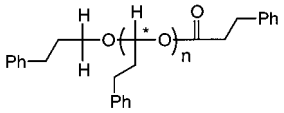
44 45 46 47 48 49

elucidated, a helical structure has been verified by NMR and crystallographic analyses of the uniform oligomers separated by chromatographic techniques.[29,118] A helical conformation has also been proposed for poly(trifluoroacetaldehyde) (**48**) and poly(tribromoacetaldehyde) (**49**).[119,120]

Optically active **44** partially resolves *trans*-stilbene oxide[121] and separates several aromatic compounds[122] when used as an HPLC stationary phase. **44** also partially resolves isotactic polymers of (*R*)-(+)- and (*S*)-(−)-α-methylbenzyl methacrylate.[123]

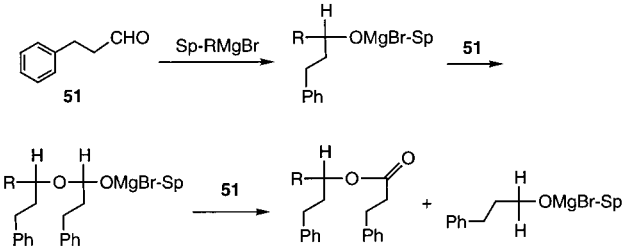
2. Other Polyaldehydes

Optically active poly(3-phenylpropanal) ($[\alpha]^{25}_{365}$ −33° to −56°) (**50**) is obtained by the anionic polymerization of 3-phenylpropanal (**51**) using the complexes of Sp with ethylmagnesium bromide (EtMgBr)



50

and *n*-octylmagnesium bromide (OctMgBr).[124] The optical activity may be based on a predominant single-handed helical conformation. Reaction of the initiator with **51** gives an ester (**52**) and the (3-phenylpropoxy)magnesium bromide−Sp complex through the Tishchenko reaction (Figure 7). The



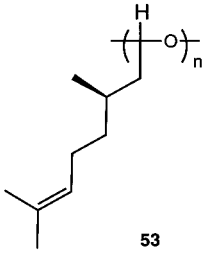
52

Figure 7. Polymerization of **51** using an Sp−Grignard reagent complex.

complex initiates the polymerization of **51**, and the termination reaction takes place through the Tishchenko reaction, resulting in the polymer structure **50**.

The major diastereomer of dimer **50** ($n = 2$) (diastereomeric stereostructure not identified) prepared by oligomerization using Sp as a chiral ligand was found to be rich in the (+)-isomer with 70% ee. This suggests that oligomer anions with a certain configuration, for instance, (*S*,*S*) or (*R*,*R*), may propagate preferentially to the polymers.

An optically active aldehyde is also considered to afford a polymer having a helical conformation.[125]



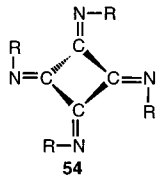
53

The polymer **53**, bearing a chiral side group, showed much larger optical activity ($[\alpha]_D$ −81° to −94°) than a model compound of the monomeric unit.[125a,b]

E. Polyisocyanides

1. Polymers of Monoisocyanides

Polyisocyanides having a 4/1-helical conformation (**54**) are obtained by the polymerization of chiral isocyanide monomers.[17,126] An optically active polyisocyanide having a chirality due to the helicity was first obtained by chromatographic resolution of poly(*tert*-butyl isocyanide) (poly-**55**) using optically active poly[(*S*)-*sec*-butyl isocyanide] as a stationary phase, and the polymer showing positive rotation was found to possess an M-helical conformation on the basis of CD spectral analysis.[127,128] Details of the helical structure of polyisocyanides have been discussed on the basis of theoretical and experimental analyses.[19−21] Optically active polymers having an excess helicity can be prepared by the polymerization of bulky isocyanides using chiral catalysts. Catalysts effective for helix-sense-selective polymerization include Ni(CNR)$_4$(ClO$_4$)$_2$/optically active amine systems,[128] the Ni(II) complexes **56**−**58**,[129] and the dinuclear complex containing Pd and Pt which has a single-handed oligomeric isocyanide chain (**59**).[130] By the polymerization of **55** using Ni(CN−Bu^t)$_4$(ClO$_4$)$_2$/(*R*)-(+)-C$_6$H$_5$-CH(CH$_3$)NH$_2$, an M-helical polymer with an ee of 62% can be synthesized,[128] and complex **58** converts **55** to a levorotatory polymer with 69% ee.[129] The complex **59** is obtained by oligomerization of *m*-(*l*)-menthoxycarbonylphenyl isocyanide with Pt−Pd di-



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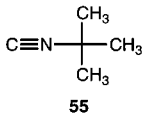

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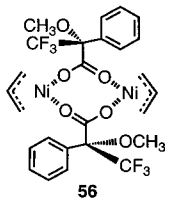

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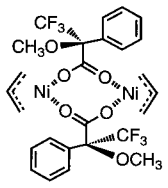

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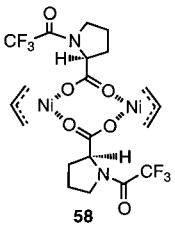

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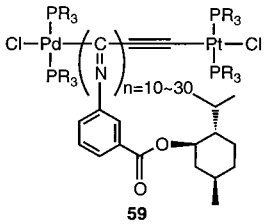

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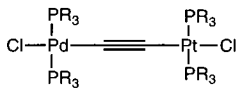

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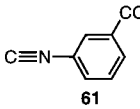

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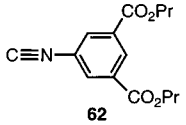

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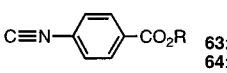


63: R = cyclohexyl
64: R = n-propyl
65: R = (l)-menthyl

63-65

nuclear complex **60**. **59** can smoothly polymerize bulky monomers **61** and **62** in a helix-sense-selective manner. For example, the polymerization of **62** with **59** ($n = 10$, $M_n = 3720$, $[\alpha]_D$ +22°) affords a polymer with $M_w = 13.5 \times 10^3$ and $[\alpha]_D$ +126°.[130] An excess helicity is also induced in the copolymerization of achiral **63** or **64** with optically active **65** using complex **60**. A nonlinear relationship exists between optical rotation and the content of the chiral monomer: the optical activity of a copolymer containing 70% chiral monomeric unit is almost the same as the optical activity of the homopolymer of the chiral monomer.[131,132] The effect of the ee of the monomer on the optical activity of the monomer in the homopolymerization of **65** using **60** has been studied; a nonlinear effect was also found in this case.[132,133]

A helical polyisocyanide bearing a porphyrin residue in the side chain has been prepared.[134] The special alignment of the porphyrin chromophores was controlled using the helical main chain as established by an absorption spectrum. In addition, helical polyisocyanides having a saccharide residue in the side chain have been designed, and the molecular recognition of the polymers by lectin was investigated.[135,136] Furthermore, block copolymers of styrene with isocyanides having L-alanine-L-alanine and L-alanine-L-histidine side chains have been synthesized; the copolymers consist of a flexible polystyrene chain and a rigid, helical, and charged isocyanide chain.[137] The copolymers were found to form rodlike aggregates having a nanometer-scale helical shape.

