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Synthesis and structure of poly(phenyl isocyanate)s bearing an optically active alkoxyl group

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ABSTRACT: Novel optically active phenyl isocyanate derivatives (**1**–**6**) bearing an *(R)*-*sec*-butoxy, *(S)*-2-methylbutoxy or *(S)*-3,7-dimethyloctyloxy group at the *meta* or *para* position on the phenyl ring were prepared and polymerized with an anionic initiator in tetrahydrofuran (THF). The resulting polymers from **1**, **2**, **4** and **6** showed much greater specific rotation than that of the corresponding monomers and an intense circular dichroism (CD) band in the main-chain absorption region, indicating that these polymers have a predominantly one-handed helical conformation in solution. On the other hand, the polymers obtained from **3** and **5** showed a much smaller specific rotation than that of the above polymers at room temperature. The polymers from **2** and **5** showed a remarkable change in optical activity with change in temperature, and the specific rotation of the polymers changed from a positive to a negative value with decrease in temperature. The CD band of the polymers in the absorption region due to the main chain changed from a positive to a negative peak with a change in specific rotation. These results indicate that poly-**2** and poly-**5** undergo a thermally induced helix–helix transition in THF. The temperature for the helix–helix transition of poly-**2** was independent of the degree of polymerization. Poly-**2** exhibited a reversible helix–helix transition in chloroform and diethyl ether and also in THF, whereas in toluene and dichloromethane such a transition was not observed. Copyright © 2000 John Wiley & Sons, Ltd.

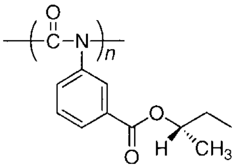
KEYWORDS: polyisocyanate; optically active polymer; aromatic isocyanate; helix; anionic polymerization; helix–helix transition

INTRODUCTION

Poly(alkyl isocyanate)s are known to have a helical structure in solution and in the solid state.[1] The helix in solution is not rigid, but dynamic, with quickly moving helix reversals in the main chain. Therefore, the asymmetric synthesis of an optically active polymer possessing a stable single-handed helical structure, which has been observed for poly(triarylmethyl methacrylate)s,[2] polyisocyanide[3] and polychloral,[4] has not yet been achieved. However, optically active polymers with a prevailing one-handed helical structure can be obtained by introducing a small amount of optically active comonomer units into an achiral isocyanate sequence through copolymerization[5a–e] or by initiating the polymerization with an optically active initiator[5f] because of the long persistence length of the helix.

On the other hand, poly(aryl isocyanate)s, which have an aryl group connected directly to the main chain, have been postulated to exist as a random coil rather than a helix in solution owing to the lack of stiffness in the main chain.[6] However, we found that the backbone of the poly(phenyl isocyanate) derivatives is rigid enough to have a helical conformation in solution as well as poly(alkyl isocyanate)s.[7] Especially, an optically active poly(phenyl isocyanate) bearing an amide group, poly{3-[((*S*)-(α-methylbenzyl)carbamoyl]phenyl isocyanate}, has an almost completely one-handed helical structure even at room temperature and showed a chiral discrimination ability toward some racemates.[8]

Recently, we also reported that the poly(phenyl isocyanate) bearing an optically active ester group, poly{3-[*(S)*-*sec*-butoxycarbonyl]phenyl isocyanate} {poly[*(S)*-3*sec*BuOCPI]}, undergoes a reversible helix–helix transition in tetrahydrofuran (THF) with change in temperature. This thermally induced helix–helix transition was specific for poly[*(S)*-3*sec*BuOCPI] and was not observed for analogous polymers bearing an optically active ester group whose structure is slightly different from that of poly[*(S)*-3*sec*BuOCPI].[9]



Poly((S)-3*sec*BuOCPI)

