Synthesis and Conformation of Optically Active Poly(phenyl isocyanate)s Bearing an ((*S*)-(α-Methylbenzyl)carbamoyl) Group

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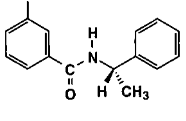
Received June 27, 1997; Revised Manuscript Received December 2, 1997

ABSTRACT: Novel optically active aromatic isocyanates, 3-((*S*)-(α-methylbenzyl)carbamoyl)phenyl isocyanate ((*S*)-3MBCPI) ($[\alpha]_{365}^{25}$ +63°) and 4-((*S*)-(α-methylbenzyl)carbamoyl)phenyl isocyanate ((*S*)-4MBCPI) ($[\alpha]_{365}^{25}$ +181°), were synthesized and homopolymerized or copolymerized with *m*-methoxyphenyl isocyanate (*m*MeOPI) with an anionic initiator in THF at −98 °C. Poly((*S*)-3MBCPI) showed a very large levorotatory specific rotation ($[\alpha]_{365}^{25}$ −1969°) and an intense CD absorption due to a predominantly one-handed helical conformation of the polymer main chain. Copolymers of (*S*)-3MBCPI with *m*MeOPI showed much larger specific rotation than that expected from the (*S*)-3MBCPI content. The intensity of the specific rotation of the copolymer of [*m*MeOPI]/[(*S*)-3MBCPI] = 91/9 greatly increased with a decrease in temperature, but that of poly((*S*)-3MBCPI) showed almost no change, suggesting that poly((*S*)-3MBCPI) may take a perfectly single-handed helical conformation in solution even at room temperature. Poly((*S*)-4MBCPI) showed a large dextrorotatory specific rotation opposite to that of poly((*S*)-3MBCPI). This rotation of poly((*S*)-4MBCPI) gradually increased in THF with time from $[\alpha]_{365}^{25}$ +1000° to a constant value ($[\alpha]_{365}^{25}$ +2059°). The GPC and CD analyses of the polymer suggest that this change in specific rotation with time may be caused by a slow conformational change. Poly((*S*)-3MBCPI) and poly((*S*)-4MBCPI) exhibited chiral recognition toward (±)-1,1′-bi-2-naphthol in ^{1}H NMR spectroscopy.

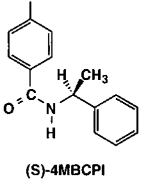
Introduction

Poly(alkyl isocyanate)s are known to have a stiff dynamic helical structure of a main chain consisting of successive amide bonds in solution.[1−3] Many optically active poly(alkyl isocyanate)s with a predominantly one-handed helical sense have been synthesized by the anionic polymerization of optically active isocyanates[4−6] or by the copolymerization of an achiral isocyanate and a small amount of an optically active isocyanate.[7] The pioneer work in optically active polyisocyanates by Goodman and Chen[4] and the studies by Green and coworkers[5−7] appear particularly important and interesting. The introduction of an optically active group at the initial chain end of the polymer chain using optically active initiators can also yield optically active poly(alkyl isocyanate)s.[8] On the other hand, poly(aromatic isocyanate)s bearing a phenyl group directly connected to the polymer main chain had been considered to take a random coil conformation in solution because of the lack of stiffness in the polymer main chain.[1] However, we recently reported that the polymerization of achiral aromatic isocyanates with an optically active anionic initiator affords optically active polymers possessing a predominantly one-handed helical structure caused by the chiral initiator residue introduced at the initial chain end and that the polymer main chain is stiff enough to maintain a helical conformation in solution.[9,10] Many optically active, helical polymers exhibit chiral recognition ability toward enantiomers and have been utilized as chiral stationary phases in HPLC to separate optical isomers.[11] However, polyisocyanates with chiral recognition ability have not yet been reported to our knowledge. Optically active poly(aromatic isocyanate)s possessing an excess one-handed helical conformation are expected to show chiral recognition ability because aromatic groups often play an important role in chiral recognition.[11,12] The optically active poly(aromatic isocyanate)s that we prepared so far have an optically active group only at the initial chain end, and the one-handedness of the polymer main chain is low. Therefore, we cannot expect high chiral recognition by these polymers.

In this study, novel optically active aromatic isocyanates ((*S*)-3MBCPI and (*S*)-4MBCPI) having an optically active substituent on the phenyl ring were synthesized and polymerized with the lithium amide (Li−piperidine) of piperidine in order to obtain the optically active poly(aromatic isocyanate) possessing a predominantly one-handed helical conformation. The optical activity and the chiral recognition ability of the obtained polymers were investigated, and we found for the first time chiral recognition by an optically active polyisocyanate. The copolymers of (*S*)-3MBCPI with *m*-methoxyphenyl isocyanate (*m*MeOPI) were also synthesized to investigate their conformation and chiral recognition ability. Polymerization of an optically active alkyl isocyanate bearing a 2-phenylpropyl group has already been reported,[4] but that of a phenyl isocyanate derivative has not.



