Synthesis and Chiral Recognition of Helical Polymers

Yoshio Okamoto[a]; Tamaki Nakano[a]; Shigeki Habaue[a]; Kei Shiohara[a]; Katsuhiro Maeda[a]

[a] Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Japan

PLEASE SCROLL DOWN FOR ARTICLE

SYNTHESIS AND CHIRAL RECOGNITION OF HELICAL POLYMERS

**Yoshio Okamoto,* Tamaki Nakano, Shigeki Habaue,
Kei Shiohara, and Katsuhiro Maeda**
Department of Applied Chemistry
School of Engineering
Nagoya University
Furo-cho, Chikusa-ku 464-01, Japan

ABSTRACT

Asymmetric syntheses of optically active polymethacrylate, poly-acrylate, polyacrylamide, and polyisocyanate with helical confor-mation and their chiral recognition abilities are described. 1-Phe-nyldibenzosuberyl methacrylate (PDBSMA) gave a purely one-handed-helical, optically active polymer ($[\alpha]_{365}$ +1670 ~ +1780°) with almost perfectly isotactic structure by anionic polymerization using optically active initiators. Radical polymerizations of PDBSMA using chiral initiators, chain transfer agents, and addi-tives also afforded optically active polymers with a prevailing one-handed helicity. Triphenylmethyl acrylate yielded an optically active, helical polymer ($[\alpha]_{365}$ +102°) having a dyad isotacticity of 70% using an optically active anionic initiator. Although the poly-acrylate demonstrated chiral recognition ability as a chiral stationary phase for HPLC, the ability was low mainly because of the low degree of one-handedness. N-(3-Chlorophenyl)-N-phenylacryl-amide gave an optically active, helical polymer ($[\alpha]_{365}$ −343°) in the asymmetric anionic polymerization; the polymer had a dyad tacticity of 77%. Optically active polyisocyanates with a predom-inantly one-handed helical conformation were prepared in homo- and co-polymerization of optically active phenyl isocyanate deriv-ative. These polyisocyanates showed the ability to discriminate en-antiomers in solution.

INTRODUCTION

Many stereoregular polymers have helical conformation in the solid state and some of them can maintain the structure even in solution. Helical structure is chiral and, therefore, one-handed helical polymer is optically active [1]. Helical polymers are interesting because they may show high chiral recognition for enant-iomers and several helical polymers including polymethacrylates and poly-saccharide derivatives have been practically used as stationary phases for HPLC to separate a wide range of enantiomers [1, 2, 3]. Optically active polymers having a prevailing one-handed helicity have been prepared through asymmetric (helix-sense-selective) polymerization of prochiral monomers such as methacrylates, acry-lates, crotonate, N,N-disubstituted acrylamides, chloral, isocyanides, and isocya-nates by using optically active initiators [1, 4]. Here, helix-sense-selective radical and anionic polymerizations of 1-phenyldibenzosuberyl methacrylate (PDBSMA), triphenylmethyl acrylate (TrA), N,N-diphenylacrylamide (DPAA), and aromatic isocyanates are mainly discussed.

Polymethacrylates

Purely one-handed helical poly(triphenylmethyl methacrylate) [poly-(TrMA)] is the first vinyl polymer of its kind [5, 6, 7]. Poly(TrMA) has an almost perfectly isotactic configuration and its helical conformation is maintained by steric repulsion between the bulky side groups. The optically active poly(TrMA) can resolve many classes of racemates when used as a chiral stationary phase for high-performance liquid chromatography (HPLC) [3]. However, the poly(TrMA) has a shortcoming that the ester linkage is readily solvolyzed by methanol which is often used as an HPLC eluent. In order to overcome this drawback, we designed 1-phenyldibenzosuberyl methacrylate (PDBSMA) [8, 9, 10]. Solvolysis of triaryl esters is considered to involve a triaryl cation as an intermediate that can be stabil-ized by delocalization of the cation by a planar resonance structure, while such a planar structure is difficult for a 1-phenyldibenzosuberyl cation due to the presence of an ethylene group tying two phenyl groups. Higher durability of PDBSMA against solvolysis compared with TrMA was evidenced by a decomposition exper-iment in a mixture of $CDCl_3$ and CD_3OD at 35°C monitored by means of ^1H NMR spectroscopy ($[PDBSMA]_o = 0.40 \ mol \cdot l^{-1}$). Half-life period for PDBSMA under aforementioned conditions was 89.0 minutes, while that for TrMA was 14.5 minutes under the same experimental conditions, which demonstrates the validity of the monomer design [9].
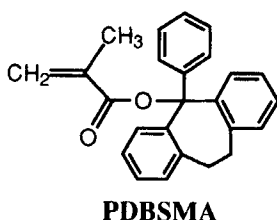
$$CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle \quad}{C}}-\overset{\displaystyle}{\underset{\displaystyle O}{C}}-O-$$