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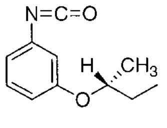
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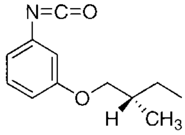
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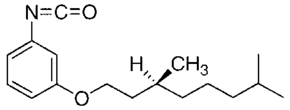
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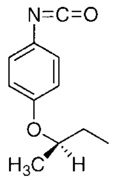
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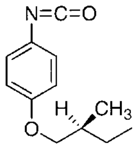
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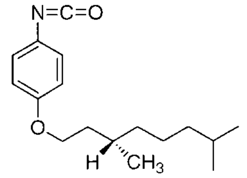
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In the present study, novel optically active phenyl isocyanates bearing a chiral alkoxyl group at the *meta* or *para* position, 3-[*(R)*-*sec*-butoxy]phenyl isocyanate (**1**), 3-[*(S)*-2-methylbutoxy]phenyl isocyanate (**2**), 3-[*(S)*-3,7-dimethyloctyloxy]phenyl isocyanate (**3**), 4-[*(R)*-*sec*-butoxy]phenyl isocyanate (**4**), 4-[*(S)*-2-methylbutoxy]-phenyl isocyanate (**5**) and 4-[*(S)*-3,7-dimethyloctyloxy]-phenyl isocyanate (**6**), were synthesized and polymerized using an achiral anionic initiator. In order to clarify the effect of the difference in the chiral groups of the side-chain and the position of the asymmetric center on the polymer main-chain conformation, chiroptical properties of the obtained polymers and their temperature and solvent dependences were investigated in detail.

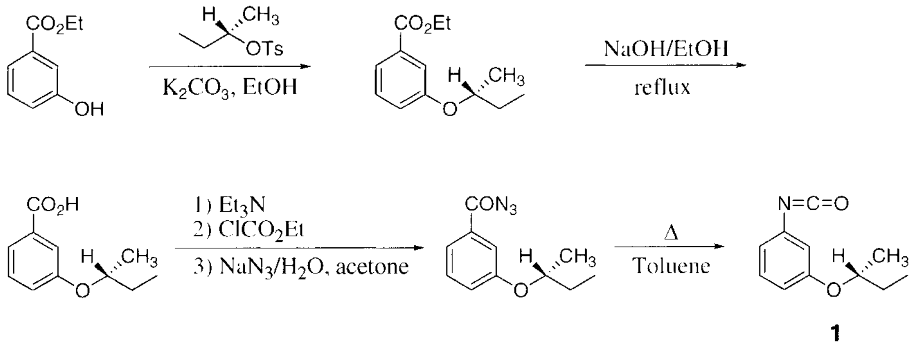
EXPERIMENTAL

Materials. *(S)*-(+)-*sec*-Butyl alcohol (Aldrich), *(S)*-(−)-2-methyl-1-butanol (Kishida), ethyl 3-hydroxybenzoate (TCI), ethyl 4-hydroxybenzoate (Aldrich), *p*-toluenesulfonyl chloride (TCI), ethyl chloroformate (Kishida) and sodium azide (Kishida) were used as purchased. *(S)*-3,7-Dimethyl-1-octanol was prepared from *(S)*-(−)-citronellol (Azmax) by hydrogenation with palladium on activated carbon (Pd, 10%) in ethanol.

THF was dried over sodium benzophenone ketyl and distilled on to CaH_2, followed by vacuum distillation on to $LiAlH_4$, and stored under nitrogen. This was distilled again under high vacuum just before use for polymerization. Piperidine (Wako) was dried over CaH_2 and distilled under reduced pressure. Lithium amide of piperidine was prepared from piperidine in THF by adding an equimolar amount of *tert*-butyllithium (1.7 M in pentane) at room temperature.

Optically active phenyl isocyanate derivative **1** was synthesized according to Scheme 1. Other optically active phenyl isocyanate derivatives were also prepared in an analogous method used for the synthesis of **1**.

3-[(R)-sec-Butoxy]benzoic acid. Treatment of (*S*)-*sec*-butanol (13.9 g) and *p*-toluenesulfonyl chloride (77.8 g) in dry pyridine at 0 °C under a nitrogen atmosphere gave (*S*)-*sec*-butyl *p*-toluenesulfonate (38.2 g). The Williamson ether synthesis using ethyl 3-hydroxybenzoate (27.4 g) and (*S*)-*sec*-butyl *p*-toluenesulfonate, followed by purification with silica gel chromatography using diethyl ether–hexane (1:10) as the eluent, provided ethyl 3-[(*R*)-*sec*-butoxy]benzoate (20.4 g). This compound was hydrolyzed with 2 M NaOH under reflux in ethanol to give 3-[(*R*)-*sec*-butoxy]benzoic acid. Yield, 15.0 g (41%). IR (neat, cm^{-1}), 1691 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 1.0 (t, 3H, CH_3), 1.3 (d, 3H, CH_3), 1.6–1.8 (m, 2H, CH_2), 4.3–4.4 (m, 1H, CH),



Scheme 1. Synthesis of **1**

7.1 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.6 (m, 1H, aromatic), 7.7 (m, 1H, aromatic), 12.4 (s, 1H, COOH).