(S)-3MBCPI



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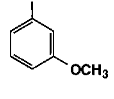
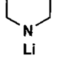


*m*MeOPI

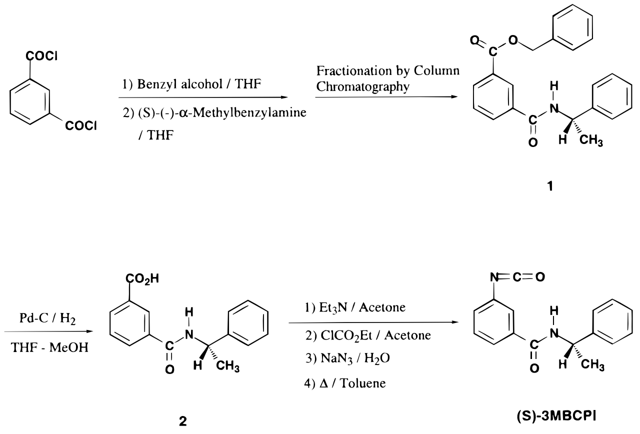


Li-piperidine

Experimental Section

Materials. Tetrahydrofuran (THF) (Wako) was dried over Na wire and distilled onto CaH_2, followed by vacuum distillation onto $LiAlH_4$ under nitrogen, and distilled again under high vacuum just before use. Piperidine (Wako) was dried over CaH_2 and distilled under reduced pressure. Toluene (Kishida)

Scheme 1



and hexane (Wako) were dried over Na wire and distilled. Pyridine and triethylamine were distilled and dried over potassium hydroxide pellets.

(*S*)-(−)-(α-Methylbenzyl)amine (Wako), isophthaloyl dichloride (Aldrich), terephthaloyl chloride (Aldrich), benzyl alcohol (Kishida), sodium azide (Kishida), and ethyl chloroformate (Kishida) were used as purchased.

The optically active aromatic isocyanate ((*S*)-3MBCPI) was synthesized according to Scheme 1.

Benzyl 3-((*S*)-(α-Methylbenzyl)carbamoyl)benzoate (1). To a solution of isophthaloyl dichloride (36.1 g, 178 mmol) in dry THF (200 mL) were added dropwise benzyl alcohol (19.2 g, 178 mmol) and pyridine (16.9 g, 213 mmol) under nitrogen. The reaction mixture was stirred for 0.5 h at room temperature and was added to a mixture of (*S*)-(α-methylbenzyl)amine (21.6 g, 178 mmol) and pyridine (16.9 g, 213 mmol) cooled to 0 °C with an ice bath under nitrogen. The reaction mixture was stirred for 17 h at room temperature, and water was added. The solution was neutralized with 1N HCl aqueous solution, washed with saturated NaCl aqueous solution and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was fractionated by column chromatography on silica gel using chloroform as the eluent. Evaporation of the solvent afforded **1** (27.0 g) in 42.2% yield; mp 142.0−143.0 °C, $[\alpha]_{365}^{25}$ +84° (*c* 1.1, THF). The enantiomeric excess of the product was determined to be nearly 100% by chiral HPLC on a chiral column packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated silica gel[12] with hexane−2-propanol (90/10) as the eluent (separation factor (α) = 1.22). IR (KBr, cm^{-1}): 1715 (C=O of ester), 1636(C=O of amide); ^1H NMR ($CDCl_3$): δ 1.62 (d, CH_3, 3H), 5.34 (q, CH, 1H), 5.38 (s, CH_2, 2H), 6.42 (d,NH, 1H), 7.26−7.53 (m, aromatic, 11H), 8.03 (d, aromatic, 1H), 8.18 (d, aromatic, 1H), 8.39 (s, aromatic, 1H).

3-((*S*)-(α-Methylbenzyl)carbamoyl)benzoic Acid (2). To a solution of **1** (27.0 g, 75 mmol) in THF−MeOH (1/1) (1.5 L) was added 10% Pd−C (2.90 g) under nitrogen. Hydrogen gas was bubbled into the mixture under vigorous stirring. After 10 h, Pd−C was removed by filtration and the solvent was evaporated under reduced pressure. The residue was recrystallized from MeOH to give **2** (15.8 g) in 78.1% yield; mp 175.5−176.0 °C. IR (KBr, cm^{-1}): 1701 (C=O of carboxylic acid), 1632 (C=O of amide); ^1H NMR (DMSO-d_6): δ 1.48 (d, CH_3, 3H), 5.18 (q, CH, 1H), 7.22−8.12 (m, aromatic, 8H), 8.47 (s, aromatic, 1H), 9.05 (d, NH, 1H).

3-((*S*)-(α-Methylbenzyl)carbamoyl)phenyl Isocyanate ((*S*)-3MBCPI). The isocyanate was prepared by the modified Curtius rearrangement.[13] **2** (5.1 g, 19 mmol) was dissolved in acetone (150 mL). The solution was cooled below 0 °C, and triethylamine (2.2 g, 22 mmol) was added. Ethyl chloroformate (2.6 g, 24 mmol) was then slowly added to the mixture while the temperature was maintained below 5 °C. After stirring for 1.5 h, a solution of sodium azide (1.9 g, 29 mmol) in water (10 mL) was added. The mixture was stirred for 1.5 h at 0 °C and then was poured into ice-cold water. The separated oil was extracted with toluene and dried over anhydrous $MgSO_4$. The toluene solution was heated and maintained at 120 °C for 2 h with stirring under nitrogen atmosphere. After the reaction was cooled to room temperature, toluene was evaporated off in vacuo to obtain a slight yellow solid. This was dissolved in dry $CHCl_3$ (80 mL), and the $CHCl_3$-insoluble part (urea) was removed by filtration under nitrogen. $CHCl_3$ was removed in vacuo, and the residue was recrystallized from dry hexane−toluene (6/1) to give (*S*)-3MBCPI (3.0 g) in 60% yield; $[\alpha]_{365}^{25}$ +63°, $[\alpha]^{25}_D$ +13° (*c* 1.1, THF). IR ($CHCl_3$ solution on NaCl plate, cm^{-1}): 2272 (N=C=O), 1659 (C=O of amide). ^1H NMR ($CDCl_3$): δ 1.61 (d, CH_3, 3H), 5.32 (q, CH, 1H), 6.26 (d, NH, 1H), 7.19−7.56 (m, aromatic, 9H).