PDBSMA

TABLE 1. Asymmetric Anionic Polymerization of PDBSMA Using DPEDA-Li Complexes[a]

Run	Ligand	Time, h	DP[b,c]	Mw/Mn[b,c]	Tacticity[b,d], mm %	$[\alpha]_{365}$[b,e]	$[\alpha]_D$[b,e]
1	(–)-Sp	24	80	1.30	>99	+1670°	+422°
2	(+)-DDB	3	48	1.07	>99	+1778°	+477°
3	(+)-PMP	3	43	1.10	>99	+1755°	+468°

[a] Conditions: monomer 1 g, toluene 20 mL, temperature –78°C,
[monomer] / [initiator] = 20.
[b] Oligomer free polymer (benzene-hexane (1/1)-insoluble part of crude products). Crude products contained oligomers showing negligible optical activity.
[c] Determined by GPC of PMMA derived from poly(PDBSMA).
[d] Determined by ^{1}H NMR of PMMA derived from poly(PDBSMA).
[e] In THF, c 1.0 g/dl.

PDBSMA leads to an optically active, one-handed helical polymers as well as TrMA by anionic polymerization using optically active initiators [9]. Table 1 shows the conditions and results of anionic polymerization using the complexes of N,N'-diphenylethylenediamine monolithium amide (DPEDA-Li) with (–)-spar-teine (Sp) , (+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), and (+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP). The obtained polymers were nearly 100% isotactic and showed high optical activity, suggesting that the polymers have helical conformation with single-handed screw sense. GPC analysis of the polymers by simultaneous UV (254 nm) and polarimetric (Hg) detections indicated that the optical activity of the polymers was almost constant regardless of molecular weight. Also, existence of (–)-component was not clearly detected in the attempted HPLC resolution of the (+)-polymers obtained in this study. This result demonstrates that the polymers are pure one-handed helical. The optically active poly(PDBSMA) exhibited chiral recognition ability to several racemic compounds.

DPEDA-Li   **Sp**   **(+)-DDB**   **(+)-PMP**
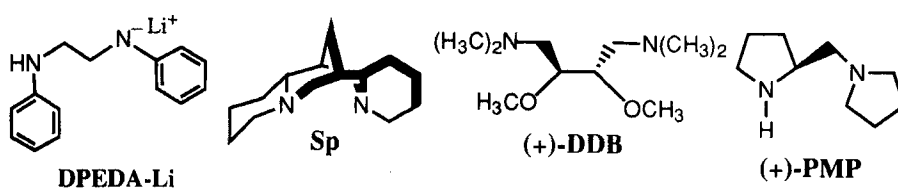
TABLE 2. Free Radical Polymerization of PDBSMA[a]

Run	Initiator	Temp. , °C	Yield[b] , %	DP[c]	Tacticity[b,d] , mm %
1	AIBN	60	76	337	>99
2	$(i\text{-PrOCO}_2)_2$	40	88	361	>99
3	$(i\text{-PrOCO}_2)_2$	30	88	554	>99

[a] Conditions: monomer 0.5 g, [monomer]$_0$ = 0.17 M, [monomer] / [initiator] = 50.

[b] Hexane-insoluble part of crude products.

[c] Determined as PMMA by GPC.

[d] Determined by ^{1}H NMR of PMMA derived from poly(PDBSMA).

Interestingly, radical polymerization of PDBSMA gives almost perfectly isotactic polymers as well as anionic polymerization (Table 2) [8]. The isotactic poly(PDBSMA) obtained with radical initiators is an equimolar mixture of right- and left-handed helices as proved by HPLC resolution. This means that optically active, helical poly(PDBSMA) with excess one-handedness can be obtained if chiral conditions are applied for radical polymerization. Based on this idea, we investigated asymmetric radical polymerization using chiral initiators, chain transfer agents, and additives (solvents) [10].