*3-[(R)-sec-Butoxy]phenyl isocyanate (**1**).* The modified Curtius rearrangement was employed to convert 3-[(*R*)-*sec*-butoxy]benzoic acid to the isocyanate **1**.[10] 3-[(*R*)-*sec*-Butoxy]benzoic acid (10.9 g) was dissolved in acetone (200 ml) and the solution was cooled in an ice-bath. To this solution were added Et_3N (7.7 g) and then ethyl chloroformate (9.2 g). After the reaction mixture had been stirred for 1.5 h at 0 °C, sodium azide (6.6 g) in H_2O (30 ml) was slowly added dropwise. The mixture was stirred for 1.5 h at 0 °C and poured into a mixture of ice–water (300 ml) and toluene (200 ml). The organic layer was separated, washed with ice-water and dried over magnesium sulfate. After filtration, the filtrate was heated under reflux for 2 h and then cooled to room temperature. The solvent was evaporated *in vacuo* and the residue was distilled under reduced pressure (b.p. 57–60 °C/0.3 mmHg) to give **1** (7.8 g) in 73% yield, $[\alpha]_{365}^{25}$ −95°, $[\alpha]_D^{25}$ −33° (*c* 1.0, THF). The enantiomeric excess of **1** was determined to be 80% by chromatographic enantioseparation on a chiral column (CHIRALCEL OD, Daicel)[11] using hexane–ethanol (99.8:0.2) as the eluent. IR (neat, cm^{-1}), 2267 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 1.0 (t, 3H, CH_3), 1.3 (d, 3H, CH_3), 1.6–1.8 (m, 2H, CH_2), 4.2–4.3 (m, 1H, CH), 6.6–6.7 (m, 2H, aromatic), 6.7–6.8 (m, 1H, aromatic), 7.2 (t, 1H, aromatic). Analysis: calculated for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.09; H, 6.96; N, 7.56%.

3-[(S)-2-Methylbutoxy]benzoic acid. This compound was prepared from (*S*)-2-methyl-1-butanol (13.5 g) according to an analogous method used for the synthesis of 3-[(*R*)-*sec*-butoxy]benzoic acid. Yield, 9.9 g (31%). IR (KBr, cm^{-1}), 1685 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 0.96 (t, 3H, CH_3), 1.03 (d, 3H, CH_3), 1.2–1.3 (m, 1H, CH_2), 1.5–1.6 (m, 1H, CH_2), 1.8–1.9 (m, 1H, CH), 3.8–3.9 (m, 2H, OCH_2), 7.2 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.6 (m, 1H, aromatic), 7.7 (m, 1H, aromatic).

*3-[(S)-2-Methylbutoxy]phenyl isocyanate (**2**).* Compound **2** was prepared from 3-[(*S*)-2-methylbutoxy]benzoic acid in the same manner as used for the synthesis of **1**. Yield, 5.6 g (58%). $[\alpha]_{365}^{25}$ +37°, $[\alpha]_D^{25}$ +9.7° (*c* 1.0, THF). IR (neat, cm^{-1}), 2270 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 0.95 (t, 3H, CH_3), 1.01 (d, 3H, CH_3), 1.2–1.3 (m, 1H, CH_2), 1.5–1.6 (m, 1H, CH_2), 1.8–1.9 (m, 1H, CH), 3.7–3.8 (m, 2H, OCH_2), 6.6 (t, 1H, aromatic), 6.65 (m, 1H, aromatic), 6.7 (m, 1H, aromatic), 7.2 (t, 1H, aromatic). Analysis: calculated for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.15; H, 7.55; N, 6.98%.

3-[(S)-3,7-Dimethyloctyloxy]benzoic acid. The acid was prepared from (*S*)-3,7-dimethyloctanol (12.1 g) according to an analogous method used for 3-[(*R*)-*sec*-butoxy]benzoic acid. Yield, 9.6 g (45%). IR (KBr, cm^{-1}), 1685 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 0.87 (d, 6H, $2CH_3$), 0.96 (d, 3H, CH_3), 1.1–1.9 (m, 10H, $4CH_2$ and 2CH), 4.1 (m, 2H, OCH_2), 7.2 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.6 (m, 1H, aromatic), 7.7 (m, 1H, aromatic).