Optically active poly-**55** shows chiral recognition ability toward several racemates including Co(acac)$_3$.[138]

2. Polymers of Diisocyanides

1,2-Diisocyanobenzene derivatives yield helical polymers via a cyclopolymerization mechanism by the polymerization with Pd and Ni complexes. Optically active polymers were initially obtained by the method illustrated in Figure 8.[139−143] Monomer **66** was reacted with an optically active Pd complex to form diastereomeric pentamers **67**, which were separated into (+)- and (−)-forms by HPLC. The polymerization of **68** using the separated **69** led to a one-handed helical polymer.[139] The polymerization of **68** using the initiators having chiral binaphthyl groups, **69**−**71**, also produced optically active polymers.[142] The helix-sense selectivity in the polymerization using **69**

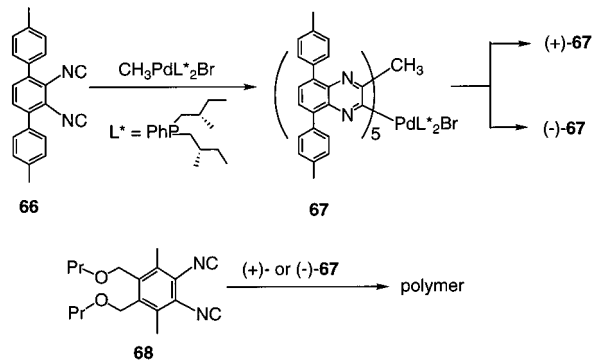
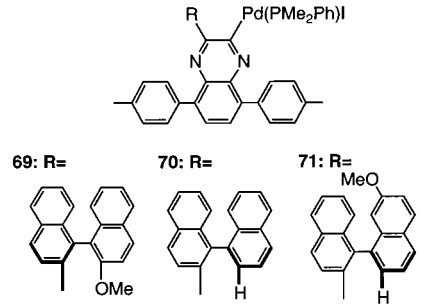


Figure 8. Helix-sense-selective polymerization of 1,2-diisocyanobezene derivatives.



depended on the polymerization procedure. The polymer obtained by direct polymerization with **69** had a much lower helix-sense excess compared with the polymer prepared using a pentamer synthesized using **69** and purified into a single-handed helical form which led to a single-handed helical structure of the obtained polymer. In contrast to **69**, **70** without purification of the intermediate oligomeric species yields poly-**68** with high helix-sense selectivity (79%). The helix-sense selectivity in the polymerization of **68** using **71** as the initiator was estimated to be over 95%.[143,144] Block copolymerization of different diisocyanide monomers was carried out, and helical triblock copolymers were synthesized.[145]

F. Polyisocyanates and Related Polymers

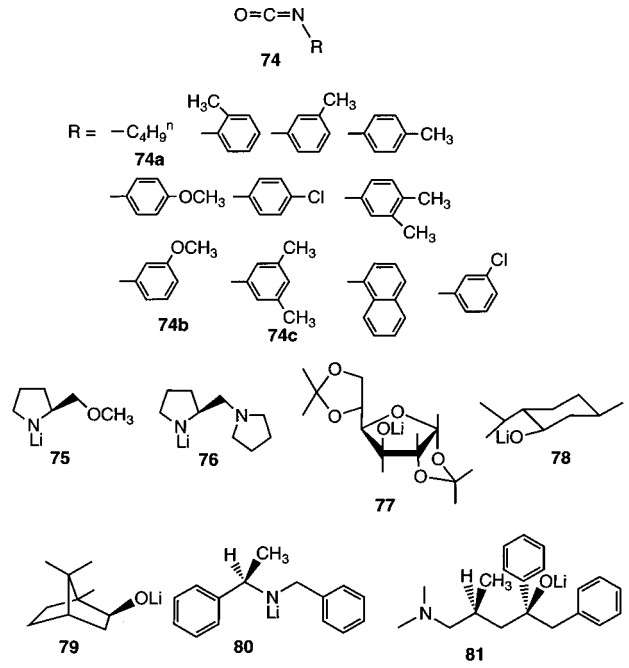
1. Polyisocyanates

Polyisocyanates are obtained by anionic polymerization using initiators such as NaCN and organolithiums and have the structure of 1-nylon (**72**).[146,147] Polymerization of hexyl isocyanate with a half-metallocene complex (**73**) leads to a living polymer,[148]

72 73

and this catalyst can be applied to the polymerization of functionalized monomers.[149] Polyisocyanates possess a dynamic helical conformation in which right-handed helical and left-handed helical parts coexist in the chain and are separated by helix-reversal points.[23,41,146,147] Hence, if a polymer is made from an achiral monomer using an achiral initiator, the polymer is optically inactive; i.e., the amounts of right- and left-handed helices are equal, although the energy barrier for the movement of the helix reversals depends on the kind of side chain.[150,151] Optically active polyisocyanates having an excess helicity are obtained by (1) polymerization of achiral isocyanates using optically active anionic initiators, (2) polymerization of optically active monomers, and (3) the interaction of a polymer chain with an optically active solvent.

The polymerization of butyl isocyanate and other achiral monomers (**74**) using optically active anionic initiators **75**−**81** affords optically active polymers.[152−156] The poly-**74a** ($M_n = 9000$) obtained using **75** exhibits $[\alpha]_{435}$ +416°. The optical activity of the polymers arises from the helical part extending from the chain terminal bearing the chiral group originat-



ing from the initiator to a certain length (persistence length) that has a single-screw sense due to the influence of the terminal chiral group. The relation between the DP and optical activity was investigated for the oligomers obtained from **74b** and **74c** using **75** as initiator (Figure 9). For this purpose, the oligomers in the DP range of 1−20 were isolated using supercritical fluid chromatography (SFC). In the figure, the optical activity of oligo-**74b** and oligo-**74c** increased with an increase in DP in the range of DP < 13 and DP < 15, respectively. This is probably because, in this DP range, the oligomers have no helix-reversal point and the helical structure becomes stiffer as the DP increases. In the higher DP range, the optical activity of the oligomers gradually decreased due to the generation of helix-reversal points, indicating that the reversal points start to be generated at the DPs mentioned above for the two oligomers.[155]

A helix-sense excess can also be realized based on the effects of a chiral side chain.[22,23,41,157−166] For example, optically active monomer (*R*)-**82**, whose chirality is based only on the difference between −H

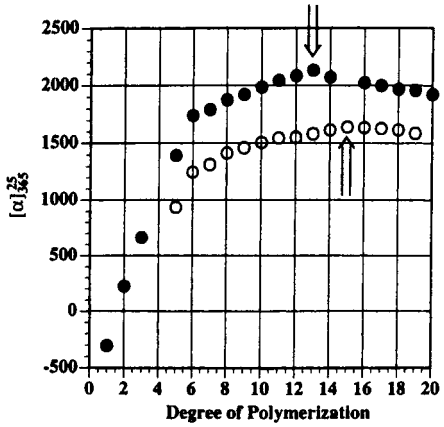


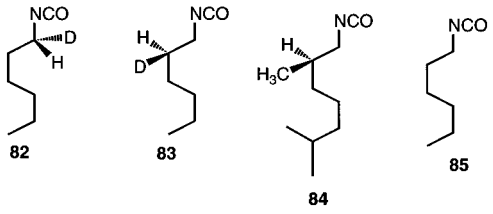
Figure 9. Specific rotation of oligomers of **74b** (upper) and **74c** (lower). Reprinted with permission from ref 155. Copyright 1998 The Society of Polymer Science, Japan.