Polymerization using chiral peroxide compounds ((−)-DMP and (−)-CMPB) gave optically active polymers ([α]$_{365}$ +40°, +20°) [10]. However, the optical activity was found to be based on the chiral initiator fragment attached to the chain terminal.
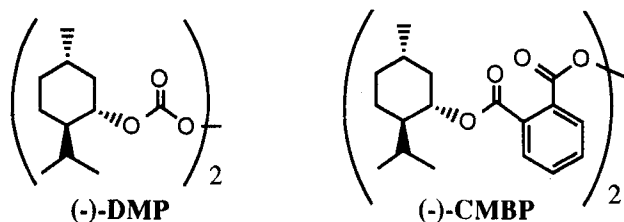

(-)-DMP   **(-)-CMBP**

TABLE 3. Polymerization of PDBSMA Using $(i\text{-PrOCO}_2)_2$ in the Presence of NMT[a]

Run	NMT	$\frac{[NMT]}{[Monomer]}$	Yield[c] , %	THF-insol. part Yield , %	DP[d]	THF-sol. part B/H[b]-insol. part Yield , %	$[\alpha]_{365}$[e]	DP[d]	B/H[b]-sol. Yield , %
1	(+)-isomer	0.05	82	73	120	2	−80°	42	7
2	(+)-isomer	0.2	71	54	84	5	−140°	42	12
3	(−)-isomer	0.4	18	~0		11	−140°	40	7
4	(−)-isomer	0.4	19	~0		10	+110°	51	9

[a] Conditions: monomer 0.5 g; toluene 8 mL, [monomer] / $[(i\text{-PrOCO}_2)_2]$ = 50; temp. 40°C; time 24h.

[b] A mixture of benzene and hexane (1/1).

[c] Hexane-insoluble products.

[d] Determined by GPC of PMMA derived from the original polymer using polystyrene standard samples.

[e] Measured in THF.

Use of optically active neomenthanethiol ((+), (−)-NMT) was effective in inducing excess single-handed helicity in polymerization of PDBSMA [10]. The conditions and results of polymerization in the presence of (+)- and (−)-NMT are summarized in Table 3. The polymerization products were fractionated into three parts, i.e., THF-insoluble part, THF-soluble and benzene/hexane (1/1) (B/H)-insoluble part, and THF-soluble and B/H-soluble part. Molecular weight of the fractions decreased in this order. The lowest molecular-weight fraction mainly contained oligomers. The THF-soluble and B/H-insoluble parts of the polymers obtained using (+)-NMT showed levorotation and their CD was quite similar in pattern to that of purely one-handed helical polymers obtained by asymmetric anionic polymerization. In addition, the polymerization using (−)-NMT gave a dextrorotatory polymer. These results indicate that the optical activity of the polymers is based on excess single-handed helicity and the helicity is controlled by NMT chirality. An insight into the chiral induction mechanism was gained from GPC analysis of the THF-soluble and B/H-insoluble fraction. GPC analysis of the (−)-polymer of run 2 in Table 3 using simultaneous concentration (UV) and polarimetric detections revealed that this polymer consisted of (−)- and (+)-fractions having higher and lower molecular weights, respectively. This suggests that chiral induction took place at least in part in the termination processes which may involve

the hydrogen transfer from NMT to a growing radical and the coupling of a grow-ing radical and a thio radical formed through the hydrogen transfer. Higher activity of helical radical leading to the (+)-polymer than its counterpart in the termination reaction can explain the GPC results. GPC fractionation (separation) gave (−)-polymer with specific rotation as high as $[\alpha]_{365}$ −750° which corresponds to a ratio of (−)- and (+)-helices of 7 to 3.

(+)-NMT   (−)-NMT
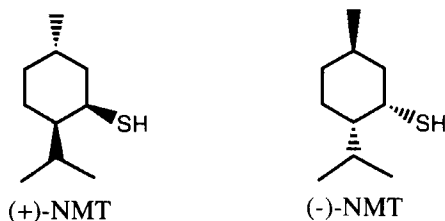
Polymerization in mixture of (+)- and (−)-menthol and toluene (conc. 2.6 g/ml) also produced the optically active polymers with excess single-handed helicity [10]. Chiral induction in this case appeared to involve chain transfer processes sim-ilarly to the polymerization in the presence of the thiols.

PDBSMA gave optically active polymer by radical polymerization in the presence of (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamin-atocobalt (II) (1) [11]. The specific rotation of the polymer increased with increas-ing molecular weight and GPC separation gave a purely one-handed helical poly-mer.