*3-[(S)-3,7-Dimethyloctyloxy]phenyl isocyanate (**3**).* Compound **3** was prepared from 3-[(*S*)-3,7-dimethyloctyloxy]benzoic acid in the same manner as **1**. Yield, 3.4 g (36%). $[\alpha]_{365}^{25}$ −8.4°, $[\alpha]_D^{25}$ −2.7° (*c* 1.3, THF). IR (neat, cm^{-1}), 2268 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 0.87 (d, 6H, $2CH_3$), 0.93 (d, 3H, CH_3), 1.1–1.9 (m, 10H, $4CH_2$ and 2CH), 3.9–4.0 (m, 2H, OCH_2), 6.61 (t, 1H, aromatic), 6.66 (m, 1H, aromatic), 6.73 (m, 1H, aromatic), 7.2 (t, 1H, aromatic). Analysis: calculated for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.99; H, 9.39; N, 5.20%.

4-[(R)-sec-Butoxy]benzoic acid. This was prepared analogously from (*S*)-*sec*-butanol (14.3 g) and ethyl 4-hydroxybenzoate (24.3 g). Yield, 10.5 g (28%). IR (KBr, cm^{-1}), 1671 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 1.0 (t, 3H, CH_3), 1.3 (d, 3H, CH_3), 1.6–1.8 (m, 2H, CH_2), 4.4 (m, 1H, CH), 6.9 (m, 2H, aromatic), 8.0 (m, 2H, aromatic).

*4-[(R)-sec-Butoxy]phenyl isocyanate (**4**).* Compound **4** was prepared from 4-[(*R*)-*sec*-butoxy]benzoic acid in the same manner as **1**. Yield, 4.0 g (39%). $[\alpha]_{365}^{25}$ −98°, $[\alpha]_D^{25}$ −28° (*c* 1.0, THF). IR (neat, cm^{-1}), 2275 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 1.0 (t, 3H, CH_3), 1.3 (d, 3H, CH_3), 1.5–1.8 (m, 2H, CH_2), 4.2 (m, 1H, CH), 6.8 (m, 2H, aromatic), 7.0 (m, 2H, aromatic). Analysis: calculated for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.04; H, 6.99; N, 7.53%.

4-[(S)-2-Methylbutoxy]benzoic acid. The acid was prepared analogously from (*S*)-2-methyl-1-butanol (16.2 g) and ethyl 4-hydroxybenzoate. Yield, 11.3 g (30%). IR (KBr, cm^{-1}), 1676 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 0.96 (t, 3H, CH_3), 1.03 (d, 3H, CH_3), 1.2–1.3 (m, 1H, CH_2), 1.5–1.6 (m, 1H, CH_2), 1.8–1.9 (m, 1H, CH), 3.8–3.9 (m, 2H, OCH_2), 6.9 (m, 2H, aromatic), 8.1 (m, 2H, aromatic).

*4-[(S)-2-Methylbutoxy]phenyl isocyanate (**5**).* Compound **5** was prepared from 4-[(*S*)-2-methylbutoxy]benzoic acid in the same manner as used for the synthesis of **1**. Yield, 4.6 g (42%). $[\alpha]_{365}^{25}$ +39°, $[\alpha]_D^{25}$ +13° (*c* 1.1, THF). IR (neat, cm^{-1}), 2276 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 0.94 (t, 3H, CH_3), 1.0 (d, 3H, CH_3), 1.2–1.3 (m, 1H, CH_2), 1.5–1.6 (m, 1H, CH_2), 1.8–1.9 (m, 1H, CH), 3.7–3.8 (m, 2H, OCH_2), 6.8 (m, 2H, aromatic), 7.0 (m, 2H, aromatic). Analysis: calculated for

Table 1. Polymerization of optically active phenyl isocyanates (**1**–**6**) bearing an alkoxyl group with Li piperidide in THF at −98 °C[a]

Run	Monomer	Yield (%)[b]	$\overline{M}_n$[c] ($\times 10^4$)	$\overline{M}_w/\overline{M}_n$[c]	$[\alpha]_{365}^{25}$[d]	$[\alpha]_{D}^{25}$[d]
1	**1**	68	2.8	1.2	−3129	−648
2	**2**	70	3.4	1.1	+1331	+283
3	**3**	100	5.3	1.3	+260	+55
4	**4**	64	5.8	1.1	+2079	+424
5	**5**	86	3.7	1.4	−20	−2
6	**6**	93	4.3	1.2	+542	+113

[a] Conditions: monomer 0.5 g, [monomer]/[initiator] = 50, THF 5 ml, time 4 h.
[b] MeOH-insoluble part.
[c] Determined by SEC with a light-scattering detector.
[d] In THF.

