Synthesis and Conformational Characteristics of Poly(phenyl isocyanate)s Bearing an Optically Active Ester Group

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Received August 28, 1998; Revised Manuscript Received November 16, 1998

ABSTRACT: Optically active phenyl isocyanates (**1**−**9**) bearing an optically active ester group were synthesized and polymerized with an achiral anionic initiator. The resulting polymers from **1** and **4**−**9** showed a much greater specific rotation than that of the corresponding monomer and an intense circular dichroism (CD) band caused by the main-chain absorption, indicating that these polymers have a predominantly one-handed helical conformation in solution. On the other hand, the polymers obtained from **2** and **3** showed a much smaller specific rotation and a weaker CD band than poly-**1**, which suggests that, as the distance between the polymer main chain and the asymmetric center on the side chain increases, the asymmetric center cannot effectively induce an excess of one helical twist sense of the polymer main chain at room temperature. However, the specific rotation and CD intensity of poly-**2** greatly increased because of a predominantly one-handed helical conformation at low temperatures. The polymers obtained from **3**−**9** did not show such a temperature effect on conformational change. Specific rotation of the copolymers of chiral **8** and achiral **10** changed from a positive to a negative value with an increase in the content of the optically active unit. The helicity of the copolymer may depend on the composition.

Introduction

Poly(alkyl isocyanate)s have a rigid rodlike main chain consisting of only amide bonds and are classified as N-substituted 1-nylon.[1] Polyisocyanates, as well as double-helical DNA, poly(aryl amide)s, and cellulose derivatives are well known as typical semiflexible polymers[2] and form liquid crystals because of stiffness of the main chain.[3] A significant amount of experimental data concerning solution properties, liquid crystallinity, and crystal structures of polyisocyanates have been reported.[1a,b,3,4] It had been difficult to control the molecular weight in the polymerzation of isocyanates.[1c,5] However, Novak and co-workers[6] recently reported that the polymerization of isocyanates with organotitanium compounds proceeds in a living manner.

Polyisocyanates are also interesting as optically active helical polymers which assume a helical conformation not only in the solid state but also in solution.[7] The helical conformation is maintained by the combination of the double-bond character of consecutive amide bonds and the steric repulsions between side groups. Although the helix is not stable but is dynamic with quickly occurring occasional reversals in the main chain, optically active polymers can be obtained by introducing a small amount of an optically active group through copolymerization with an optically active monomer[8a−e] or by initiating polymerization with an optically active initiator because of the long-persistence length of the helix.[8f] On the other hand, poly(phenyl isocyanate)s, in which the phenyl ring is connected directly to the main chain, had been considered to be more flexible and to exist as a random coil in solution because of the lack of stiffness of the main chain.[1a] However, we recently demonstrated that poly(phenyl isocyanate)s exhibit clear optical activity caused by a prevailing one-handed helical structure when an optically active group is introduced at the initial polymer end.[9] We also reported that an optically active poly(phenyl isocyanate) bearing an amide group, poly(3-((*S*)-(α-methylbenzyl)carbamoyl)phenyl isocyanate), obtained with an achiral initiator, has an almost completely one-handed helical structure even in solution, which enables the discrimination of enantiomers.[10] This is the first example of chiral discrimination by a polyisocyanate.

Very recently, we also found that poly(3-((*S*)-*sec*-butoxycarbonyl)phenyl isocyanate) (poly-**1**) shows a reversible helix−helix transition on changing temperature in tetrahydrofuran (THF).[11] In the present study, novel optically active phenyl isocyanates bearing an ester group (Scheme 1), 3-((*S*)-(2-methylbutoxy)carbonyl)phenyl isocyanate (**2**), 3-((*S*)-(3,7-dimethyloctyloxy)carbonyl)phenyl isocyanate (**3**), 3-((−)-menthoxycarbonyl)phenyl isocyanate (**4**), 3-((*S*)-(2-octyloxy)carbonyl)phenyl isocyanate (**5**), 3-((*S*)-(1-(methoxycarbonyl)ethoxy)carbonyl)phenyl isocyanate (**6**), 4-((*S*)-*sec*-butoxycarbonyl)phenyl isocyanate (**7**), 3-((*S*)-(α-methylbenzyloxy)carbonyl)phenyl isocyanate (**8**), and 4-((*S*)-(α-methylbenzyloxy)carbonyl)phenyl isocyanate (**9**), were synthesized and polymerized with the lithium amide (Li-piperidine) of piperidine. Chiroptical properties of the obtained polymers were investigated to clarify the effect of the side-chain ester groups on the main-chain conformation.