1
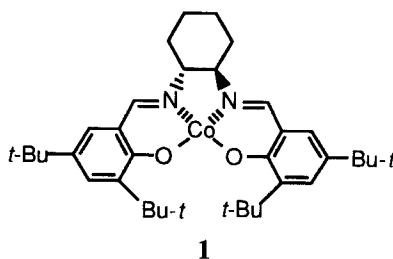
Polyacrylates [12,13]

In general, tacticity control in the polymerization of acrylates is more difficult than that of methacrylates. For example, it has been reported that triphenylmethyl acrylate (TrA) forms a polymer with much less isotacticity in anionic polymer-ization as well as in radical polymerization in comparison with TrMA [14]. How-ever, TrA can also afford an optically active polymer having a stable helical conf-ormation in the asymmetric polymerization with chiral anionic initiators.

TrA
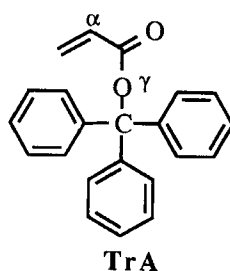
Optically active poly(TrA) is obtained in the polymerization using the complexes of DPEDA-Li with chiral ligands, (–)-Sp, (+)-DDB, and (+)-PMP in toluene at –78°C for 24 hours (Table 4) [12]. The polymerization proceeds quantitatively in all cases, and the tacticity and specific rotation of polymers are greatly affected by the ligands. The specific rotation of the polymers seems to increase with an increase of the isotacticity, and the (+)-PMP system affords the polymer of the highest specific rotation ($[\alpha]_{365}$ +102°) and isotacticity (m = 0.70) (Run 1). However, these values are much smaller than those ($[\alpha]_{365}$ +1500°, mm > 0.99) of one-handed helical, optically active poly(TrMA) [6].

The CD spectrum of (+)-poly(TrA) (Run 1 in Table 4) is shown in Figure 1(a). The spectrum demonstrates the positive peaks at 210 and 230 nm which may be ascribed to the absorption due to the aromatic and carbonyl groups, respectively. This spectral pattern is quite similar to that of the one-handed helical, optically active poly(TrMA). This suggests that the optical activity of the poly(TrA) may be attributed to a partially one-handed helical structure of the polymer chain. The degree of one-handedness must be lower than that of the poly(TrMA) judging from the smaller optical activity and isotacticity of the polymer.

The specific rotation ($[\alpha]_{365}$ +85°, c = 0.91) of (+)-poly(TrA) in THF did not change in 50 minutes at 25°C. However, the optical activity gradually increased at 60°C and reached about +138° after 20 minutes. Then the solution became turbid. These results indicate that the (+)-poly(TrA) is conformationally stable at room temperature but some conformational change and association occur at a higher temperature. In chloroform, the (+)-poly(TrA) precipitated immediately after the dissolution.

To obtain information about the contribution of a configurational factor to the chiroptical property of the polymer, the (+)-poly(TrA) (Run 1 in Table 4) was converted to poly(methyl acrylate) (PMA) by hydrolysis in methanol containing a small amount of hydrochloric acid followed by methylation with diazomethane. The PMA showed a small negative specific rotation ($[\alpha]_{365}$ –18°), which is opposite in sign to that of the (+)-poly(TrA). The CD spectrum of the PMA was

TABLE 4. Polymerization of TrA by DPEDA-Li Complexes in Toluene at −78°C for 24h[a]

Run	Chiral ligand	Yield[b], %	DP[c]	Mw / Mn^c	Tacticity, $m : r$	$[\alpha]_{365}$[d]
1	(+)-PMP	96	46	1.28	0.70 : 0.30	+102° [e]
2	(−)-Sp	98	57	2.94	0.64 : 0.36	n.d.[f]
3	(+)-DDB	100	61	1.38	0.49 : 0.51	−7°

[a] [TrA] / [Initiator] = 20.

[b] Methanol-insoluble part.

[c] Determined by GPC (polystyrene standard).

[d] Measured in CHCl3 at 25°C.

[e] $[\alpha]_D$ = +22° (c = 1.53).