Table 6. Specific Rotation of Copolymers of 84 and 85[a]

[**85**] (%)[b]	[**84**] (%)[b]	$[\alpha]^{-20}_D$ (deg)	$[\alpha]^{+20}_D$ (deg)
100	0	0	0
99.5	0.5	−140	−66
97.7	2.3	−379	−231
85	15	−532	−480
0	100	−514	−500

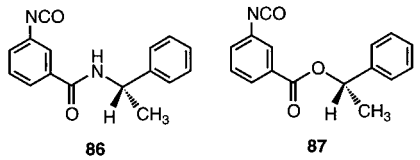
[a] Measured in $CHCl_3$ (c = 0.5 mg mL^{-1}). Reprinted with permission from ref 41. Copyright 1999 Wiley-VCH. [b] Mole percent.

and −D ($[\alpha]_D$ < 1°), gives a polymer showing $[\alpha]_D$ −367° by anionic polymerization with NaCN.[23,157] The preferential helical sense is sensitive to the side-chain structure; **82** and **83** with the same absolute configuration and very similar structures result in an opposite helical sense of the polymers.[161] A screw-sense excess is also realized in copolymers of chiral and achiral monomers. Only a small amount of chiral **84** randomly incorporated into a polymer chain consisting mainly of achiral monomeric units based on **85** effectively induces a helical-sense excess ("ser-



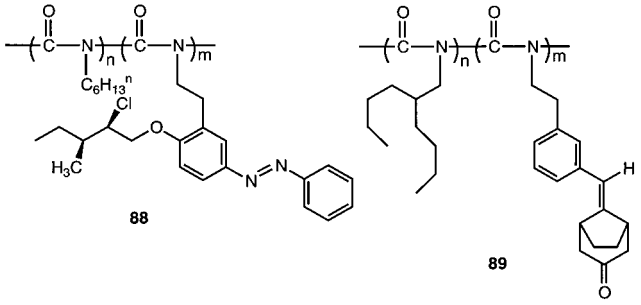
geants and soldiers" effect) (Table 6). The data shown in Table 6 indicate that only 0.5% **84** units can induce an excess helical sense and that 15% **84** units induces the excess helicity essentially the same as that of the homopolymer of **84**. Using structurally different enantiomers along one chain gives rise to an unusual relationship of optical activity and temperature in the polyisocyanates.[164] Optically active block copolymers have been created using the living polymerization catalyst **73** mentioned earlier.[165]

Optically active aromatic isocyanates have been synthesized and polymerized.[152−156,166−169] Poly-(*S*)-**86** prepared by the polymerization using the lithium amide of piperidine showed a very large levorotation ($[\alpha]_{365}$ −1969° to −2014°) which was only slightly affected by temperature.[167] This is in contrast to the fact that the optical activity of polyisocyanates with chiral side chains is often greatly dependent on temperature and may suggest that the poly-(*S*)-**86** has a perfectly single-handed helical conformation. The polymer showed chiral discrimination ability toward 1,1′-bi-2-naphthol and mandelic acid.[167] In the copolymers of **87** with **74b**, the predominant helicity was reversed depending on the ratio of the monomeric units.[169] The polymer having 10% chiral **87**



units showed $[\alpha]^{25}_{365}$ +733°, while the one having 80% **87** units showed $[\alpha]^{25}_{365}$ −1278°.

The helical sense of polyisocyanates **88** and **89** can be controlled in terms of photoinduced isomerization of the side chain chromophores.[165,170] For **88**, photoirradiation causes the cis−trans isomerization of the azo moiety, which induces a change in the helix population of the main chain.[165] In the case of **89** having a chiral bicyclo[3.2.1]octan-3-one group in the side chain, photoirradiation results in rotation around the styryl double bond in the side chain. When (+)- or (−)-circularly-polarized light is used for irradiation, the chirality of the bicyclo[3.2.1]octan-3-one is controlled, leading to a change in the predominant helicity.[170]



An excess helicity is induced by the effect of a chiral solvent or additive.[41,161,171,172] In the case of poly(hexyl isocyanate), a CD spectrum based on an excess helicity was observed in chiral chloroalkane solvents (Figure 10), and the sign and intensity of the CD absorptions changed depending on the kind of solvent.[171] A minute difference in the solvation energy for right- and left-handed helical parts is considered to cause the screw-sense excess. The addition of chiral amino alcohols and amines to polymer **90** having a carboxylic acid residue induced an excess screw sense probably through an acid−base interaction.[172]

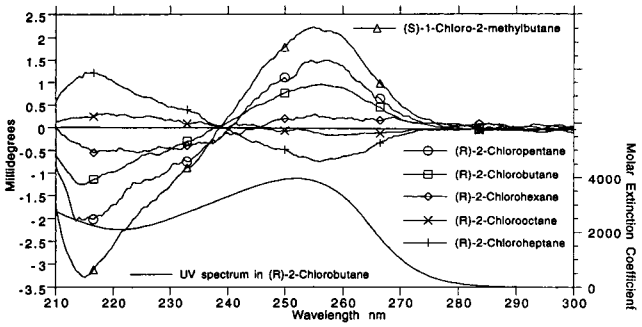
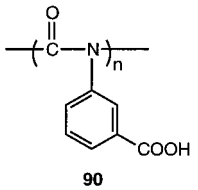
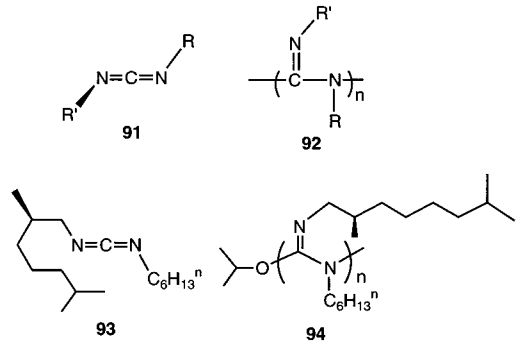


Figure 10. CD spectra of poly(*n*-hexylisocyanate) (poly-**85**) dissolved in optically active solvents at 20 °C. Ultraviolet spectrum (bottom) shown only for (*R*)-2-chlorobutane (polymer concentration 1.9 mg/mL). (Reprinted with permission from ref 171. Copyright 1993 American Chemical Society.)



2. Polycarbodiimides

Carbodiimide **91** gives helical polymer **92** through living polymerization with titanium and copper catalysts.[173,174] The conformation of a polycarbodiimide has been studied by means of NMR.[175] An optically active carbodiimide, (*R*)-**93** ($[\alpha]_{365}$ +7.6°), gives polymer **94** by the polymerization using a titanium catalyst.[176] The polymer showed optical activity essentially identical to that of the monomer; however, on heating, the polymer indicated mutarotation and the specific rotation reached a plateau value of $[\alpha]_{365}$ −157.5° probably based on the excess helical sense of the main chain. The mutarotation has been ascribed to a conformational transition from a kinetically controlled one to a thermodynamically controlled one. An excess single-handed helical conformation can be induced for poly(di-*n*-hexylcarbodiimide) (**95**) by protonating the polymer with (*R*)- or (*S*)-camphorsulfonic acid (**96**) (Figure 11).[176]