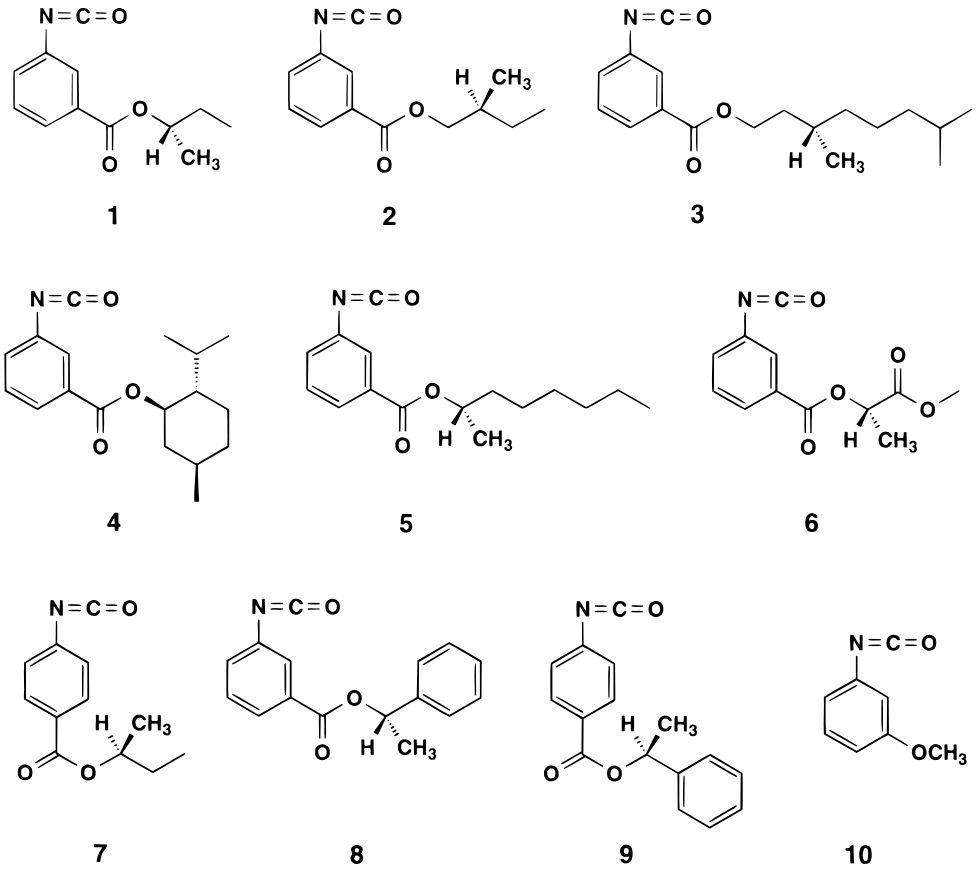
Experimental Section

Materials. (*S*)-(+)-*sec*-Butyl alcohol, methyl (*S*)-(−)-lactate, and isophthaloyl dichloride were purchased from Aldrich. (*S*)-(−)-α-Methylbenzyl alcohol and (*S*)-(+)-2-octanol were obtained from Azmax (Japan). (−)-Menthol, ethyl chloroformate, and sodium azide were purchased from Kishida (Japan). (*S*)-2-Methyl-1-butanol was purchased from Kodak, and terephthaloyl chloride from Wako (Japan). These reagents were used as obtained. *m*-Methoxyphenyl isocyanate was obtained from Aldrich, dried over CaH_2, and distilled under reduced pressure. (*S*)-3,7-Dimethyl-1-octanol was prepared from (*S*)-citronellol (Azmax) by hydrogenation with palladium on activated carbon (Pd, 10%) in ethanol.

THF used in polymerization was dried over sodium benzophenone ketyl, distilled onto $LiAlH_4$, and then distilled again

10.1021/ma981362i CCC: $18.00
Published on Web 01/28/1999

Scheme 1



under high vacuum just before use. 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.

Synthesis of **1** has been presented previously.[11] Novel optically active phenyl isocyanate derivatives **2**−**9** were synthesized as follows by Curtius rearrangement of the corresponding azide compounds.[12]

3-((*S*)-(2-Methylbutoxy)carbonyl)benzoic Acid. A mixture of (*S*)-2-methyl-1-butanol (18.4 g, 208 mmol) and pyridine (18.1 g, 229 mmol) was slowly added dropwise to a THF (250 mL) solution of isophthaloyl dichloride (42.3 g, 208 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4.5 h, pyridine (18.1 g, 229 mmol) and water (100 mL) were added and the mixture was heated for 4 h under reflux. After cooling to room temperature, the solution was washed with 0.2 N HCl (500 mL) and water (500 mL × 2), and dried over $MgSO_4$. After evaporating the solvent, the residue was dissolved in 300 mL of chloroform, and insoluble isophthalic acid was removed by filtration on a glass filter packed with Celite. The solvent was removed under reduced pressure, and the residual oily product was chromatographed over silica gel with use of chloroform as the eluent to remove the diester. 3-((*S*)-(2-Methylbutoxy)carbonyl)benzoic acid was obtained as a colorless solid in 41% yield. $[\alpha]_{365}^{25}$ +15.6°, $[\alpha]_D^{25}$ +4.5° (*c* 1.2, THF). IR (KBr, cm^{-1}) 1718 (C═O of ester), 1691 (C═O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, 3H, CH_3), 1.04 (d, 3H, CH_3), 1.2−1.6 (m, 2H, CH_2), 1.9 (m, 1H, CH), 4.1−4.3 (m, 2H, OCH_2), 7.6 (t, 1H, aromatic), 8.3−8.8 (m, 3H, aromatic).

3-((*S*)-(2-Methylbutoxy)carbonyl)phenyl Isocyanate (2). To 3-((*S*)-(2-methylbutoxy)carbonyl)benzoic acid (11.2 g, 47.3 mmol) dissolved in acetone (150 mL), Et_3N (5.9 g, 58.2 mmol), and then ethyl chloroformate (6.3 g, 58.2 mmol) were added at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, sodium azide (5.4 g, 82.8 mmol) in H_2O (30 mL) was slowly added. After stirring for 1.5 h at 0 °C, the reaction mixture was 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 $MgSO_4$. The toluene solution was heated under reflux for 2 h until the evolution of nitrogen gas stopped. The solvent was evaporated in vacuo and the residue was distilled under reduced pressure (94 °C at 0.25 mmHg) to give **2** (4.4 g, 19.0 mmol) in 40% yield. $[\alpha]_{365}^{25}$ +15°, $[\alpha]_D^{25}$ +1.8° (*c* 2.5, THF). IR (neat, cm^{-1}) 2270 (N═C═O), 1723 (C═O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, 3H, CH_3), 1.02 (d, 3H, CH_3), 1.2−1.6 (m, 2H, CH_2), 1.9 (m, 1H, CH), 4.1−4.3 (m, 2H, OCH_2), 7.2−7.3 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.7−7.9 (m, 2H, aromatic). Anal. Calcd for $C_{13}H_{15}NO_3$: N, 6.00; C, 66.94; H, 6.48. Found: N, 6.14; C, 66.86; H, 6.68.