(*S*)-4MBCPI was prepared in the same way as the synthesis of (*S*)-3MBCPI.

Benzyl 4-((*S*)-(α-Methylbenzyl)carbamoyl)benzoate (3). This compound was prepared from terephthaloyl chloride; yield 37.6%, $[\alpha]_{365}^{25}$ +84° (*c* 1.1, THF). The enantiomeric excess of the product was determined to be nearly 100% by chiral HPLC on cellulose tris(3,5-dimethylphenylcarbamate) with hexane−2-propanol (80/20) as the eluent (separation factor (α) = 2.50). ^1H NMR ($CDCl_3$): δ 1.61 (d, CH_3, 3H), 5.33 (q, CH, 1H), 5.37 (s, CH_2, 2H), 6.41 (d, NH, 1H), 7.25−7.50 (m, aromatic, 10H), 7.80 (d, aromatic, 2H), 8.09 (d, aromatic, 2H).

4-((*S*)-(α-Methylbenzyl)carbamoyl)benzoic Acid (4). **4** was synthesized from **3** by the same method used for the synthesis of **2**. The crude product was recrystallized from EtOH; yield 78.1%, mp 196.5−197.0 °C. IR (KBr, cm^{-1}): 1684 (C=O of carboxylic acid), 1636(C=O of amide); ^1H NMR (DMSO-d_6): δ 1.48 (d, CH_3, 3H), 5.18 (q, CH, 1H), 7.21−8.03 (m, aromatic, 9H), 8.99 (d,NH, 1H), 13.23 (s, CO_2H, 1H).

4-((*S*)-(α-Methylbenzyl)carbamoyl)phenyl Isocyanate ((*S*)-4MBCPI). (*S*)-4MBCPI was also prepared by the modified Curtius rearrangement[13] described in the synthesis of (*S*)-3MBCPI. The crude product was purified by recrystallization from hexane−toluene (2/1): yield 42%; $[\alpha]_{365}^{25}$ +181°, $[\alpha]^{25}_D$ +13° (*c* 1.1, THF). IR ($CHCl_3$ solution on NaCl plate, cm^{-1}): 2270 (N=C=O), 1659 (C=O of amide). ^1H NMR ($CDCl_3$): δ 1.60 (d, CH_3, 3H), 5.32 (m, CH, 1H), 6.28 (s, NH, 1H), 7.12−7.75 (m, aromatic, 9H).

Preparation of Initiator Solution. The lithium amide (Li−piperidine) of piperidine was prepared by adding an equimolar amount of *tert*-butyllithium in pentane to a solution of piperidine in THF at room temperature immediately before use.

Polymerization. Polymerization was carried out in a glass ampule under dry nitrogen atmosphere. In the glass ampule, the monomer and THF were placed and cooled to −98 °C. The polymerization reaction was initiated by adding the initiator solution with a syringe. The polymerization was terminated by adding a 10-fold excess of HCl in MeOH to the initiator, and the resulting polymer was precipitated into a large amount of MeOH, collected by centrifugation, and dried in vacuo at room temperature overnight.

Evaluation of Chiral Recognition Ability by ^1H NMR Measurement. A polymer (10 mg) was dissolved in $CDCl_3$ (0.9 mL) and a racemate at one-third equivalent to the monomeric unit of the polymer was added. ^1H NMR measurement was carried out at room temperature (ca.. 20−22 °C). When the peak separation due to a pair of enantiomers was observed, the assignment of each peak was performed with an optically pure enantiomer.

Measurement. Optical rotation was measured on a Jasco DIP-181 polarimeter. ^1H NMR spectra were measured on a Varian VXR-500 (500 MHz) or Gemini-2000 (400 MHz) spectrometer using tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were measured with a Varian Gemini-2000 (100 MHz) spectrometer. IR spectra were recorded on a Jasco FT/IR-7000 spectrometer. Circular dichroism (CD) spectra were measured with a Jasco J-720 spectrometer. The molecular weight of the polymer was determined by GPC measurement on a Shodex System-21 GPC system equipped

Table 1. Polymerization of 3-((*S*)-(α-Methylbenzyl)carbamoyl)phenyl Isocyanate ((*S*)-3MBCPI) with Li−Piperidine in THF at −98 °C[a]

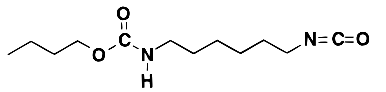
run	[M]/[I]	yield (%)[b]	$[\alpha]_{365}^{25}$ [c] (deg)	M_n[d] ($\times 10^4$)	M_w/M_n[d]
1	50	40	−1969[e]	2.3	2.1
2	100	41	−1995	7.6	2.1
3	200	43	−2041	13	2.1
4	500	53	−1990	23	1.8
5	1000	60	−2014	33	1.8

[a] Conditions: (run 1) monomer 0.5 g, THF 5 mL; (runs 2−5) monomer 0.2 g, THF 2 mL, 4 h. [b] MeOH-insoluble part. [c] In THF. [d] Determined by GPC with LS. [e] $[\alpha]^{25}_D$ −504° ($CHCl_3$).

with a Shodex RI-71S detector and a Wyatt Technology DAWN DSP-F multiangle light scattering detector using THF as an eluent at 40 °C. Two GPC columns, Shodex KF-803 and KF-806L, were connected in series. The determination of the enantiomeric excess (% ee) of the chiral monomers was performed on a Jasco PU-986 liquid chromatograph equipped with Jasco MD-910 UV and Jasco OR-990 polarimetric detectors using a chiral column packed with cellulose tris(3,5-dimethylphenylcarbamate)-coated silica gel (CHIRALCEL OD, Daicel)[12] using hexane−2-propanol as the eluent.