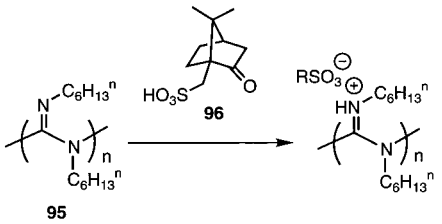


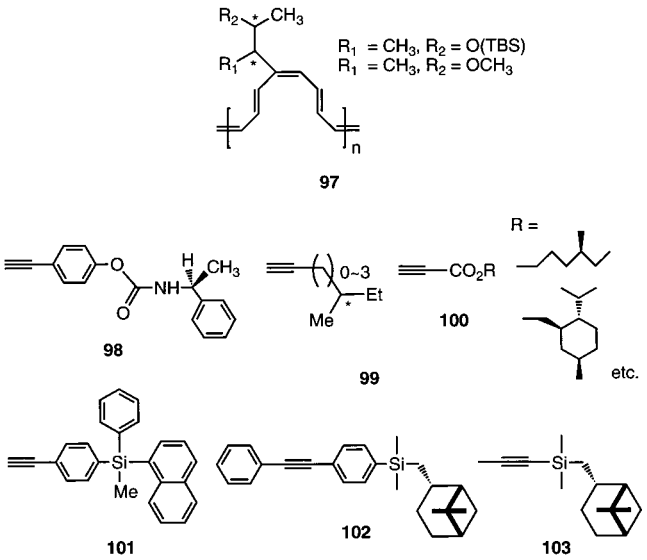
Figure 11. Induction of an excess helix sense for carbodiimide polymer by complexation with camphorsulfonic acid.

G. Polyacetylene Derivatives and Related Polymers

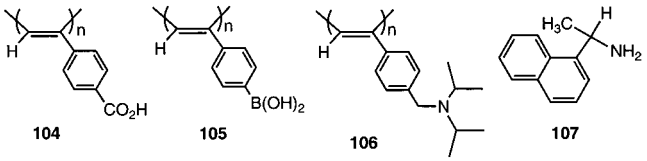
1. Polyacetylene Derivatives

Optically active polyacetylene derivatives **97** were synthesized through ring-opening polymerization of the corresponding cyclooctatetraene derivatives.[25] A twisted conformation of the main chain was proposed on the basis of CD and UV absorptions. Various optically active polyacetylenes have also been prepared from chiral monomers.[24,25,26a,177−183] The examples include a phenylacetylene derivative (**98**),[26a] alkylacetylenes **99**,[24] propionic esters such as **100**,[177,178] a Si-containing monomer (**101**),[179] and disubstituted monomers such as **102**.[180] Poly-(*R*)-**98** synthesized using a $[RhCl(norbornadiene)]_2$ catalyst shows intense CD bands in the UV−vis region, probably based on a predominant helical sense of the main chain.[26a] This polymer effectively resolves several racemic

compounds including Tröger's base, *trans*-stilbene oxide, and methyl phenyl sulfoxide when coated on silica gel and used as chiral packing material for HPLC.[181] More examples of chiral recognition by optically active poly(phenylacetylene) derivatives are known.[182] Chiral recognition by a membrane prepared from optically active poly-**103** has been reported.[183]



Poly(phenylacetylene) derivatives **104**−**106** bearing achiral functional side groups have been synthesized. The polymers possess a stereoregular cis-transoidal structure. Excess single-handed helicity of the main chain can be induced for the polymers by the interaction with chiral molecules.[26b,184−188] For example, **104** shows intense CD bands in the presence of optically active amines and amino alcohols including **107**



(Figure 12).[26b,184] In Figure 12, mirror images of CD spectra were obtained in the presence of the (*R*)- and (*S*)-amine. The CD absorptions are not based on the chiral amine but on the excess helicity of the main chain of **104** as clearly understood from the wavelength range. These results indicate that **104** originally having a rather irregular twist of the adjacent double bonds around a single bond may be transformed into the helical conformation with an excess screw sense by the interaction with the chiral amines (Figure 13). Helicity induction was also found for the Na salt of **104** by the interaction of a natural amino acid including L- and D-methionine.[185]

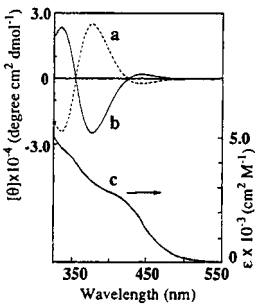


Figure 12. CD spectra of **104** in the presence of (*R*)-**107** (a) and (*S*)-**107** (b) and absorption spectrum (c) in the presence of (*R*)-**107** in DMSO (the molar ratio of **107** to **104** is 50). (Reprinted with permission from ref 26b. Copyright 1995 American Chemical Society.)

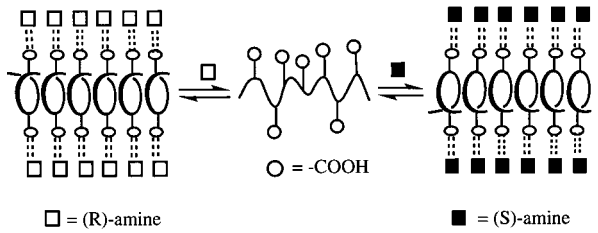


Figure 13. Helix formation of poly(phenylacetylene) derivatives through the interaction with added chiral amine.

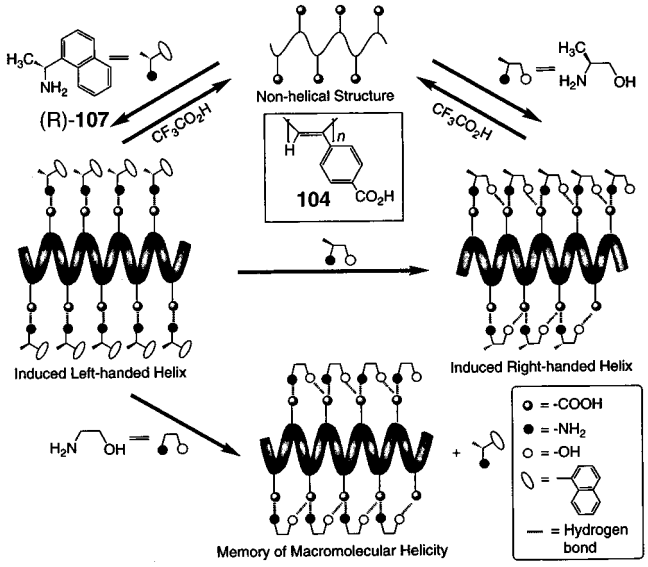
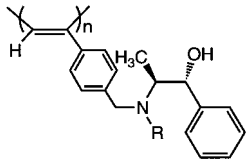


Figure 14. Concept of memory of macromolecular helicity. (Reprinted with permission from Nature (http://www.nature.com), ref 186. Copyright 1999 Macmillan Magazines.)

The concept of "memory of macromolecular helicity" has been introduced for **104** (Figure 14).[186] As discussed above, a right- or left-handed helical conformation is induced for **104** with the interaction with chiral additives. For this system, it was found that the helical conformation is not lost even after the chiral additives are replaced with achiral additives. In the case shown in Figure 14, chiral **107** is replaced with achiral 2-aminoethanol. Hence, the helicity is memorized. The effectiveness of the memory depends sensitively on the structure of the achiral additive replacing the chiral additive. It should be noted that the memorized helical-sense excess increased on storage with *achiral* 2-aminoethanol complexed to **104**.