3-((*S*)-(3,7-Dimethyloctyloxy)carbonyl)benzoic Acid. The acid was prepared from (*S*)-3,7-dimethyloctanol (15.0 g, 95 mmol) according to an analogous method used for the synthesis of 3-((*S*)-(2-methylbutoxy)carbonyl)benzoic acid and was purified by gradient chromatography on silica gel using ether−hexane (1/4−1/1) as the eluent. Yield, 16.9 g (58%). $[\alpha]_{365}^{25}$ −3.7°, $[\alpha]_D^{25}$ −0.7° (*c* 1.2, THF). IR (KBr, cm^{-1}) 1719 (C═O of ester), 1687 (C═O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 0.9 (d, 6H, $2CH_3$), 1.0 (d, 3H, CH_3), 1.1−1.9 (m, 10H, $4CH_2$ and 2CH), 4.4 (m, 2H, OCH_2), 7.6 (t, 1H, aromatic), 8.3 (m, 2H, aromatic), 8.8 (s, 1H, aromatic).

3-((*S*)-(3,7-Dimethyloctyloxy)carbonyl)phenyl Isocyanate (3). **3** was prepared from 3-((*S*)-(3,7-dimethyloctyloxy)-carbonyl)benzoic acid in the same manner used for the synthesis of **2**. Yield, 10.8 g (66%). $[\alpha]_{365}^{25}$ −8.1°, $[\alpha]_D^{25}$ -1.6° (*c* 0.4, THF). IR (neat, cm^{-1}) 2264 (N═C═O), 1724 (C═O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 0.8 (d, 6H, $2CH_3$), 1.0 (d, 3H, CH_3), 1.1−1.9 (m, 10H, $4CH_2$ and 2CH), 4.4 (m, 2H, OCH_2), 7.2−7.3 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.8 (s, 1H, aromatic), 7.9 (d, 1H, aromatic). Anal. Calcd for $C_{18}H_{25}NO_3$: N, 4.62; C, 71.26; H, 8.31. Found: N, 4.72; C, 71.13; H, 8.50.

3-((−)-Menthoxycarbonyl)benzoic Acid. This was obtained from (−)-menthol (23.0 g, 148 mmol) analogously to the method used for the synthesis of 3-((*S*)-(3,7-dimethyloctyloxy)-carbonyl)benzoic acid and was purified by gradient chromatography on silica gel using chloroform−hexane (1/1, chloro-

form only) as the eluent. Yield, 20.5 g (43%). $[\alpha]_{365}^{25}$ −221.2°, $[\alpha]_D^{25}$ −70.5° (*c* 1.1, THF). IR (KBr, cm^{-1}) 1718 (C=O of ester), 1698 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 0.8 (d, 3H, CH_3), 0.8 (q, 6H, $2CH_3$), 1.5−2.1 (m, 8H, $3CH_2$ and 2CH), 5.0 (m, 1H, OCH), 7.6 (t, 1H, aromatic), 8.3 (dd, 2H, aromatic), 8.8 (m, 1H, aromatic).

3-((−)-Menthoxycarbonyl)phenyl Isocyanate (4). 4 was obtained from 3-((−)-menthoxycarbonyl)benzoic acid (10.0 g, 32.9 mmol) in the same manner as **2**. Yield, 2.9 g (29%). $[\alpha]_{365}^{25}$ −204.2°, $[\alpha]_D^{25}$ -67.5° (*c* 0.6, THF). IR (neat, cm^{-1}) 2268 (N=C=O), 1717 (C=O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 0.8 (d, 3H, CH_3), 0.9 (q, 6H, $2CH_3$), 1.1−2.1 (m, 8H, $3CH_2$ and 2CH), 4.9 (m, 1H, OCH), 7.2−7.3 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.7−7.9 (m, 2H, aromatic). Anal. Calcd for $C_{18}H_{23}NO_3$: N, 4.65; C, 71.73; H, 7.69. Found: N, 4.78; C, 71.73; H, 7.87.

3-((S)-(2-Octyloxy)carbonyl)benzoic Acid. The acid was prepared from (*S*)-(+)-2-octanol (14.5 g, 112 mmol) according to a method analogous to that described for the synthesis of 3-((*S*)−(3,7-dimethyloctyloxy)carbonyl)benzoic acid and was purified by chromatography over silica gel with ether−hexane (1/6) as the eluent. Yield, 13.1 g (38%). $[\alpha]_{365}^{25}$ +117°, $[\alpha]_D^{25}$ +35.6° (*c* 1.5, THF). IR (KBr, cm^{-1}) 1717 (C=O of ester), 1695 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 0.9 (t, 3H, CH_3), 1.2−1.8 (m, 10H, $5CH_2$), 5.2 (q, 1H, CH), 7.6 (t, 1H, aromatic), 8.3 (d, 2H, aromatic), 8.8 (s, 1H, aromatic).