Results and Discussion

Polymerization of (*S*)-3MBCPI and Copolymerization with *m*MeOPI. Table 1 shows the results of the polymerization of optically active (*S*)-3MBCPI with Li−piperidine in THF at −98 °C. The polymerization reaction proceeded very rapidly and the reaction system became a gel within a few minutes after adding the initiator. However, the isolated polymers were soluble in THF and $CHCl_3$. The polymers of various molecular weights were obtained by changing the feed ratio of monomer to initiator ([M]/[I]), and the polymer yield increased with an increase in the [M]/[I] ratio. Although in this polymerization a transfer reaction of the growing chain end to the carbamoyl NH group of the monomer or polymer might occur, this result indicates that such a transfer reaction rarely occurs. Recently, we reported that the polymerization of alkyl isocyanate (**5**) bearing a carbamate group under analogous conditions to those described in Table 1 affords the polymer mainly consisting of a 1-nylon structure and that almost no transfer reaction of the propagation end to the carbamate group takes place.[14]



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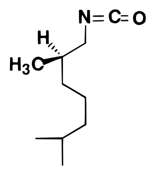

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The ^1H NMR spectra of (*S*)-3MBCPI and poly((*S*)-3MBCPI) (run 1 in Table 1) are shown in Figure 1. The spectrum of poly((*S*)-3MBCPI) is reasonably assigned, although each peak is very broad. This broadening is probably because the mobility of the polymer chain is reduced by the intramolecular hydrogen bonding among the carbamoyl groups in the side chain.

The polymers showed very large specific rotation which is opposite in sign to that of the monomer (*S*)-3MBCPI. The values are almost the same as that of poly((*R*)-2,6-dimethylheptyl isocyanate) (**6**) which has been considered to take a perfectly single-handed helical conformation in solution.[7,15] The polymers in Table 1 showed almost the same specific rotation regardless of molecular weight. The CD and UV spectra of (*S*)-3MBCPI and poly((*S*)-3MBCPI) (run 1 in Table 1) are shown in Figure 2. The CD spectral pattern of poly((*S*)-3MBCPI) around 250 nm is quite different from that of the monomer (*S*)-3MBCPI but similar to that of optically active one-handed helical poly(alkyl isocyanate)s.[5] These results indicate that the poly((*S*)-3MBCPI) has a predominantly one-handed helical structure, and

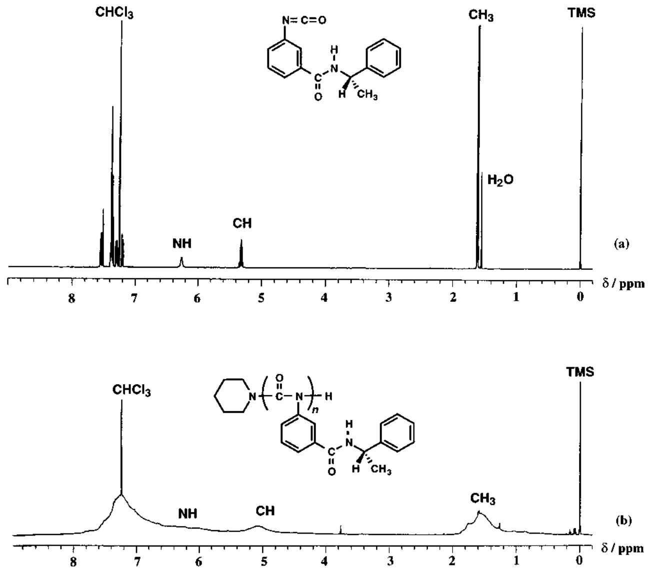


Figure 1. ^1H NMR spectra of (*S*)-3MBCPI (a) and poly((*S*)-3MBCPI) (run 1 in Table 1) (b) in $CDCl_3$ at 60 °C (500 MHz).

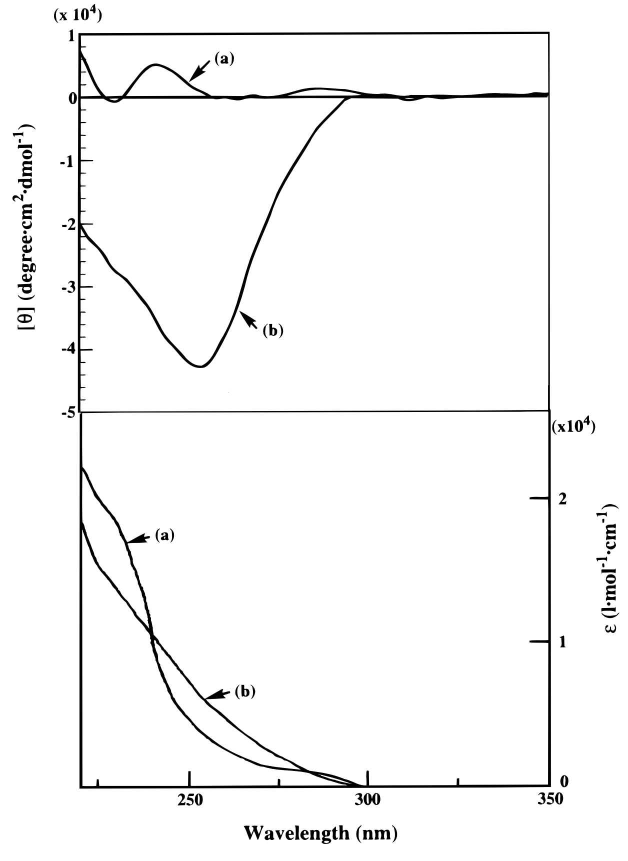


Figure 2. CD (top) and UV (bottom) spectra of (*S*)-3MBCPI (a) and poly((*S*)-3MBCPI) (run 1 in Table 1) (b) in THF.