$C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.09; H, 7.56; N, 7.05%.

4-[(S)-3,7-Dimethyloctyloxy]benzoic acid. This compound was prepared from (*S*)-3,7-dimethyloctanol (20.0 g) and ethyl 4-hydroxybenzoate according to an analogous method described above. Yield, 11.0 g (31%). IR (KBr, cm^{-1}), 1664 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$), δ 0.87 (d, 6H, $2CH_3$), 0.95 (d, 3H, CH_3), 1.1–1.9 (m, 10H, $4CH_2$ and 2CH), 4.0–4.1 (m, 2H, OCH_2), 6.9 (m, 2H, aromatic), 8.0 (m, 2H, aromatic).

4-[(S)-3,7-Dimethyloctyloxy]phenyl isocyanate (6). Compound **6** was prepared from 4-[(*S*)-3,7-dimethyloctyloxy]benzoic acid in the same manner as **1**. Yield, 4.5 g (41%). $[\alpha]_{365}^{25}$ −11° $[\alpha]_D^{25}$ −3.1° (*c* 1.2, THF). IR (neat, cm^{-1}), 2276 (N=C=O); ^1H NMR (400 MHz, $CDCl_3$), δ 0.87 (d, 6H, $2CH_3$), 0.93 (d, 3H, CH_3), 1.1–1.8 (m, 10H, $4CH_2$ and 2CH), 3.9–4.0 (m, 2H, OCH_2), 6.8 (m, 2H, aromatic), 7.0 (m, 2H, aromatic). Analysis: calculated for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.91; H, 9.29; N, 5.36%.

Polymerization. Polymerization was carried out in a glass ampule under a dry nitrogen atmosphere in THF at −98 °C. The lithium amide of piperidine was used as an initiator. The monomer and THF were placed in a glass ampule and cooled to −98 °C. The polymerization reaction was initiated by adding the initiator solution with a syringe. After 4 h, the reaction was terminated by adding a 10-fold excess of HCl in methanol to the initiator, then the polymer was precipitated in a large amount of methanol. The polymer was collected by centrifugation and dried *in vacuo* at room temperature.

Measurement. Optical rotation was measured on a Jasco DIP-181 polarimeter. CD spectra were measured with a Jasco J-720 spectrometer. ^1H NMR spectra were taken on a Varian Gemini-2000 (400 MHz for ^1H) spectrometer with tetramethylsilane (TMS) as the internal standard in

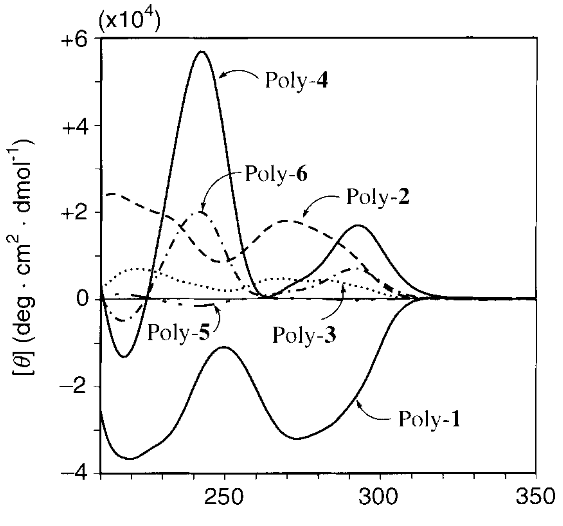


Figure 1. CD spectra of poly(phenyl isocyanate)s bearing an alkoxyl group in THF at ambient temperature (*ca* 23–25 °C)