3-((*S*)-(2-Octyloxy)carbonyl)phenyl Isocyanate (5). 5 was obtained from 3-((S)−(2-octyloxy)carbonyl)benzoic acid (12.1 g, 43.4 mmol) in the same manner as **2**. Yield, 7.3 g (62%). $[\alpha]_{365}^{25}$ +122.8°, $[\alpha]_D^{25}$ +36.6° (*c* 3.6, THF). IR (neat, cm^{-1}) 2268 (N=C=O), 1717 (C=O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 0.9 (t, 3H, CH_3), 1.2−1.8 (m, 10H, $5CH_2$), 5.1−5.2 (q, 1H, CH), 7.2−7.3 (m, 1H, aromatic), 7.4 (t, 1H, aromatic), 7.8 (s, 1H, aromatic), 7.8−7.9 (m, 1H, aromatic). Anal. Calcd for $C_{16}H_{21}NO_3$: N, 5.09; C, 69.79; H, 7.69. Found: N, 5.27; C, 69.79; H, 7.82.

3-((*S*)-(1-(Methoxycarbonyl)ethoxy)carbonyl)benzoic Acid. This was prepared from methyl (*S*)-lactate (30.1 g, 148 mmol) according to a method analogous to the synthesis of 3-((*S*)-(2-methylbutoxy)carbonyl)benzoic acid and was purified by recrystallization (twice) from benzene−hexane (1/1). Yield, 11.9 g (33%). $[\alpha]_{365}^{25}$ +82.7°, $[\alpha]_D^{25}$ +12.8° (*c* 1.0, THF). IR (KBr, cm^{-1}) 1757, 1733 (C=O of ester), 1695 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 1.7 (d, 3H, CH_3), 3.8 (s, 3H, OCH_3), 5.4 (q, 1H, CH), 7.6 (t, 1H, aromatic), 8.3−8.4 (m, 2H, aromatic), 8.8 (s, 1H, aromatic).

3-((*S*)-(1-(Methoxycarbonyl)ethoxy)carbonyl)phenyl Isocyanate (6). 6 was synthesized from 3-((S)−(1-(methoxycarbonyl)ethoxy)carbonyl)benzoic acid in the same manner as **2**. Yield, 7.7 g (69%). $[\alpha]_{365}^{25}$ +78.8°, $[\alpha]_D^{25}$ +12.9° (*c* 3.5, THF). IR (neat, cm^{-1}) 2266 (N=C=O), 1762, 1729 (C=O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 1.6 (t, 3H, CH_3), 3.8 (s, 3H, OCH_3), 5.3−5.4 (q, 1H, CH), 7.3−7.5 (m, 2H, aromatic), 7.8−8.0 (m, 2H, aromatic). Anal. Calcd for $C_{12}H_{11}NO_5$: N, 5.62; C, 57.83; H, 4.45. Found: N, 5.81; C, 57.64; H, 4.50.

4-((*S*)-*sec*-Butoxycarbonyl)benzoic Acid. This was prepared from (*S*)-*sec*-butyl alcohol (9.9 g, 133 mmol) analogously to the method used for the synthesis of 3-((*S*)-(2-methylbutoxy)-carbonyl)benzoic acid and was purified by recrystallization from hexane. Yield, 10.8 g (37%). $[\alpha]_{365}^{25}$ +85.7°, $[\alpha]_D^{25}$ +29.1° (*c* 0.9, THF). IR (KBr, cm^{-1}) 1714 (C=O of ester), 1691 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 1.0 (t, 3H, CH_3), 1.4 (d, 3H, CH_3), 1.6−1.8 (m, 2H, CH_2), 5.1 (m, 1H, CH), 8.1−8.2 (m, 4H, aromatic).

4-((*S*)-*sec*-Butoxycarbonyl)phenyl Isocyanate (7). 7 was synthesized from 4-((*S*)-*sec*-butoxycarbonyl)benzoic acid in the same manner as **2**. Yield, 6.8 g (67%). $[\alpha]_{365}^{25}$ +95.6°, $[\alpha]_D^{25}$ +30.6° (*c* 3.6, THF). IR (neat, cm^{-1}) 2264 (N=C=O), 1718 (C=O of ester); ^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), 5.1 (m, 1H, CH), 7.1, 8.0 (m, 4H, aromatic). Anal. Calcd for $C_{12}H_{13}NO_3$: N, 6.39; C, 65.74; H, 5.98. Found: N, 6.52; C, 65.63; H, 6.15.

3-((*S*)-(α-Methylbenzyloxy)carbonyl)benzoic Acid. This was obtained from (*S*)-(−)-α-methylbenzyl alcohol (12.5 g, 103 mmol) according to a method analogous to that used for the synthesis of 3-((*S*)-(3,7-dimethyloctyloxy)carbonyl)benzoic acid and was purified by gradient chromatography on silica gel using ether−hexane (7/3−1/1) as the eluent. Yield, 11.9 g (45%). $[\alpha]_{365}^{25}$ +217°, $[\alpha]_D^{25}$ +46.3° (*c* 1.8, THF). IR (KBr, cm^{-1}) 1725 (C=O of ester), 1699 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 1.7 (d, 3H, CH_3), 6.2 (q, 1H, CH), 7.3−7.6 (m, 6H, aromatic), 8.3 (m, 2H, aromatic), 8.8 (s, 1H, aromatic).

3-((*S*)-(α-Methylbenzyloxy)carbonyl)phenyl Isocyanate (8). 8 was synthesized from 3-((*S*)-(α-methylbenzyloxy)-carbonyl)benzoic acid (11.0 g, 40.8 mmol) in the same manner as **2**. Yield, 6.5 g (60%). $[\alpha]_{365}^{25}$ +222.7°, $[\alpha]_D^{25}$ +48.0° (*c* 0.8, THF). IR (neat, cm^{-1}) 2270 (N=C=O), 1721 (C=O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 1.7 (d, 3H, CH_3), 6.1 (q, 1H, CH), 7.3−7.5 (m, 7H, aromatic), 7.8−7.9 (m, 2H, aromatic). Anal. Calcd for $C_{16}H_{13}NO_3$: N, 5.24; C, 71.90; H, 4.90. Found: N, 5.38; C, 71.90; H, 5.13.