In the case of **105**, carbohydrates and steroids induced the helicity.[187] A reverse combination of acid and base compared to the helix induction using **104** was achieved using **106**, whose interaction with various chiral carboxylic acids led to an excess screw sense of the main chain.[188,189]

Polymer **108** having a chiral side chain possesses a helical conformation with a predominant helicity due to the effect of the side groups. The predominant helicity was reversed by the interaction with (*R*)-



108a: R = -H
108b: R = -CH_3

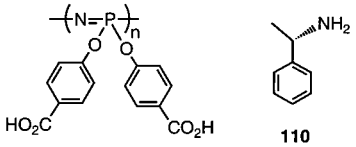
mandelic acid (helix−helix transition), while (*S*)-mandelic acid only slightly affected the conformation of the polymer. The diastereomeric acid−base interaction causes the conformational transition.[190] Complexes of **108** with R_2Zn effectively catalyze the asymmetric alkylation of benzaldehyde.[191]

The poly(phenylacetylene) derivatives discussed here are considered to be molecular probes for chirality detection of various chiral molecules.

As another example of a helical polyacetylene, the single-handed helical polyacetylene fibril, whose structure was studied by SEM, was prepared by the polymerization of acetylene within a chiral nematic liquid crystalline phase.[192]

2. Polyphosphazene

Helicity induction was also realized for polyphosphazene derivative **109** using (*R*)-1-phenethylamine (**110**) as the chiral additive.[193]

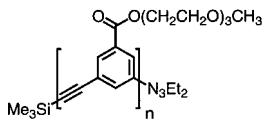


109

110

H. Poly(aryleneethynylene)s

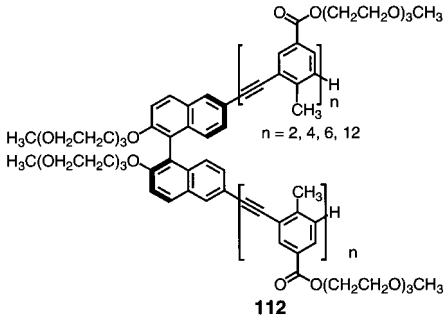
Oligo(*m*-phenyleneethynylene)s **111** have been shown to adopt a helical conformation in acetonitrile, although they do not in chloroform.[33,194] The helix



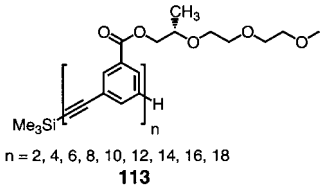
n = 2, 4, 6, 8, 10, 12, 14, 16, 18
111

formation is thought to be a result of the solvatophobic effect: the oligomers fold into a compact, helical structure in a poorer solvent such as acetonitrile. The conformation was proposed on the basis of the hypochromic effect. In acetonitrile and chloroform, the oligomers show a different dependence of the molar extinction coefficient (ϵ) on the DP. In the range of DP = 2−8, ϵ values in acetonitrile are close to those in chloroform in which the ϵ−DP plot is linear. However, in the DP range larger than 8, the slope of the ϵ−DP plot in acetonitrile becomes smaller than that in chloroform, indicating that the overlap of phenylene groups driven by the helix formation (folding of the molecule) causes the hypochromicity in acetonitrile. The absorption spectral pattern also differs depending on the solvent. Intermolecular interaction was ruled out by the spectral studies at various concentrations, and the helical structure was supported by the ^1H NMR measurement, which showed a remarkable upfield shift of the aromatic protons, an indication of overlap of the phenylene groups.

Oligomers **112**[195] and **113**[196] having chiral groups in the main or side chain have an excess helicity. A **112** analogue having a flexible chiral group in place of the binaphthyl group has also been reported.[197] Although the exact values of the helical-sense excess are not known, the chiral oligomers show the characteristic CD bands in acetonitrile, which are not seen in chloroform.

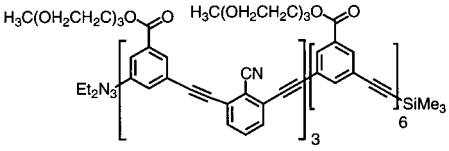


n = 2, 4, 6, 12
112



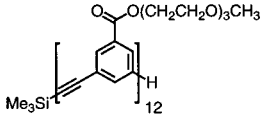
n = 2, 4, 6, 8, 10, 12, 14, 16, 18
113

In the case of oligomer **114**, Ag^+ ions are taken into the interior part of the helix and stabilize the helical conformation.[198]



114

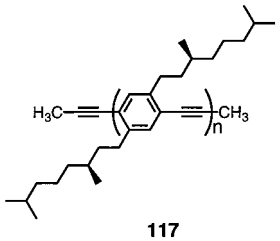
Chiral monoterpenes including (+)-β-pinene (**116**) can induce an excess helicity to achiral **115**. The chiral terpene forms a complex preferentially with right- or left-handed helical **115**, which exists in a dynamic racemic form. This can be regarded as chiral recognition by the helical oligo(phenyleneethynylene).[199]



115

116

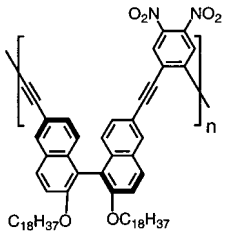
Poly(*p*-phenyleneethynylene) (DP ≈ 500) (**117**) having two chiral side chains per *p*-phenylene unit



117

has been synthesized by alkyne metathesis of the corresponding monomer having two acetylene moieties.[200] The polymer forms aggregates in a poor solvent such as decanol and shows a characteristic bisignate CD spectrum, which is not seen in a solution of chloroform, a good solvent. The contribution of a chiral conformation including the helix of the aggregate to the CD absorptions has been proposed.

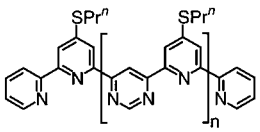
Several poly(aryleneethynylene)s having chiral binaphthylene moieties in the main chain have been prepared.[40,201,202] A propeller-like conformation has been proposed for **118** as one of the possible structures.[201]



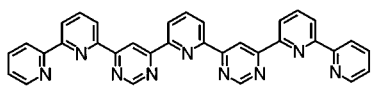
118

I. Polyarylenes

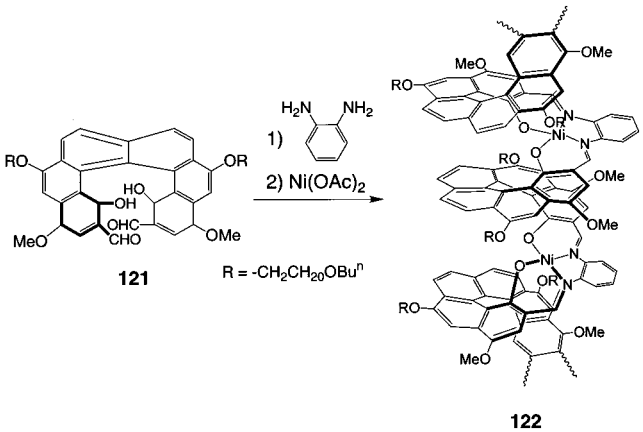
Conformations of oligo(pyridine-*alt*-pyrimidine)s **119** have been studied. On the basis of NMR analysis and the fluorescence spectrum in solution, the oligomers were found to take a helical conformation.[203] The conformation was characterized by distinct chemical shifts (upfield shift), NOE effects, and excimer emission arising from the overlap of aromatic groups. The helical structure was confirmed for **120** in the solid state by X-ray single-crystal analysis.[32] By variable-temperature NMR analyses of **119** ($n = 5$, 8, 12), the oligomers were found to be in an equilibrium of the right- and left-handed helical conformations in solution and the barrier for helix reversal was revealed to be independent of the chain length. This suggests that the helix reversal may take place not through a helix-to-random-to-helix transition including an unwrapping process of the entire chain (a global wrap−unwrap process) but through a stepwise folding mechanism where the transition state is common to **119** with different chain lengths. In the proposed transition state, the right- and left-handed helical parts are connected through a perpendicularly twisted 2,2′-bipyridine moiety. Shorter oligomeric chains were also shown to adopt a helical conformation.[204] Several oligomers with structures similar to those discussed here form polymeric aggregates as described later. A helical structure has also been proposed for poly(*m*-phenylene) on the basis of X-ray diffraction data.[205]