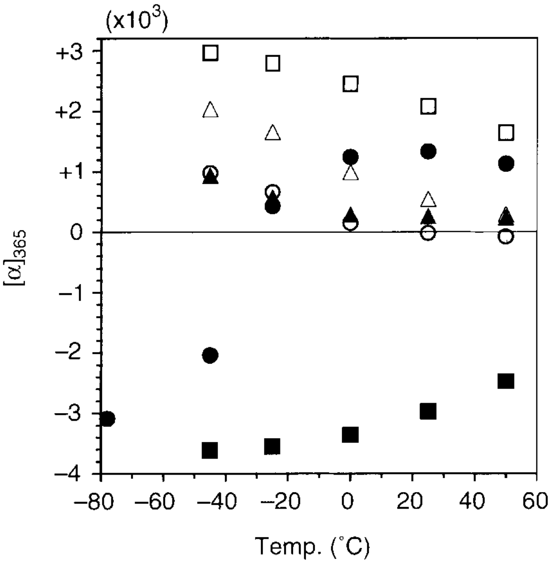


Figure 2. Temperature dependence of specific rotation of poly-**1** (■), poly-**2** (●), poly-**3** (▲), poly-**4** (□), poly-**5** (○) and poly-**6** (△) in THF. The concentration of the polymers was 1.0 g dl^{-1}

$CDCl_3$ at ambient temperature or 60 °C. IR spectra were recorded on a Jasco FT/IR-620 spectrometer. The molecular weight of the polymer was determined by SEC measurement on a Shodex System-21 GPC system equipped with a Shodex RI-71S detector and a Wyatt Technology DAWN DSP-F multi-angle light-scattering detector using THF as an eluent at 40 °C. Two SEC columns, Shodex KF-803 and KF-806L, were connected in series. The determination of the enantiomeric excess (%e.e.) of the chiral monomers was performed on a Jasco PU-980 liquid chromatograph equipped with Jasco 970-UV and Jasco OR-990 polarimetric detectors using a chiral column (CHIRALCEL OD, Daicel)[11] using hexane–ethanol as the eluent.

RESULTS AND DISCUSSION

Table 1 shows the results of the polymerization of **1–6** with the lithium amide of piperidine as an initiator in THF at −98 °C. Among the polymers obtained with an optically active group at the *meta* position of the aromatic ring, poly-**1** and poly-**2** showed a much greater specific rotation than that of the corresponding monomer, and the specific rotation of poly-**1** ($[\alpha]_D^{25}$ −648°) is the largest one in the optically active polyisocyanates so far reported, to the best of our knowledge. The CD spectra of poly-**1–6** (runs 1–6 in Table 1) in THF at room temperature are shown in Fig. 1. Poly-**1** and poly-**2** showed a very intense CD band in the region of the main-chain absorption (210–310 nm), indicating that these polymers have a predominantly one-handed helical conformation in solution. Poly-**3** also showed a CD band in the main-chain region, but its intensity was much lower than those of poly-**1** and poly-**2**. For the polymers bearing an optically active group at the *meta* position on the aromatic ring, the optical rotation decreased as the asymmetric center on the side chain moves away from the polymer main chain. On the other hand, the polymers with an optically active group at the *para* position, poly-**4** and poly-**6**, showed a much greater specific rotation and CD band compared with the corresponding monomers, whereas those of poly-**5** were very small. The optical activity of the *para*-substituted polymers may follow the odd–even rule.

Figure 2 shows the temperature dependence of the specific rotation of the polymers in THF. The absolute values of the specific rotation of poly-**1**, poly-**3**, poly-**4**, and poly-**6** increased with decrease in temperature. This may be because the persistence length of the helical structure of the polymer chain increases as the temperature decreases, as already reported for poly(alkyl isocyanate)s and other poly(phenyl isocyanate)s.[5,7ab] On the other hand, the specific rotations of poly-**2** and poly-**5** exhibited an unusual temperature dependence. The specific rotation of poly-**2** changed from a positive to a large negative value on decreasing the temperature, and then quickly returned back to the original positive value when the sample solution was restored to 25 °C. The CD spectra of poly-**2** in THF at 25 °C and at −45 °C are shown in Fig. 3. At −45 °C, the polymer showed an intense negative peak in the absorption region due to the main chain, and at 25 °C a positive peak, and this CD spectral change was accompanied by only minor changes in the UV spectra. These results indicate that poly-**2** undergoes a reversible helix–helix transition with change in temperature. The specific rotation of poly-**5** also changed reversibly from a small negative to a positive value with decrease in temperature, and the CD spectral pattern was reversed along with the change in the specific rotation. Poly-**5** also appears to undergo a reversible helix–helix transition in THF, although the change in the optical activity of poly-**5** was not as significant as that in poly-**2**.