Table 2. Copolymerization of 3-((*S*)-(α-Methylbenzyl)carbamoyl)phenyl Isocyanate (M_1) and *m*-Methoxyphenyl Isocyanate (M_2) with Li–Piperidine in THF at −98 °C[a]

run	M_1 fraction in monomer (mol %)	yield[b] (%)	M_1 fraction in polymer (mol %)[c]	$[\alpha]_{365}^{25}$ [d]	M_n[e] ($\times 10^4$)	M_w/M_n[e]
1	80	68	82	−2015	1.6	1.5
2	70	69	73	−2161	2.0	1.2
3	60	72	59	−2206	1.8	1.2
4	50	71	50	−2298	1.4	1.3
5	40	77	38	−2108	1.7	1.3
6	30	83	27	−1878	1.8	1.3
7	10	79	9	−1094	1.4	1.4
8	5	78	6	−670	1.3	1.6
9	1	78	1	−92	1.6	1.6

[a] Conditions: (runs 1–8) monomer 0.2 g, THF 2 mL, [M]/[I] = 50; (run 9) monomer 0.5 g, THF 5 mL, [M]/[I] = 50, 4 h. [b] MeOH-insoluble part. [c] Estimated by ^{1}H NMR. [d] In THF. [e] Determined by GPC with LS.

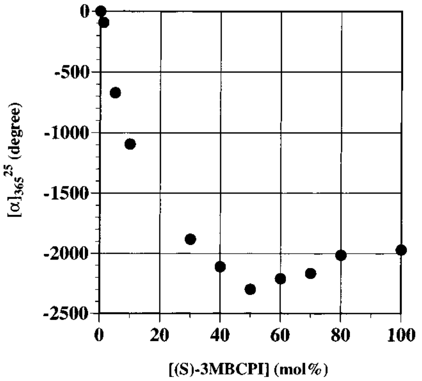


Figure 3. Plots of $[\alpha]_{365}^{25}$ (in THF) of poly(*m*MeOPI-*co*-(*S*)-3MBCPI) against (*S*)-3MBCPI content (mol %).

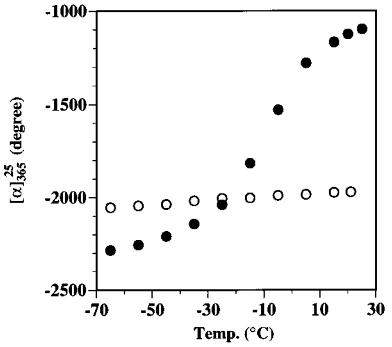


Figure 4. Temperature dependence of specific rotation of poly(*m*MeOPI-*co*-(*S*)-3MBCPI) (*m*MeOPI/(*S*)-3MBCPI = 91/9) (run 7 in Table 2) (●) and poly((*S*)-3MBCPI) (run 1 in Table 1) (○) on temperature in THF.

from the sign of the Cotton effect, the sense of the helix is assigned to be left-handed.[15]

The results of the copolymerization of (*S*)-3MBCPI with *m*MeOPI are summarized in Table 2. The composition of the copolymer agreed well with that of the fed monomer, suggesting that the monomer distribution in the copolymers may be at random. In Figure 3, the specific rotation of the copolymers is plotted against the composition of the copolymers. The specific rotation of the copolymers drastically increased with an increase in the content of (*S*)-3MBCPI and at about 30% (*S*)-3MBCPI content, it became as large as that of poly((*S*)-3MBCPI). It has been reported that the copolymer of optically active **6** (15%) with achiral hexyl isocyanate (85%) shows a specific rotation as large as that of the homopolymer of **6**.[7] These results indicate that poly(aromatic isocyanate)s have a smaller persistence length and higher flexibility than poly(alkyl isocyanate)s. This agrees well with previous reports.[1,10] The copolymer with 50% (*S*)-3MBCPI content showed the largest specific rotation. This is probably because the specific rotation of the one-handed helix of poly(*m*MeOPI) may be larger than that of poly((*S*)-3MBCPI).

Table 3. Polymerization of 4((*S*)-(α-Methylbenzyl)carbamoyl)phenyl Isocyanate ((*S*)-4MBCPI) with Li–Piperidine in THF at −98 °C[a]

run	time (h)	yield (%)[b]	$[\alpha]_{365}^{25}$ [c]	M_n[d] ($\times 10^4$)	M_w/M_n[d]
1	0.5	74	+1703	2.9	1.5
2	1	55	+1640[e]	2.8	1.6
3	4	34	+1615[f]	2.4	1.5

[a] Conditions: (runs 1, 2) monomer 0.3 g, THF 3 mL; (run 3) monomer 0.5 g, THF 5 mL, [M]/[I] = 50. [b] MeOH-insoluble part. [c] In $CHCl_3$. [d] Determined by GPC with LS. [e] $[\alpha]^{25}_D$ +387° (in $CHCl_3$). [f] $[\alpha]_{365}^{25}$ +2059° (82 h after dissolved in THF).