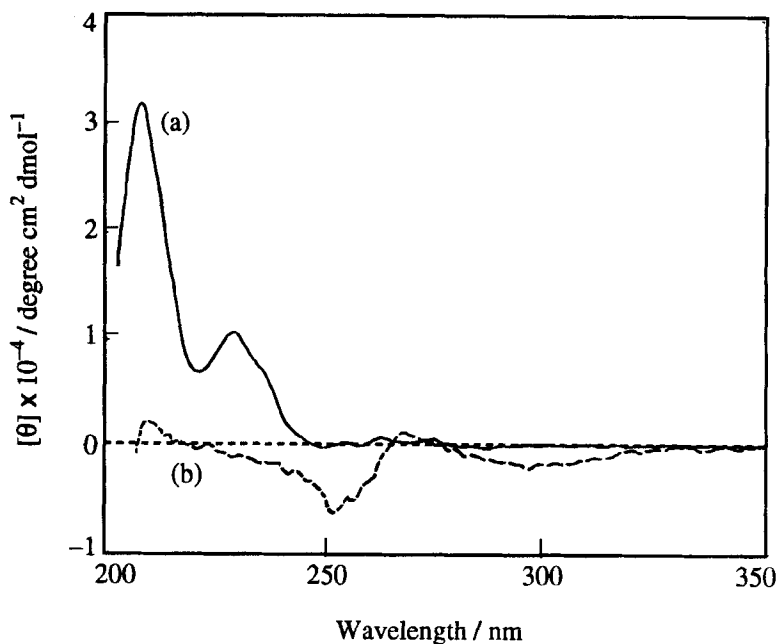[f] Not determined. The obtained polymer was partly insoluble in common organic solvents.

Figure 1.   CD spectra of (+)-poly(TrA) (a) and (−)-PMA (b) derived from the (+)-poly(TrA) in THF. The molar concentration of (+)-poly(TrA) was calculated on the basis of the monomeric unit (Mw = 314) and that of (−)-PMA on the basis of the polymer molecules (Mw = 4.9 x 10³).

quite different in pattern from that of poly(TrA) (Figure 1). The optical activity of the PMA may be mainly due to the chirality near polymer ends because the CD peaks of PMA are attributed mainly to the absorption of the initiator residue, an N,N'-diphenylethylenediamino group. The induction of the configurational asymmetry clearly occurs at the initial stage of the polymerization and may continue through the polymerization to produce the prevailing conformational asymmetry in the polymer chain.

The chiral recognition ability as a chiral stationary phase for HPLC of the poly(TrA) prepared with (+)-PMP-DPEDA-Li complex (run 1 in Table 4) was investigated. Packing material was prepared in the same procedure as that for poly(TrMA) using macroporous silica gel [3]. The poly(TrA) phase separated *trans*-stilbene oxide with a capacity factor for the first eluted enantiome $k'_1 = 4.9$ (−) and separation factor $\alpha = 1.16$ (eluent: MeOH, flow rate: 0.5 mL/min). However, the ability of poly(TrA) is much lower than that of poly(TrMA) with high chiral recognition ability for a broad range of racemates [3]. This lower chiral recognition of poly(TrA) is explained mainly by the lower degree of one-handedness of poly(TrA). Purely one-handed poly(TrA) would show high chiral recognition as well as poly(TrMA).

Poly(*N,N*-diphenylacrylamides) (DPAA) [15, 16, 17]

N,N-Diphenylamino group of DPAA is smaller than triphenylmethyl group of TrA, but the former is in the b-position with respect to the C=C double bond while the latter is in the β-position. Therefore, there exists a possibility to form an optically active polymer with a helical conformation in the asymmetric polymerization. Actually, optically active polymers have been obtained in the asymmetric anionic polymerization of various DPAA derivatives, using the complexes of fluorenyllithium (FlLi) with (−)-Sp in toluene at −98°C. The tacticity of the obtained polymer was determined by ^{1}H NMR analysis of poly(methyl acrylate) (PMA), which was carefully derived from poly(DPAA) by solvolysis in a mixture of sulfuric acid and methanol followed by methylation with diazomethane [16].
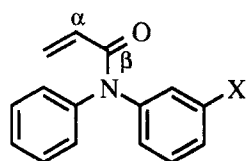
3-XDPAA
(X = H, OMe, Me, Cl)

TABLE 5. Polymerization of 3-XDPAAs with (–)-Sp-FlLi in Toluene at $-98°C^a$

Run	X	Time , h	Yield[b] , %	DP[c]	Mw / Mn^c	Tacticity[d] , $m : r$	$[\alpha]_{365}{}^c$
1	H	2	93	54	1.25	0.74 : 0.26	–249° [g]
2[f]	H	1	91	48	1.16	0.64 : 0.36	–201° [g]
3	OMe	2	93	52	1.06	0.58 : 0.42	–130°
4	Me	2	75	43	1.10	0.57 : 0.43	–142°
5	Cl	2	82	41	1.15	0.77 : 0.23	–343° [h]

[a] [Monomer] / [Initiator] = 20.