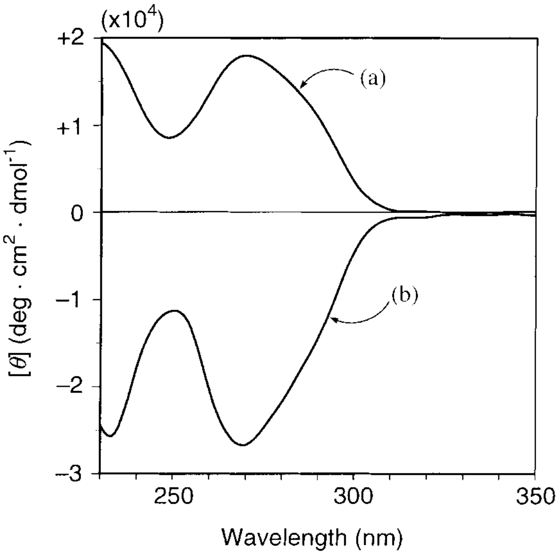


Figure 3. CD spectra of poly-**2** (1.1 mg ml^{-1}) at ambient temperature (*ca* 23–25 °C) (a) and −45 °C (b) in THF

As reported in previous papers,[9] the temperature-induced helix–helix transition of poly(phenyl isocyanate)s bearing an optically active ester group occurred only in poly[(*S*)-3*sec*BuOCPI], which has an asymmetric center at the γ-position from the phenyl group. For the poly(phenyl isocyanate)s bearing an optically active alkoxyl group, only poly-**2** and poly-**5**, whose structure and position of the asymmetric center are equivalent to those of poly[(*S*)-3*sec*BuOCPI], exhibited a reversible helix–helix transition. These results indicate that the important factor for the helix–helix transition is the existence of the chiral *sec*-butyl group at the γ-position from the phenyl group.

In order to investigate the effect of molecular weight on the main-chain conformation of poly-**2**, a series of poly-**2** with various molecular weights were prepared. In Fig. 4, the specific rotations of the polymers at 25 °C in

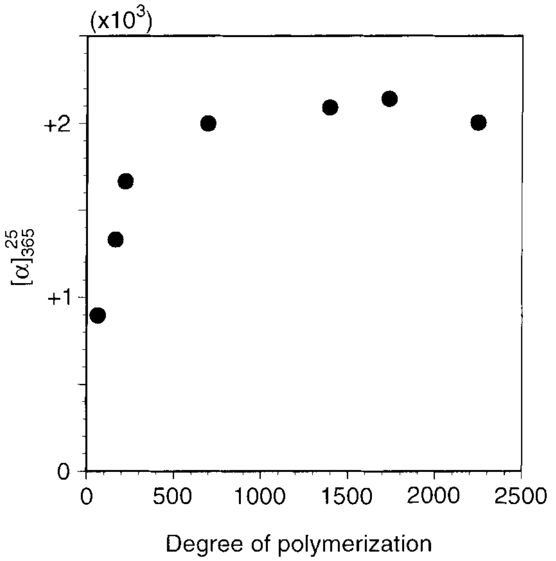


Figure 4. Plots of specific rotation versus degree of polymerization of poly-**2** in THF

THF are plotted versus the degree of polymerization (DP). The specific rotation of the polymers increased with increase in DP, up to DP = 700, and reached a plateau value ($[\alpha]_{365}^{25} \approx +2100°$). Green *et al.* reported an analogous relationship between the molecular weights and $[\alpha]_{300}$ for the optically active poly(alkyl isocyanate) poly[(*R*)-1-deutero-1-hexyl isocyanate], with chirality arising from the difference in deuterium and hydrogen, in which $[\alpha]_{300}$ increased up to DP ≈ 500 and then maintained a constant value.[5b] These results suggest that poly-**2** may have a long persistence length of the helical structure, which is comparable to that of poly[(*R*)-1-deutero-1-hexyl isocyanate].