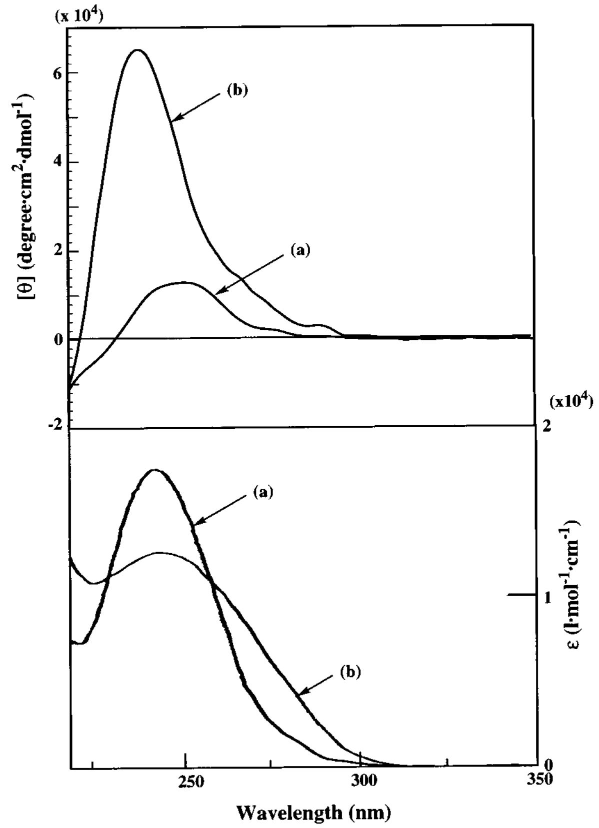


Figure 5. CD (top) and UV (bottom) spectra of (*S*)-4MBCPI (a) and poly((*S*)-4MBCPI) (b) (run 3 in Table 3) in $CHCl_3$.

The specific rotations of poly((*S*)-3MBCPI) and the copolymer (poly((*S*)-3MBCPI-*co*-*m*MeOPI)) of (*S*)-3MBCPI with *m*MeOPI ((*S*)-3MBCPI/*m*MeOPI = 9/91) (run 7 in Table 2) were measured at various temperatures, and the results are shown in Figure 4. The absolute value of the specific rotation of poly((*S*)-3MBCPI-*co*-*m*MeOPI) steeply increased with a decrease in temperature, and this change was very fast and reversible. This must be ascribed to the fact that at lower temperature the persistence length of the helical structure becomes longer and the optically active group of (*S*)-3MBCPI residue can induce a one-handed helical structure over a longer distance. An analogous temperature effect has been reported in the poly(aromatic isocyanate) bearing an optically active group at the initial chain end.[10] On

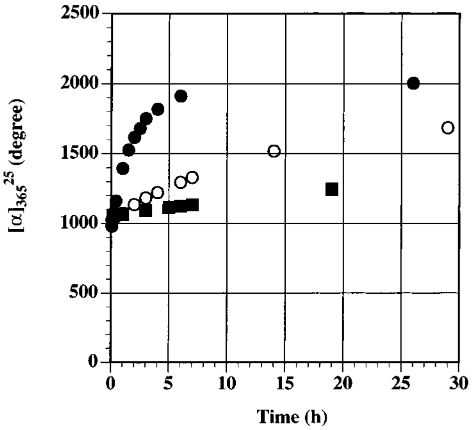
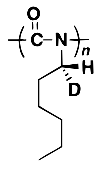


Figure 6. Change of $[\alpha]_{365}^{25}$ of poly((*S*)-4MBCPI) (run 3 in Table 3) in THF (●), in THF-MeOH (9:1) (○), and in THF−MeOH (8:2) (■).

the other hand, poly((*S*)-3MBCPI) showed almost no influence of temperature, indicating that poly((*S*)-3MBCPI) has an almost completely single-handed helical conformation around room temperature.

Polymerization of (*S*)-4MBCPI. Table 3 shows the results of the polymerization of optically active (*S*)-4MBCPI. The polymerization for 0.5 h afforded the polymer in 74% yield while that for 4 h was in 30% yield. The polymerization reaction seems to proceed very fast and is completed within 0.5 h. The infrared spectrum of the methanol-soluble part for 4 h showed the bands characteristic of the cyclic trimer. As shown in the earlier study,[16] poly(aromatic isocyanate)s with an electron-withdrawing group on the phenyl ring are subject to depolymerization especially under basic conditions. The decrease in the polymer yield with polymerization time probably occurs because, after the completion of the propagation reaction, the depolymerization reaction accompanied by the formation of the cyclic trimer proceeds.

The poly((*S*)-4MBCPI) showed a very large specific rotation, whose sign was opposite to that of poly((*S*)-3MBCPI). The CD and UV spectra of (*S*)-4MBCPI and poly((*S*)-4MBCPI) (run 3 in Table 3) are shown in Figure 5. The sign of the Cotton effect of poly((*S*)-4MBCPI) was opposite to that of poly((*S*)-3MBCPI). The poly((*S*)-4MBCPI) appears to have a predominantly right-handed helical structure.[15] Poly((*S*)-4MBCPI) and poly((*S*)-3MBCPI) probably have opposite helical structures despite the same absolute configuration of the optically active group in the side chain. Green et al. has already reported that poly(alkyl isocyanate)s **7** and **8** are predominantly one-handed helices with an opposite helical sense although the absolute configuration of the asymmetric centers **7** and **8** are the same.[17]



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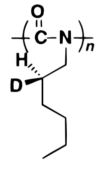

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Interestingly, the specific rotation of poly((*S*)-4MBCPI) changed with time in THF, although in $CHCl_3$ such a change was not observed. The change in the specific rotation of poly((*S*)-4MBCPI) (run 3 in Table 3) in THF is shown in Figure 6. The specific rotation of poly((*S*)-4MBCPI) increased with time, and after 60 h, it reached a constant value ($[\alpha]_{365}^{25}$ +2059°). After the specific rotation of poly((*S*)-4MBCPI) reached a constant value in THF, the polymer was recovered by reprecipitation in a large amount of methanol followed by centrifugation. This recovered polymer also showed the same change in the specific rotation with time in THF, indicating that this change is reversible. However, in $CHCl_3$, a constant $[\alpha]_{365}^{25}$ +1610° was observed. To obtain information on this rotation change in poly((*S*)-4MBCPI) in THF, CD and GPC measurements were performed at various times after poly((*S*)-4MBCPI) had been dissolved in THF. In Figure 7 are shown the GPC curves of the poly((*S*)-4MBCPI) measured at 0.5 h (A) and 15 h (B) after dissolution. The chromatographic patterns are similar, and the broadening of the peak and the shift to higher molecular-weight were not