4-((*S*)-(α-Methylbenzyloxy)carbonyl)benzoic Acid. This compound was obtained from (*S*)-(−)-α-methylbenzyl alcohol (11.9 g, 97.2 mmol) according to a method analogous to that described for the synthesis of 3-((*S*)-(1-methoxycarbonylethoxy)-carbonyl)benzoic acid and was purified by recrystallization (twice) from benzene−hexane (1/3). Yield, 14.2 g (51%). $[\alpha]_{365}^{25}$ +280°, $[\alpha]_D^{25}$ +56° (*c* 1.3, THF). IR (KBr, cm^{-1}) 1716 (C=O of ester), 1680 (C=O of carboxylic acid); ^1H NMR (400 MHz, $CDCl_3$) δ 1.7 (d, 3H, CH_3), 6.2 (q, 1H, CH), 7.3−7.5 (m, 5H, aromatic), 8.2 (s, 4H, aromatic).

4-((*S*)-(α-Methylbenzyloxy)carbonyl)phenyl Isocyanate (9). 9 was synthesized from 4-((*S*)-(α-methylbenzyloxy)-carbonyl)benzoic acid (10.0 g, 37.0 mmol) in the same manner as **2**. Yield, 7.0 g (71%). $[\alpha]_{365}^{25}$ +377.0°, $[\alpha]_D^{25}$ +72.9° (*c* 0.5, THF). IR (neat, cm^{-1}) 2268 (N=C=O), 1717 (C=O of ester); ^1H NMR (400 MHz, $CDCl_3$) δ 1.7 (d, 3H, CH_3), 6.1 (q, 1H, CH), 7.1−7.5 (m, 7H, aromatic), 8.1 (m, 2H, aromatic). Anal. Calcd for $C_{16}H_{13}NO_3$: N, 5.24; C, 71.90; H, 4.90. Found: N, 5.28; C, 71.91; H, 5.04.

Polymerization. Polymerization was carried out in a glass ampule under a dry nitrogen atmosphere in THF at −98 °C. The lithium amide of piperidine, which was prepared by adding an equimolar amount of *tert*-butyllithium in pentane to a THF solution of piperidine at room temperature, was used as an initiator. A typical polymerization procedure was as follows. The monomer and THF were placed, with use of a syringe, in a glass ampule with a three-way stopcock and cooled to −98 °C. The polymerization was initiated by adding the initiator with a syringe. The reaction was terminated by adding a 10-fold excess of HCl in methanol to the initiator, and then the polymer was precipitated in a large amount of methanol. The polymer was collected by centrifugation and dried in vacuo at room temperature.

Fractionation of Poly-7. Poly-**7** was isolated from the methanol-soluble part obtained in the polymerization performed for 0.25 h. Fractionation was carried out on two JASCO Finepak GEL S101C columns connected in series with a GPC instrument (JASCO 880-PU) equipped with a JASCO 875-UV. Chloroform was used as an eluent at a flow rate of 0.5 mL/min. The molecular weight of the isolated polymer was determined using a calibration curve obtained with standard polystyrenes (Tosoh).

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 $CDCl_3$ 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 GPC measurement on a Shodex System-21 GPC system equipped 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.

Results and Discussion

Influence of Distance of Asymmetric Center from Main Chain. To investigate the effect of the

Table 1. Polymerization of Optically Active Phenyl Isocyanates (1−3) Bearing an Ester Group with Li-piperidine in THF at −98 °C[a]

run	monomer	yield (%)[b]	$[\alpha]_{365}^{25}$[c]	M_n ($\times 10^{-4}$)[d]	M_w/M_n[d]
1	**1**	40	+1272°[e]	2.6	1.1
2	**2**	51	+58°[f]	2.7	1.1
3	**3**	50	+225°[g]	1.6	1.3

[a] Conditions: monomer 0.5 g, $[M]/[I] = 50$, THF 5 mL, time 4 h. [b] MeOH-insoluble part. [c] In THF. [d] Determined by GPC with a light-scattering detector (LS). [e] $[\alpha]_D^{25}$ +286° (THF). [f] $[\alpha]_D^{25}$ +4° (THF). [g] $[\alpha]_D^{25}$ +52° (THF).

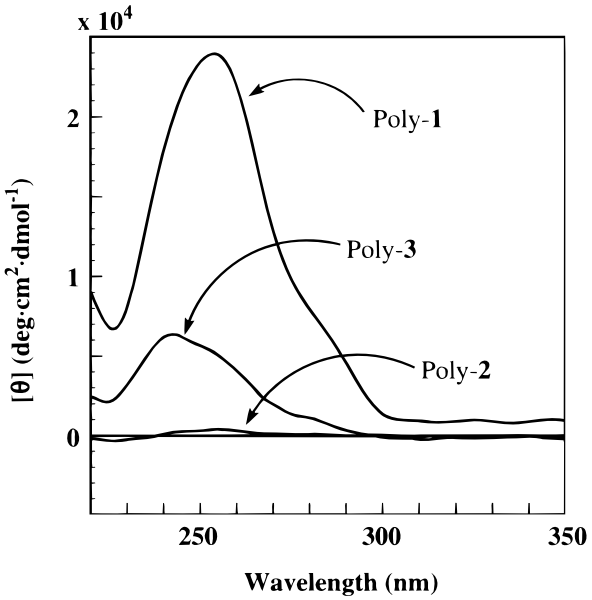


Figure 1. CD spectra of poly-**1**, poly-**2**, and poly-**3** at 25 °C in THF.