119 (n = 5, 8, 9, 12)



120



121

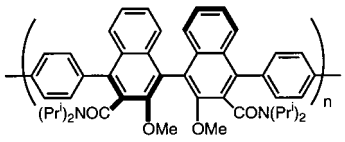
R = -$CH_2CH_2OBu^n$

122

Figure 15. Synthesis of a Schiff-base-type helical polymer.

The reaction of optically active, helicene derivative **121** first with *o*-phenylenediamine and then with $Ni(OAc)_2$ led to a helical polymer ($M_n \approx 7000$) (**122**) having a unique ladder-type structure with Schiff base moieties immersed in the main chain (Figure 15).[206] The polymer showed red-shifted absorptions with respect to nickel salophene, the parent compound for the polymer, supporting the formation of a long conjugation system. Intense CD bands were reported for the polymer.

A polyarylene, **123**, containing a chiral binaphthyl group has been synthesized via the Suzuki coupling reaction.[207] The polymer may have a helical structure segmented by a phenylene group. Another optically active polyarylene has been synthesized and its conformation has been considered.[208]

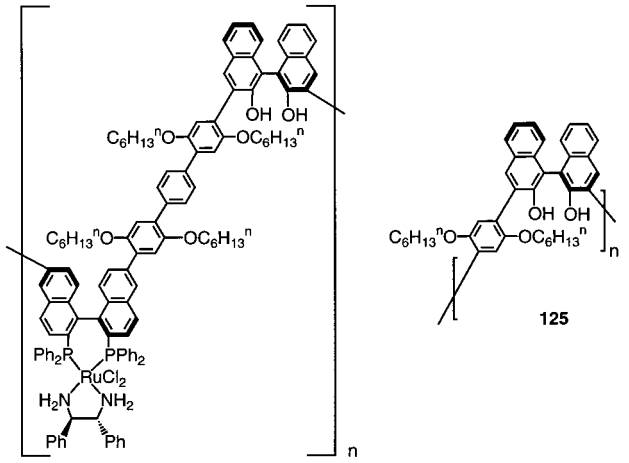


123

Binaphthyl-based polyarylene **124** bearing the Ru−Binaph sites has been synthesized. This polymer has a structural similarity to poly(aryleneethynylene) **118** discussed above and therefore may have a similar propeller-like conformation. **124** complexed with Et_2Z catalyzes a tandem asymmetric reaction involving Et_2N addition and hydrogenation that converts *p*-acetylbenzaldehyde into chiral 1-(1-hydroxypropyl)-4-(1-hydroxyethyl)benzene.[209] Polyarylene **125** bearing a binaphthol unit was also prepared as a polymer ligand. **125** catalyzed the asymmetric reaction of aldehydes with Et_2N. Related binaphthyl-based polyarylenes have been reported.[210] Some more examples using similar polymers are known.[211,212]

A helical structure has been proposed for an oligo(β-pyrrole) on the basis of NMR data and conforma-

tional calculation.[213] The NMR analysis of a trimer having a chiral group at the chain terminal suggested that two diastereomeric conformers existed, which may be right- and left-handed helical ones.



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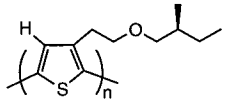
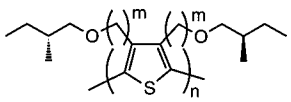
125

Polythiophenes **126** and **127** having chiral side groups have been synthesized, and their conformation has been studied by means of CD absorption and fluorescent spectra.[214,215] For example, polymer **126**



126



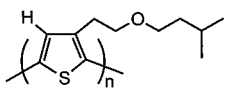
m = 2~7

127

shows a characteristic CD spectrum in a methanol/chloroform mixture, a poor solvent, while no CD absorption is seen in chloroform, a good solvent. In a poor solvent, the polymer forms an aggregate (microcrystalline) in which the polymer chains are stacked on top of each other to have a single-handed helical conformation. The conformation has been reported to be as rigid as that in the solid phase (crystalline phase). In a good solvent, such an aggregate does not form. In addition, the dominant helicity for **126** depends on the solvent. The chiroptical properties of **126** also depended on the ee of the monomeric units, and the dependence was nonlinear. This effect may be based on a cooperative effect of the chiral side chain and may be explained by the "majority rules" concept originally introduced for polyisocyanates.[41]

For polymer **127** with two chiral side chains per monomeric unit, a right-handed helical order of the aggregates has been proposed by interpreting their CD spectra on the basis of the exciton theory and model studies.[216,217]

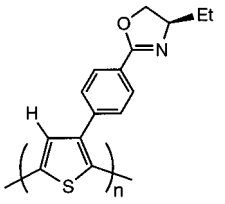
For the mixed aggregates of **126** and **128**, the CD intensity showed a nonlinear relation with the content of **128**.[218] This behavior has a similarity to the optical activity of a copolymer of chiral and achiral



128

isocyanates, which has been interpreted by the sergeants and soldiers theory.[41]

A regioregular polymer, **129**, having chiral monomeric units has been synthesized. This polymer does not show CD absorption in chloroform, a good solvent.



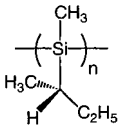
129

However, on addition of $Cu(OTf)_2$ to the solution, the resulting suspension showed strong CD bands.[219] Because no gelling effect was observed and the absorption position did not change on addition of $Cu(OTf)_2$, the CD bands which appeared due to the effect of Cu^{2+} are not based on the π-stacked aggregate suggested for **126**−**128** but on a helical conformation of a single molecule induced by the complexation with Cu^{2+}.

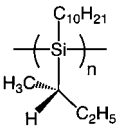
J. Si-Containing Polymers

1. Polysilanes

Polysilanes adopt a helical conformation. This class of polymers has the Si σ conjugating backbone, which allows the conformational study by means of photophysical analysis of the polymers.[30,220−226] Two polysilanes, **130** and **131**, were synthesized by the Na-



130



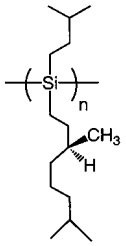
131

mediated condensation reaction of the corresponding chiral dichlorosilanes in the presence of 15-crown-5. **130** consists of right- and left-handed helical parts coexisting in one polymer chain, while **131** is a single-handed helix.[30a,221] **130** showed a positive and a negative peak in the CD spectra corresponding to P-helical and M-helical segments, respectively (the P- and M-notations do not mean the absolute conformation), a rather broad absorption band, and a fluorescent peak whose half-peak width was close to that of the negative peak in the CD spectrum. In addition, the fluorescent anisotropy depended greatly on the wavelength. These features support the belief that a polymer chain of **130** has energetically different P- and M-helical parts. In contrast, **131** exhibited a narrow absorption peak, a CD peak whose spectral profiles match, and a fluorescent peak which is an mirror image of the absorption peak. A slight dependence of the fluorescent anisotropy on the wavelength indicates the presence of an ordered, single-handed helical conformation of **131** with a homogeneous photophysical profile along the chain. Although the tacticity of these polymers is not known, the molecular mechanics calculation on iso- and syndiotactic

models indicated that either configuration can yield a similar helical structure.