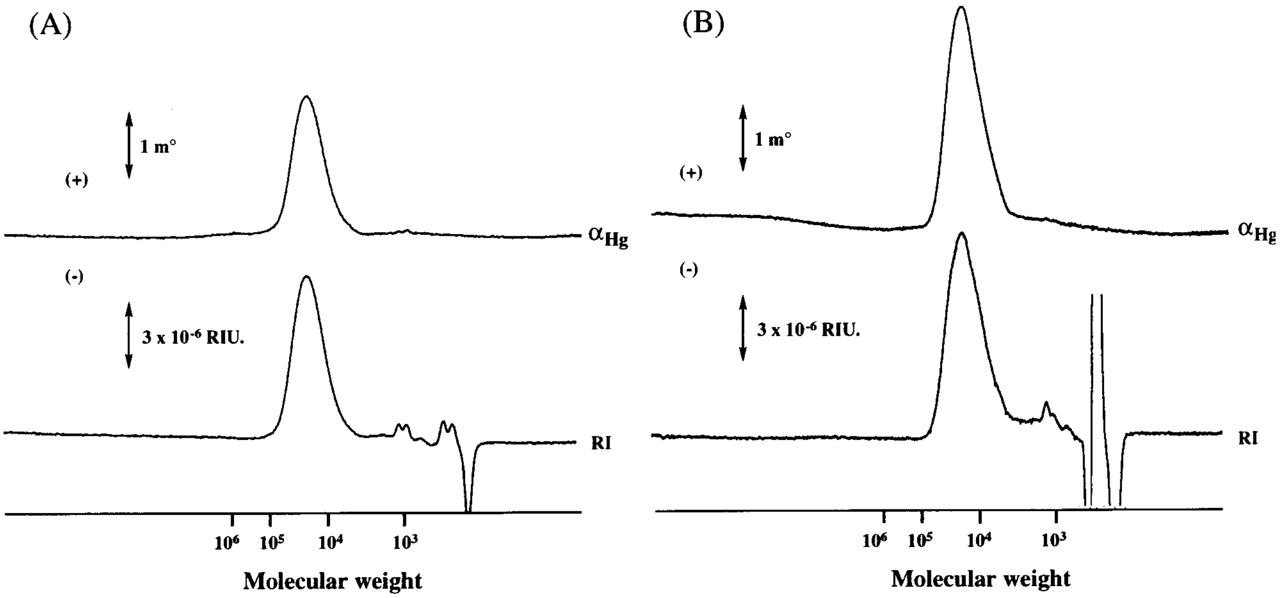


Figure 7. GPC curves of poly((*S*)-4MBCPI) (run 3 in Table 3) at 0.5 h (A) and 15 h (B) after dissolution in THF monitored with RI and polarimetric detectors (eluent: THF).

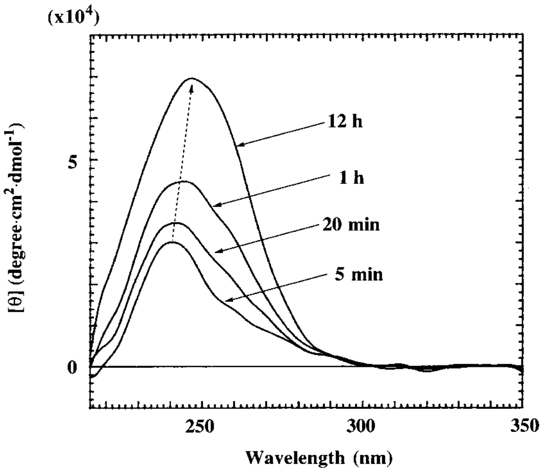


Figure 8. CD spectra of poly((*S*)-4MBCPI) (run 3 in Table 3) in THF.

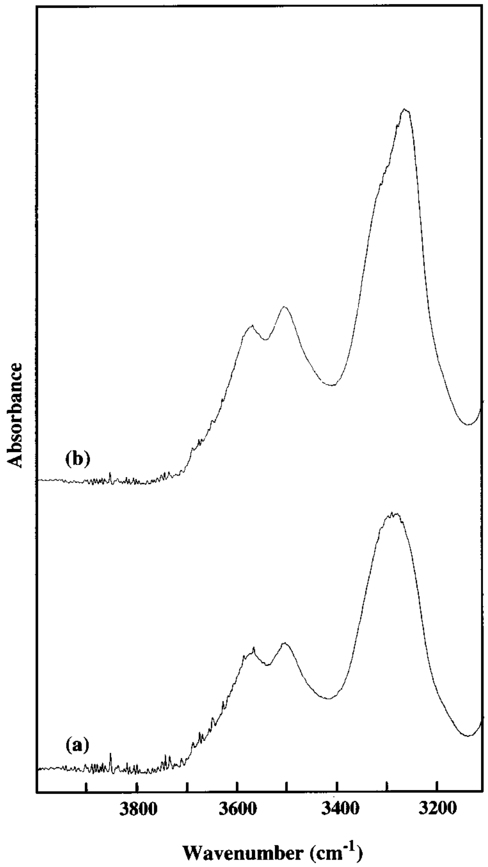


Figure 9. IR spectra of poly((*S*)-4MBCPI) (run 3 in Table 3) measured at 5 min (a) and 24 h (b) after dissolution in THF (in NaCl cell).

observed, indicating that poly((*S*)-4MBCPI) does not associate in THF and that the change in specific rotation of poly((*S*)-4MBCPI) is not due to aggregation.