[b] Methanol-insoluble part.

[c] Determined by GPC (polystyrene standard).

[d] Determined by ^1H NMR using poly(methyl acrylate) derived from the original polymer.

[e] Measured in $CHCl_3$ (c = 1.0, 25°C).

[f] Polymerization temp.: –78°C.

[g] In $CHCl_3-CF_3CO_2H$ (c = 0.5, 25°C).

[h] $[\alpha]_D = -52°$ ($CHCl_3$, c = 1.0, 25°C).

Table 5 shows the results of the polymerization of 3-XDPAA's [17]. The polymerization was proceeded in good yields to afford the polymers of negative optical rotation with a narrow molecular weight distribution (Mw/Mn = 1.06 ~ 1.25). Optically active poly(3-XDPAA)s (X = Me, OMe, Cl) are soluble in common organic solvents such as chloroform and THF, whereas the optically active poly(DPAA) is less soluble. Some characteristic features of the polymerization are as follows: (1) The specific rotation of the obtained polymers increases with an increase of the isotacticity, and reached to –343° ($[\alpha]_{365}$) when the dyad isotacticity (m) was 0.77. (2) The specific rotation of the polymers de-pends on the *meta*-substituents and increases in the order of Cl > Me > MeO. (3) The CD measurement of the polymer indicates that the optical activity of the obtained polymer may be attributed to the partially constructed one-handed helical structure produced through the polymerization process. These results suggest that the polymer with a higher optical rotation will be obtained if the tacticity of the polymers is more strictly controlled.

The conformational stability of (–)-poly(3-ClDPAA) ($[\alpha]_{365}$ –343° in $CHCl_3$) was investigated in $CHCl_3$ at 60°C. The optical activity did not change for 7 hours at 60°C, demonstrating that the optical active poly(3-ClDPAA) is con-formationally stable.

Poly(aromatic isocyanate)

Poly(alkyl isocyanates) are well known to have a helical, stiff polymer chain and have been extensively studied [18]. On the other hand, poly(aromatic iso-cyanates) had been considered to be flexible polymers which would not have a helical polymer chain [19]. However, we recently demonstrated that optically active polymers can be obtained from aromatic isocyanates such as *m*-methylphenyl isocyanate **2** by using optically active anionic initiators, for instance lithium salts of optically active amines (–)-MMP and (+)-PMP [20]. The optical activity of the polymers is due to the prevailing one-handed helicity which is induced on the polymers due to the initiator residues on a polymer chain end. This result indicates that the main chains of poly(aromatic isocyanates) are also rather stiff.

$$N=C=O$$

2   (–)-**MMP**
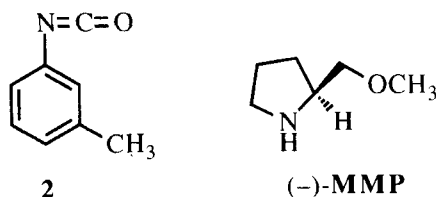
An optically active phenyl isocyanate derivative **3** ($[\alpha]_{365}$ +63° was polymerized and copolymerized with achiral *m*-methoxyphenyl isocyanate **4** by using the lithium salt of piperidine in THF at –98°C [21]. The obtained homopolymer showed a very large specific rotation ($[\alpha]_{365}$ –1969°), whose sign is opposite to that of **3**, and an intense CD band in the absorption range of the polymer backbone was observed. These results indicate that this polymer has a predominant one-handed helical conformation. The specific rotation ($[\alpha]_{365}$ –1094°) of the copolymer (**3/4** = 0.1/0.9) showed a large temperature dependence and increased with a decrease in temperature. This is probably due to the fact that at lower temperature the persistence length of the polymer chain may increase. On the other hand, the specific rotation of the homopolymer showed little temperature dependence. These results suggest that the homopolymer may be perfectly one-handed at room temperature.