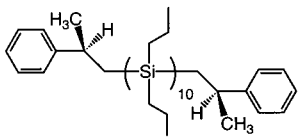
In addition to the polymers described above, the polysilanes having aromatic side groups[222,225] and the copolymers of a chiral monomer and an achiral monomer[224−228] have been shown to adopt a helical conformation. A water-soluble, helical polysilane having an ammonium moiety has also been prepared.[229]

Furthermore, a helix−helix transition was found for polysilane **132** and some copolymers having a 3,7-dimethyloctyl group as a chiral group.[230] In the stereomutation of **132** in an isooctane solution, the ratio of right- and left-handed helices depends on temperature and is 1/1 at −20 °C.



132

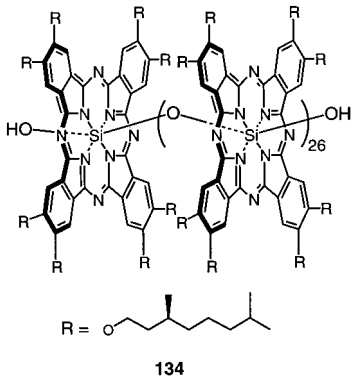
An excess helicity was induced not only by the chirality of the side chain but also by the terminal group. **133** shows the CD absorptions based on an excess helicity at 85K in an isopentane/methylcyclohexane matrix.[231]



133

2. Polysiloxane

Polysiloxane **134** having chiral phthalocyanine moieties as repeating constituents takes a helical conformation in a chloroform solution.[232] The helical structure was indicated to be stable at up to 120 °C in a dodecane solution. On the basis of the CD spectra, the helix was found to be left-handed.



134

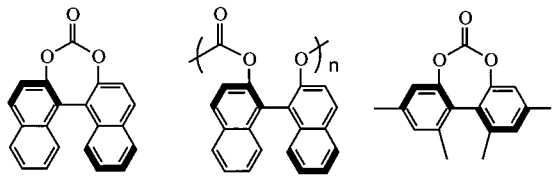
K. Other Types of Polymers

1. Miscellaneous Examples

The electropolymerization of *o*-methoxyaniline in the presence of (+)-(1*S*)- or (−)-(1*R*)-camphorsulfonic acid yields an optically active polyaniline derivative. The polymer shows intense CD bands as a film deposited on an electrode.[233] The polymer is soluble in NMP, $CHCl_3$, DMF, DMSO, and MeOH, and the polymer also showed a CD absorption in solution probably based on a chiral main chain conformation such as a helix. A film made by spin-coating a mixture of polyaniline with camphorsulfonic acid also showed strong CD absorptions that may be based on a helical conformation of the main chain.[233c] The electopolymerization method has been applied to the synthesis of an optically active polypyrrole which may have a helical conformation.[234]

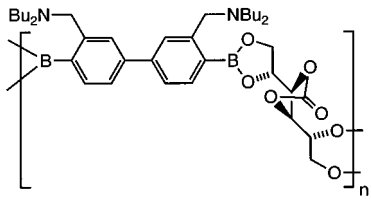
A polyaniline film prepared by doping an emeraldine base with optically active CSA showed a CD spectrum. Even after dedoping, the film exhibited CD bands which were different in pattern from those of the original dedoped film, suggesting that a chiral conformation such as a helix remains in the polymer chain. The dedoped film exhibited chiral recognition ability toward phenylalanine.[235]

By anionic polymerization using *t*-BuOK, an optically active, binaphthyl-based carbonate monomer (**135**) gives polymer poly-**135**, which has a single-handed 4_1-helical conformation.[236] An analogous polymer has been synthesized from a biphenyl-based monomer, **136**.[237,238]



135 poly-**135** **136**

Polycondensation of a corresponding tetraol compound derived from D-mannitol with a bisboric acid compound produces polymer **137**.[239] The M_w of the



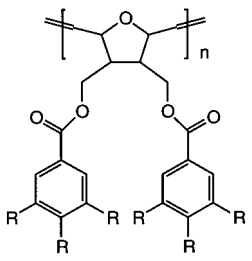
137

polymer was estimated to be 14000 by a light scattering method. The CD spectrum of the polymer had a pattern clearly different from that of the model compound for the monomeric unit and was indicative of a single-handed helical structure. The conformation was supported by MO calculation.

A poly(7-oxabicyclo[2.2.1]hept-2-ene) derivative (polymerization using $RuCl_3$), **138**, and a poly(*N*-phenylmaleimide) derivative (radical polymerization) bearing phenyl groups having long alkyl chains form a hexagonal columnar liquid crystalline phase.[240] The polymers are proposed to take a helical conformation that may be stabilized by the intra- and intermolecular interaction of the side chains.

There are some examples of polyamides, poly(arylene ether)s,[241] polyimides,[242,243] and poly-

amides[244,245] having 1,1′-binaphthylene-2,2′-diyl or biphenylene units that introduce chiral twists in the polymer chain. The chiral groups are expected to make the entire chain take a helical conformation. Earlier studies based on similar molecular designs are referenced in ref 243.



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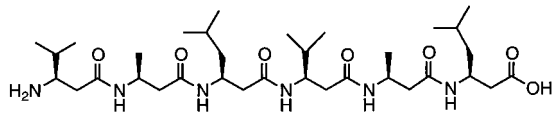
Support for a helical structure of polyketones arose from chiroptical studies as a function of temperature in the glassy state.[246]

2. Mimics and Analogues of Biopolymers

β-Peptides form well-defined, stable secondary structures including a helical structure as well as α-peptides.[7−10,247] A helical structure was proved for *β*-peptide 139 in solution by NMR studies.[9,248−251] The fact that **139** consisting of only six monomeric units has a stable helical conformation is interesting because a longer monomeric sequence (10−15-mer) is generally needed for α-peptides except for those containing proline or a 2-amino-2-methylpropanoic acid residue. A similar helical structure has been found for *β*-peptide **140** in the solid state and in



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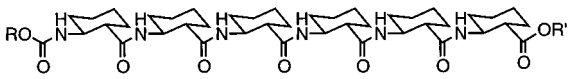
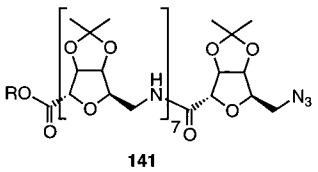


140

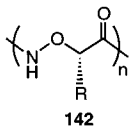
solution.[10,252,253] These two *β*-peptides form a 3/1-helix, while an α-helix for α-peptides is a 3.6/1-helix. A series of **140** analogues having different cyclic structures in the main chain have been synthesized; the helical pitch depends on the ring structures.[253,254]