Figure 8 depicts the change in the CD spectra of poly((*S*)-4MBCPI) in THF with time. The CD intensity increased, and the peak maximum shifted to a longer wavelength with time. These results indicate that the change in specific rotation of poly((*S*)-4MBCPI) is attributable to the change in conformation. The specific rotation change in poly((*S*)-4MBCPI) in THF containing a small amount of MeOH is shown in Figure 6. As the MeOH content increased, the change slowed, and the final values appear to be smaller than that in pure THF.

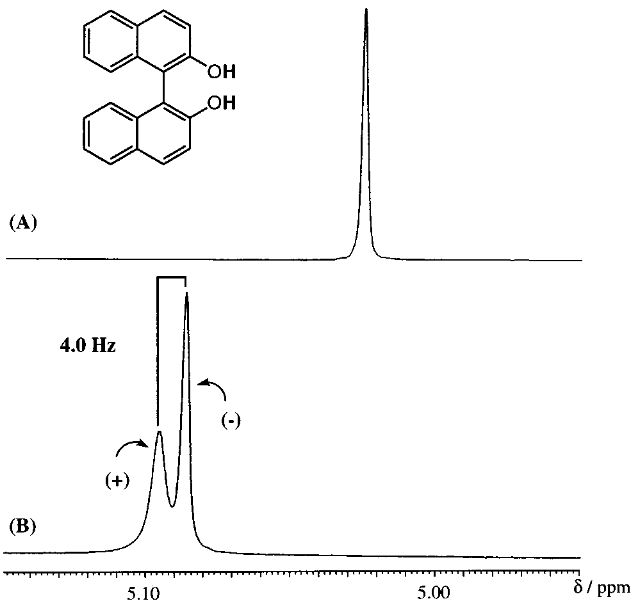
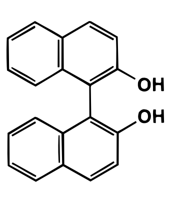


Figure 10. 500 MHz ^{1}H NMR spectra of hydroxy proton of (±)-1,1′-bi-2-naphthol (9) in the absence (A) and in the presence (B) of poly((*S*)-3MBCPI) ([poly((*S*)-3MBCPI)]/[9] = 3/1) in $CDCl_3$ at 25 °C.

In Figure 9 are shown IR spectra of the poly((*S*)-4MBCPI) measured at 5 min and 24 h after dissolution in THF. After 24 h, a new peak was observed at 3260 cm^{-1}, which indicates that a stronger hydrogen bond was formed with time. These results suggest that this slow conformational change may be caused by the formation of intramolecular hydrogen bonds among the amide groups in the side chain. Although a slow conformational change in poly(alkyl isocyanate) from a helix to a random structure in solution has been reported,[18] such a slow change to a one-handed helical structure as shown in Figure 6 has not been reported. In this respect, the present result of the poly(aromatic isocyanate) is unique and interesting.

Chiral Discrimination. To elucidate the chiral discrimination ability of the optically active poly(aromatic isocyanate)s, ^{1}H NMR measurements of some racemates were performed in the presence of poly((*S*)-3MBCPI) or poly((*S*)-4MBCPI) in $CDCl_3$. Figure 10 shows the ^{1}H NMR spectra of racemic 1,1′-bi-2-naphthol (**9**) in the absence (A) and presence (B) of poly((*S*)-3MBCPI (run 1 in Table 1). The hydroxy protons of **9** are separated into two singlet resonances in the presence of poly((*S*)-3MBCPI). This result clearly indicates that poly((*S*)-3MBCPI) can discriminate the enantiomers of **9** in $CDCl_3$. The measurement using enantiomerically pure **9** revealed that the downfield peak is due to the proton of the (+)-(*R*)-isomer. The (+)-(*R*)-isomer must be absorbed more strongly on poly((*S*)-3MBCPI) probably through the hydrogen bonding, which rationalizes the broadening of the peak width of the (+)-(*R*)-isomer.



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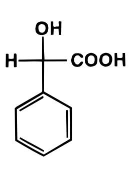

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However, other protons of **9** were not split. The carboxy proton of mandelic acid (**10**) was also separated into two singlet resonances in the presence of poly((*S*)-3MBCPI). To investigate the effect of poly((*S*)-3MBCPI) as a polymer, the ^{1}H NMR was measured in the presence of optically active **1** ($[\alpha]_{365}^{25}$ +84° (*c* 1.1, THF)) shown in Scheme 1. However, in the presence of **1**, a peak split due to the enantiomers was not observed under the same conditions. The chiral discrimination ability of poly((*S*)-3MBCPI) appears to be based on the helical structure of its main chain. The copolymer of (*S*)-3MBCPI and *m*MeOPI ((*S*)-3MBCPI/*m*MeOPI = 50/50) (run 4 in Table 2) also exhibited splitting due to enantiomers for **9** and **10**. The degree of the splitting was larger than that in the presence of poly((*S*)-3MBCPI). Poly((*S*)-4MBCPI) also showed similar chiral discrimination ability for **9** and **10**. Chiral discrimination of polyisocyanate has not yet been reported to our knowledge, and this may be the first example of the chiral discrimination of polyisocyanates.

Acknowledgment. K.M. is thankful for the support by a Grant-in-Aid for JSPS Fellows (No. 0574) from the Ministry of Education, Science, Sports, and Culture of Japan.

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MA970948M