distance of an asymmetric center from the polymer backbone on polymer conformation, optically active phenyl isocyanates **1**−**3** with similar structures (Scheme 1) were synthesized and polymerized. The asymmetric centers of these polymers are separated from the main chain by six, seven, or eight bonds. The results of the polymerization are summarized in Table 1. Poly-**1** showed a very large positive specific rotation compared with monomer **1**. On the other hand, poly-**2** and poly-**3** showed much smaller specific rotation compared with poly-**1**. CD spectra of these polymers in THF at room temperature are shown in Figure 1. Poly-**1** showed a very intense CD band in the region of the main-chain absorption (around 255 nm),[8c−d] indicating that poly-**1** has a helical conformation with a predominantly single screw sense in solution. Poly-**3** also showed a CD band in the main-chain region; however, the intensity of poly-**3** is only about a quarter of that of poly-**1**. Poly-**2** did not show a clear CD absorption in the range of 220−350 nm. These results indicate that, when the distance between the polymer main chain and the chiral center on the side chain is longer than that in poly-**1**, the chiral center cannot effectively induce an excess of one helical twist sense of the polymer main chain at room temperature.

We have already reported that the specific rotation of poly-**1** changed completely reversibly from a high positive value to a high negative value with decreasing temperature and this change can be ascribed to a reversible helix−helix transition.[11] In Figure 2, the temperature dependence of the specific rotation of poly-**2** and poly-**3** in THF is shown together with the previous

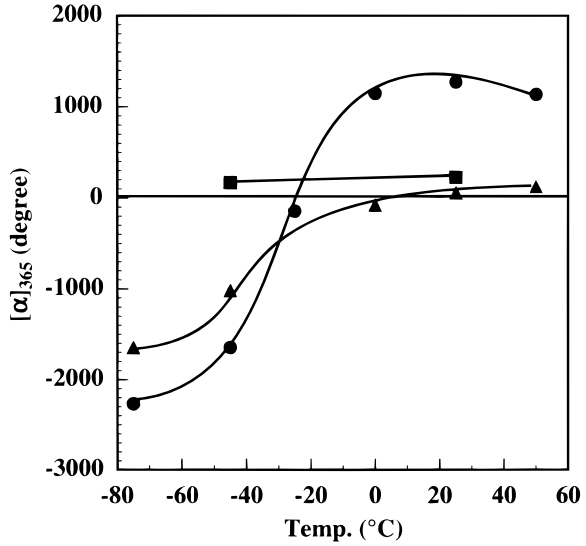


Figure 2. Temperature dependence of specific rotation of poly-**1** (●), poly-**2** (▲), poly-**3** (■) in THF.

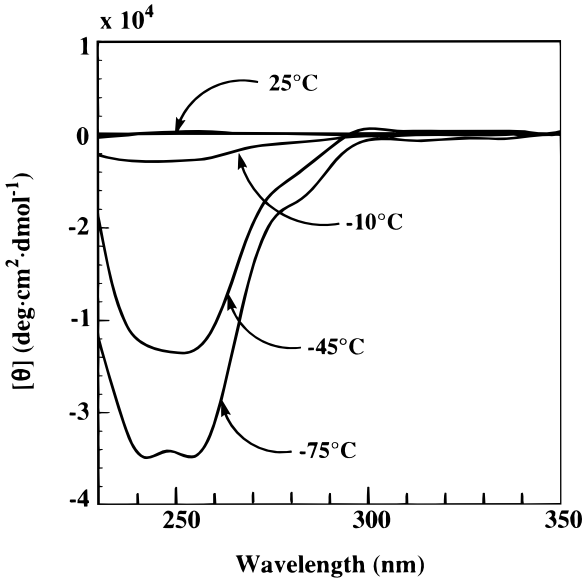


Figure 3. CD spectra of poly-**2** in THF at 25 °C, −10 °C, −45 °C, and −75 °C.

data on poly-**1** for comparison.[11] The specific rotation of poly-**2** significantly increased in the negative direction at low temperature, and this change was also reversible. The CD spectra of poly-**2** in THF at various temperatures are shown in Figure 3. Poly-**2** showed almost no CD band caused by the main-chain absorption at room temperature, but at low temperatures, an intense CD band caused by the main-chain amide was observed. This means that poly-**2** posesses a predominantly one-handed helical conformation (left-handed helix[13]) at low temperature, whereas at room temperature, it exists in an almost random helical conformation which has equal amounts of right- and left-handed helical sequences in the polymer chain. Therefore, this change can be regarded as a kind of transition of a random helix to a one-handed helix. In other words, at low temperatures, the persistence length of left-hand helical poly-**2** preferentially increases over that of the right-handed helix. On the other hand, poly-**3**, which has a chiral center at a one σ-bond remote position from the polymer backbone compared to poly-**2**, did not show any significant change in specific rotation even at low temperatures. These

Table 2. Polymerization of Optically Active Phenyl Isocyanates (4−9) Bearing an Ester Group with Li-piperidine in THF at −98 °C[a]

run	monomer	time	yield (%)[b]	$[\alpha]_{365}^{25}$ [c]	M_n ($\times 10^{-4}$)[d]	M_w/M_n[d]
1	**4**	4	64	−1924°	2.1	1.2
2	**5**	4	55	−1511°	1.6	1.3
3	**6**	4	57	−1827°	2.1	1.4
4	**7**	4	0	−	−	−
5	**7**	0.5	0	−	−	−
6	**7**	0.25	11[e]	−1684° [e]	0.7[e]	1.2[e]
7	**8**	4	77	−1783°	3.4	1.5
8	**9**	4	0	−	−	−
9	**9**	0.5	56	−1309°	3.1	1.5

[a] Conditions: monomer 0.5 g, $[M]/[I] = 50$, THF 5 mL. [b] MeOH-insoluble part. [c] In THF. [d] Determined by GPC with LS. [e] Methanol-soluble polymer fractionated by GPC.

results suggest that, when the asymmteric center exists at a further remote position than that in poly-**3**, the chirality in the side chain may no longer effectively induce an excess of one helical twist sense of the polymer main chain even at low temperatures.