The specific rotations of poly-**2** of DP = 160 and 2200 were measured at various temperatures and the results are shown in Fig. 5. The inversion of optical activity took place at almost the same temperature regardless of the DP, indicating that the helix–helix transition of poly-**2** proceeds independently of the molecular weight. Specific rotation and CD measurements were also performed at a lower concentration (specific rotation, 0.2 g dl^{-1}; CD, 0.03 mg ml^{-1}) in THF at various temperatures. The changes in the specific rotation and CD spectra of poly-**2** (DP = 160) at a low concentration were nearly the same as those in Figs. 2 and 3, respectively. These results exclude the possibility of the aggregation of the polymer chains for the reason of the above inversion of optical activity, although it has been reported that an analogous change in the optical activity of a polypeptide can be ascribed to an aggregation of polymer chains.[12]

To examine the solvent effect on the helix–helix transition of poly-**2**, the temperature dependence of the specific rotation was investigated in various solvents, such as toluene, dichloromethane and diethyl ether (Fig. 6). The specific rotation in toluene changed slightly without crossing zero at low temperature. In dichloromethane, the specific rotation increased monotonically as the temperature decreased from 35 to −45 °C. On the other hand, the change in the specific rotation in diethyl ether was similar in pattern to that in THF, and the specific rotation crossed zero at a lower temperature than in THF. In chloroform, an inversion of the sign for the optical activity was also observed, although a small positive optical activity was observed only above 40 °C. These results indicate that the conformational change of poly-**2** with change in temperature depends significantly on the solvents and clear inversion of the helices occurs in some solvents such as THF and diethyl ether.

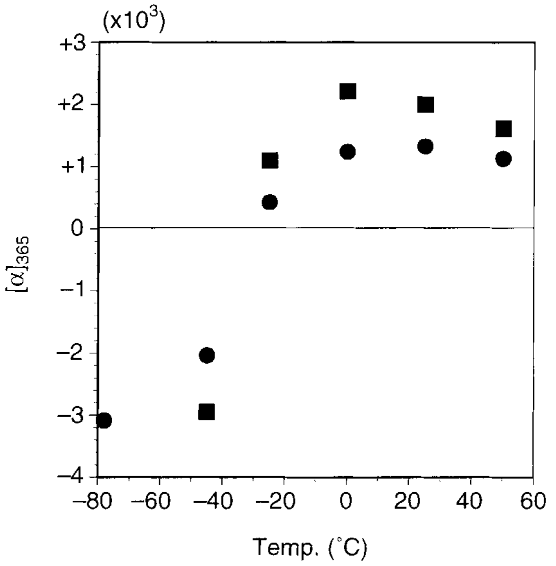


Figure 5. Temperature dependence of specific rotation of poly-**2** in THF [(●) DP = 160 and (■) DP = 2200] (*c* = 1.0 g dl^{-1})

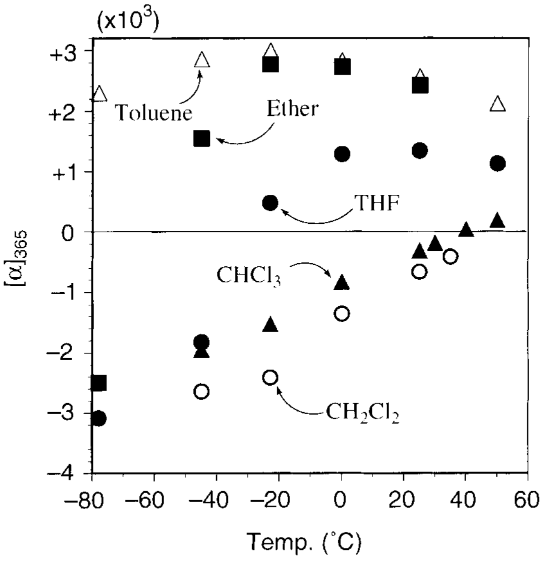


Figure 6. Temperature dependence of specific rotation of poly-**2** in toluene (△), diethyl ether (■), THF (●), $CHCl_3$ (▲) and CH_2Cl_2 (○)

Although at present it is not clear why poly-**2** and poly-**5** exhibit a temperature-induced helix–helix transition, it could be correlated with the enthalpy and entropy factors of solvation. The left- and right-handed helical structures of the poly-**2**s are diastereomers, which means that they possess different polarities. The polarity or dielectric constant of the solvents changes depending on temperature.[13] This means that the influence of the solvents on the two diastereomeric structures are not identical and must be temperature dependent. The polarity of THF is known to increase with decrease in temperature.[13] The more polar helical structure of poly-**2** is expected to be more stabilized at lower temperature in THF, which may be the main reason for the inversion of the helix.

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