Helical conformations have also been found or postulated for peptide analogues including *γ*-peptides,[255] an octameric 5-(aminomethyl)tetrahydrofuran-2-carboxylate (**141**),[256] a vinylogous peptide,[257] vinylogous sulfonamidopeptides,[258] peptides of α-aminoxy acids (**142**),[259] and polypeptoids (*N*-substituted glycine oligomers) **143**.[260] The oligoanthranilamide **144** was found to have a helical conformation in the solid state by X-ray analysis.[261,262] **144** also takes a helical conformation in solution as proved by NMR analysis. An analogous oligomer has been studied.[263]

Gene analogues have been synthesized, and their conformational aspects have been studied.[264] Peptide nucleic acid (PNA) **145** and pentopyranosyl-(2′→4′) oligonucleotides **146** and their analogues form DNA- or RNA-like double-helical strands.[265]



141



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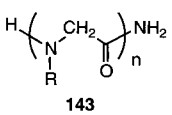

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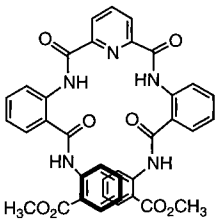

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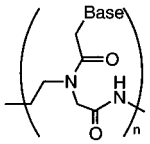
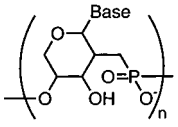


145



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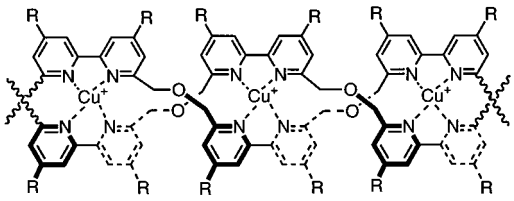
III. Helical Polymeric Complexes and Aggregates

A. Helicates

There is a class of metallic complexes called helicates.[31,266−271] Such complexes typically consist of two or three oligomeric chains containing bipyridine moieties and transition metals. The oligomeric chains form a double- or triple-helical complex with the metallic species inside the complex coordinated by the pyridyl moieties. Intensive studies have been preformed in this area, and there are comprehensive reviews covering various aspects.[31,266−270] As an interesting example, the helicates with a generic structure, **147**, have been synthesized: the helicates have nucleoside residues in the positions of R and may be regarded as an artificial system mimicking the double-helical structure of DNA.[271]

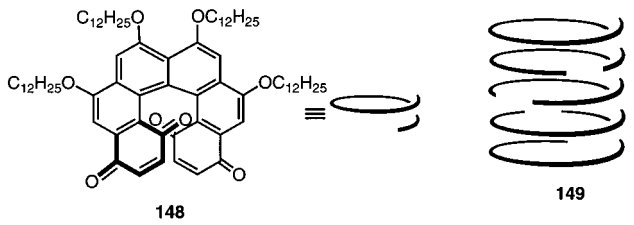


147

B. Helical Aggregates

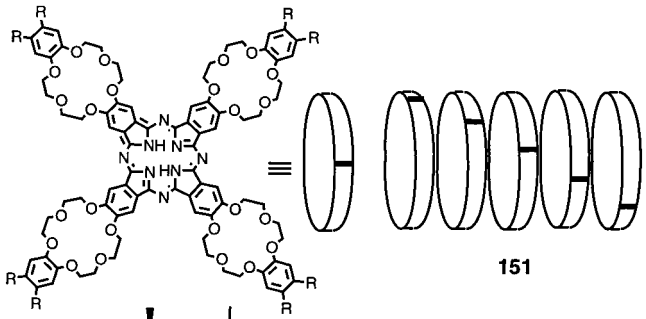
Polymeric aggregates having a helical structure are known though they are not in the category of conventional polymers. Hexahelicenequinone **148** (ee 98−99.5%) and its analogues cause aggregation in a concentrated solution in *n*-dodecane and show intense CD absorptions.[272−274] The aggregate formation was studied by NMR, UV−vis spectra, light scattering, and viscosity. A polymeric columnar aggregate

(**149**) in which the molecules are stacked along their helix axes has been proposed.



148 149

A chiral crown ether compound based on phthalocyanine (**150**) forms a linear polymeric aggregate (**151**) in which the π-electron systems are stacked on top of each other in a mixture of chloroform and

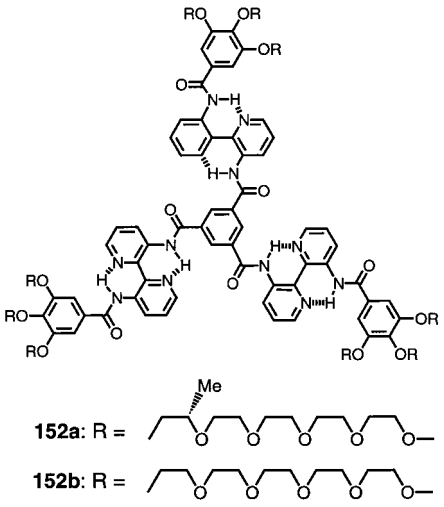


150 151

methanol.[275] The addition of excess K^+ ion to the aggregate destroys the helical structure; the complexation between the crown ether moiety and K^+ weakens the interaction between the chromophores.

Similar helical aggregates have been constructed for oligo(pyridine−pyrimidine)s and a oligo(pyridine−pyridazine) in a solution of chloroform, dichloromethane, or pyridine.[276,277] The helical structure was elucidated by NMR spectroscopy, vapor pressure osmometry, and freeze-fracture electron micrography and was supported by molecular modeling.

Compounds **152a,b** having a planar structure stabilized by intramolecular hydrogen bonds form rodlike aggregates in which **152a** or **152b** molecules are densely stacked.[278,279] The aggregate of **152a** in water showed a CD spectrum which suggested a



helical chirality within the aggregate. Moreover, an aggregate consisting of 8% chiral **152a** and 92% achiral **152b** also showed CD absorptions whose intensity was comparable with that of the spectrum of the **152a** aggregate. This means that a small amount of **152a** incorporated into an aggregate consisting mostly of **152b** can induce an excess helicity in the aggregate.

IV. Summary and Outlook

A wide spectrum of synthetic polymers, polymeric complexes, and aggregates that have or may have a helical conformation were reviewed. The synthetic method varies from the addition polymerization methods for the vinyl and related polymers to the simple mixing methods for the aggregates. Some of the polymers exhibited functions based on the helical structure such as chiral recognition and asymmetric catalyses.

Since our last review was published in 1994, a large volume of research work has been published in this field, and the structural variation of helical polymers has been significantly broadened. The relatively new examples include polyacetylene derivatives, poly(aryleneethynylene)s, polyarylenes, silane-containing polymers, polycarbonates, biopolymer-mimicking oligomers, and some aggregates and complexes. Apart from the structural variation, notable progress lies in the introduction of the concept of dynamic helices through the studies on the polyacetylene derivatives, which are not helical themselves but become helical on the basis of relatively weak interaction with chiral additives. This finding implies that basically any flexible polymer such as PMMA or polystyrene may take a dynamic helical conformation in solution if an adequate additive is chosen, though the configurational control of the polymer chain may be prerequisite.

Knowing that the field of synthetic chemistry is always expanding and that so many new variations of chemical reactions are being made possible using new catalyses, newer helical polymers may be introduced by incorporating the advanced synthetic techniques into polymer synthesis in the future.[280] In addition, by taking full advantage of the structural variation of helical polymers so far realized and the sophisticated functions of natural macromolecules with a helical conformation, the spectrum of their applications will also be broadened.

V. Acknowledgments

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VI. References

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