Influence of Chiral Groups. The structure effect of the chiral groups on a side chain on the helicity induction to a main chain was investigated. Six new optically active phenyl isocyanates **4**−**9** (Scheme 1) were synthesized and polymerized with Li-piperidine. The results of the polymerization are summarized in Table 2. The polymerization of **7** and **9** for 4 h afforded no methanol-insoluble polymer and the methanol-soluble part mainly consisted of a cyclic trimer, which is formed by a back-biting reaction.[1b] This result indicates that even at low temperatures the polymers of phenyl isocyanate derivatives that have an electron-withdrawing substituent at the para position are very unstable and tend to depolymerize into a cyclic trimer under basic conditions. By reducing the polymerization time for 0.5 h, the polymerization of **9** afforded a methanol-insoluble polymer, whereas a methanol-insoluble polymer was not obtained from **7** even at 0.25 h. However, the formation of a small amount of high-molecular-weight polymer was observed by GPC analysis of the methanol-soluble part in the polymerization of **7** for 0.25 h. This fraction ($M_n = 0.7 \times 10^4$, $M_n/M_w = 1.2$) was isolated with use of GPC. The polymers of **4**−**9** showed large negative specific rotation and an intense negative CD band at 25 °C in THF, indicating that these polymers have predominantly one-handed helical conformation. The temperature dependence of the specific rotation of these polymers in THF is shown in Figure 4. The absolute values of the specific rotation of all the polymers increased with a decrease in temperature as expected from previous reports.[8,9a−b] The inversion of optical activity, which was found for poly-**1**, was not observed even for poly-**5** and poly-**7**. Therefore, the helix−helix transition observed for poly-**1** seems to be a very rare case. To observe such a transition, precise selection of the chiral group and the position seems necessary.

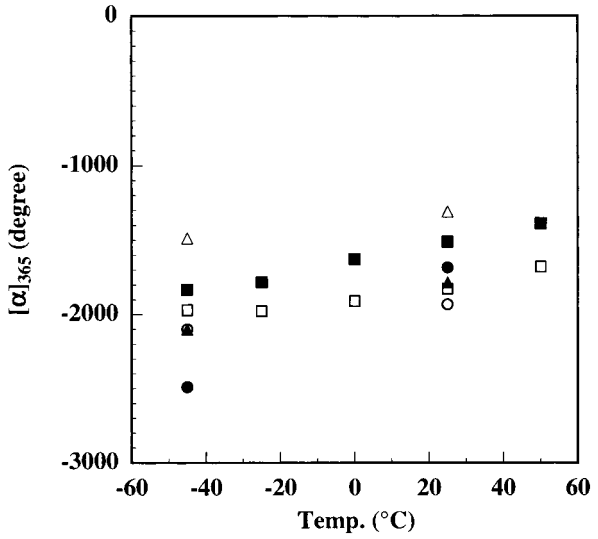


Figure 4. Temperature dependence of specific rotation of poly-**4** (○), poly-**5** (■), poly-**6** (□), poly-**7** (●), poly-**8** (▲), and poly-**9** (△) in THF.

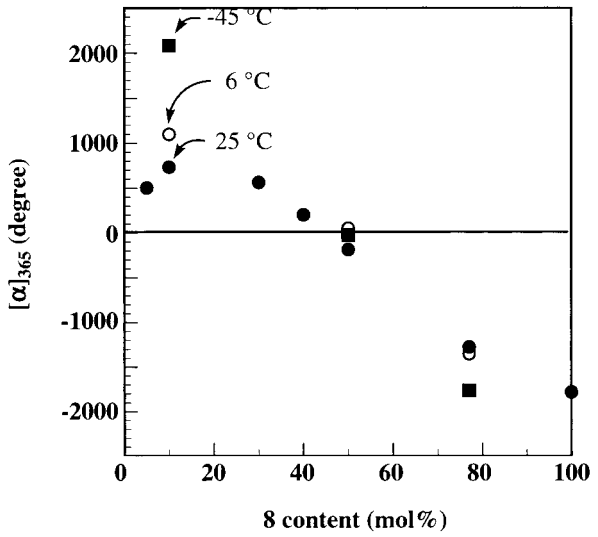


Figure 5. Plots of specific rotation of poly(**8**-*co*-**10**) against the content of **8** at 25 °C (●), 6 °C (○), and −45 °C (■) (in THF).