3   4
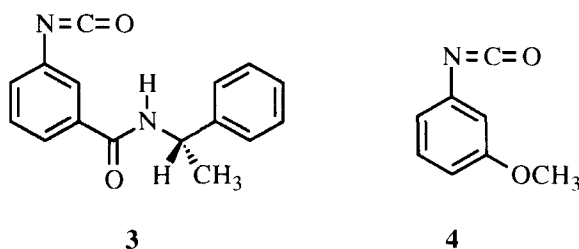
In the presence of poly(3) or poly(3-*co*-4) (3/4 = 0.5/0.5) in CDCl$_3$, the ^{1}H NMR spectra of (±)-1,1'-bi-2-naphthol and (±)-mandelic acid showed the peaks due to enantiomers. This clearly indicates that poly(3) and poly(3-*co*-4) can discriminate the enantiomers even in the solution. This may be the first example of the chiral discrimination by poly(isocyanates).

CONCLUSION

Optically active polymers with helical structure were synthesized by asymmetric anionic polymerization of the acrylic monomers and aromatic isocyanates. Optically active poly(methacrylate)s with prevailing one-handed helicity were also prepared by radical methods using chiral initiators, chain transfer agents, and additives. The helical structure of the obtained polymers from acrylic monomers is maintained by steric repulsion between the bulky side groups. The prevailing one-handed helical conformation of the obtained optically active poly(iso-cyanate)s is induced by the chiral substituent on phenyl group as well as chiral initiator residues attached to the polymer chain end. The obtained optically active polymers exhibited chiral recognition in NMR and HPLC.

REFERENCES

[1]   Y. Okamoto and T. Nakano, *Chem., Rev.,* 94, 349 (1994).

[2]   Y. Okamoto and Y. Kaida, *J. Chromatogr.,* 666, 403 (1994); E. Yashima and Y. Okamoto, *Bull. Chem. Soc. Jpn.,* 68, 3289 (1995).

[3]   Y. Okamoto and K. Hatada, *J. Liq. Chromotogr.,* 9, 369 (1986).

[4]   K. Ute, T. Asada, Y. Nabeshima, and K. Hatada, *Acta. Polym.,* 46, 458 (1995).

[5]   Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and Y. Yuki, *J. Am. Chem. Soc., 101*, 4763 (1979).

[6]   T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc., 114*, 1318 (1992).

[7]   T. Nakano, A. Matsuda, and Y. Okamoto, *Polym. J., 28*, 556 (1996).

[8]   T. Nakano, M. Mori, and Y. Okamoto, *Macromolecules, 26*, 867 (1993).

[9]   T. Nakano, A. Matsuda, M. Mori, and Y. Okamoto, *Polym. J., 28*, 330 (1996).

[10]   T. Nakano, Y. Shikisai, and Y. Okamoto, *Polym. J., 28*, 51 (1996).

[11]   T. Nakano and Y. Okamoto, Presentation at Fourth Pacific Polymer
         Conference, December 1995 (preprint p. 399).

[12]   S. Habaue, T. Tanaka, and Y. Okamoto, *Macromolecules, 28*, 5973
         (1995).

[13]   T. Tanaka, S. Habaue, and Y. Okamoto, *Polym. J., 27*, 1202 (1995).

[14]   K. Matsuzaki, T. Uryu, T. Kanai, K. Hosonuma, T. Matsubara, H.
         Tachikawa, M. Yamada, and S. Okuzono, *Makromol. Chem., 178*, 11
         (1977).

[15]   Y. Okamoto, M. Adachi, H. Shohi, and H. Yuki, *Polym. J., 13*, 175
         (1981); Y. Okamoto, H. Hayashida, and K. Hatada, *Polym. J., 21*, 543
         (1989).

[16]   K. Shiohara, S. Habaue, and Y. Okamoto, *Polym. J., 28*, 682 (1996).

[17]   S. Habaue, K. Shiohara, T. Uno, and Y. Okamoto, *Enantiomer, 1*, 55
         (1996).

[18]   M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, and S.
         Lifson, *Science, 268*, 1860 (1995).

[19]   A. J. Bur and L. S. Fetters, *Chem. Rev., 76*, 727 (1976).

[20]   Y. Okamoto, M. Matsuda, T. Nakano, and E. Yashima, *J. Polym. Sci.,
         Part A, Polym. Chem., 32*, 309 (1994).

[21]   K. Maeda and Y. Okamoto, *Polym. Prepr. Jpn., 45*, 1365 (1996).