Copolymerization with Achiral *m*MeOPI. The results of the copolymerization of optically active **8** with achiral **10** are summarized in Table 3. The optical activity of the obtained copolymers changed from positive to negative values with an increase in the content of optically active **8** unit and crossed zero degree around 50 mol % content of **8** (Figure 5). The CD and UV spectra of poly($\mathbf{8}_{10}$-*co*-$\mathbf{10}_{90}$) (run 5 in Table 3) and poly($\mathbf{8}_{80}$-*co*-$\mathbf{10}_{20}$) (run 1 in Table 3) at 25 °C in THF are shown in Figure 6. The CD bands of poly($\mathbf{8}_{10}$-*co*-$\mathbf{10}_{90}$) and poly($\mathbf{8}_{80}$-*co*-$\mathbf{10}_{20}$) are opposite in sign to each other, indicating that they exist in a predominantly one-

Table 3. Copolymerization of 8 (M_1) and 10 (M_2) with Li-piperidine in THF at −98 °C for 4 h[a]

run	$[M_1]/([M_1]+[M_2])$ in feed (mol%)	yield (%)	$[M_1]/([M_1]+[M_2])$ in polymer (mol%)[b]	$[\alpha]_{365}^{25}$ [c]	M_n[d] ($\times 10^{-4}$)	M_w/M_n[d]
1	78	81	80	−1278°	2.0	1.3
2	50	83	51	−187°	1.8	1.2
3	40	85	39	+201°	1.8	1.2
4	30	86	29	+563°	1.5	1.2
5	11	88	10	+733°	1.9	1.2
6	5	90	5	+501°	1.5	1.4

[a] Conditions: (runs 1−4) monomer 0.25 g, THF 2.5 mL, (runs 5, 6) monomer 0.5 g, THF 5 mL, $[M]/[I] = 50$. [b] Estimated by ^{1}H NMR. [c] In THF. [d] Determined by GPC with LS.

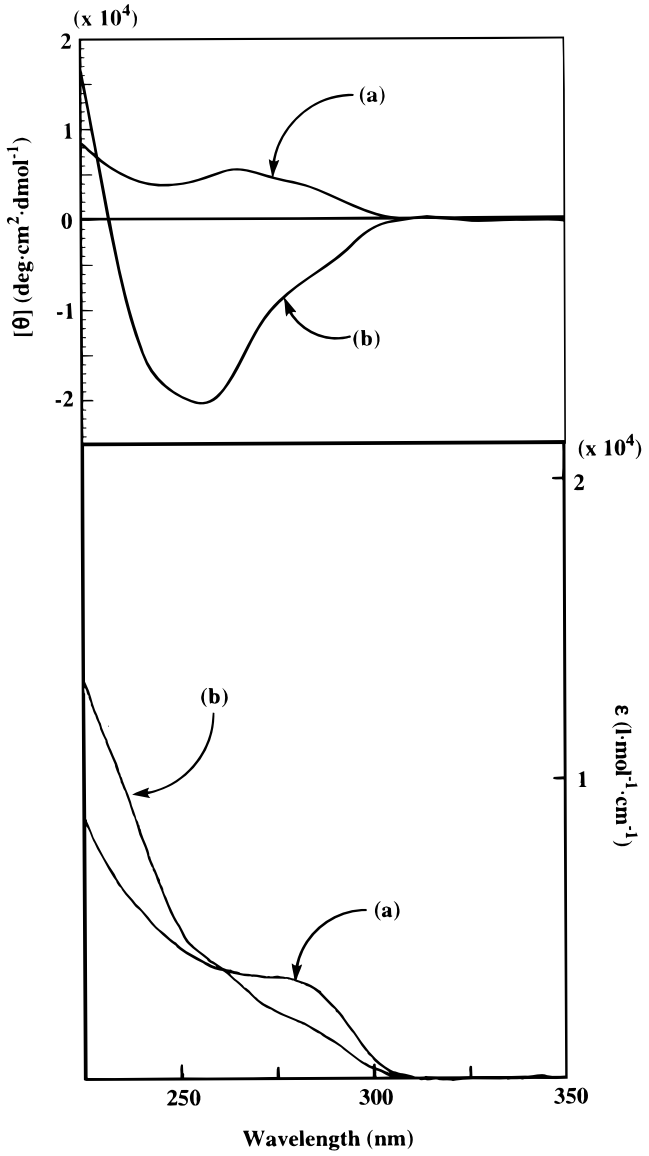
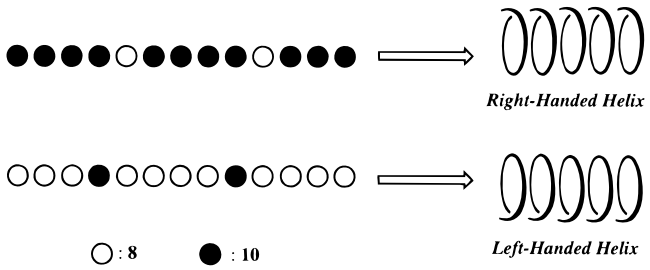


Figure 6. CD (top) and UV (bottom) spectra of poly($\mathbf{8}_{10}$-*co*-$\mathbf{10}_{90}$) (run 5 in Table 3) (a) and poly($\mathbf{8}_{80}$-*co*-$\mathbf{10}_{20}$) (run 1 in Table 3) (b) in THF.

handed helical conformation with an opposite screw sense. The temperature effect on the optical activity of these copolymers was also examined in THF. The magnitude of the specific rotation of poly($\mathbf{8}_{10}$-*co*-$\mathbf{10}_{90}$) and poly($\mathbf{8}_{80}$-*co*-$\mathbf{10}_{20}$) increased at low temperatues as expected from previous studies,[8,9a−b] whereas that of poly($\mathbf{8}_{51}$-*co*-$\mathbf{10}_{49}$) showed almost no change (Figure 5). The sequence of successively bonded optically active **8** units and of achiral **10** units including a sporadic optically active **8** unit may induce a helical conformation with an opposite twist sense to each other as illustrated in Scheme 2, where the sense of the helix is asigned to left-handedness for the polymer showing a negative CD band and right-handedness for that showing a positive one referring to the previous studies.[13] Therefore, at about 50 mol % content of **8**, the effect arising from these two species on the polymer main chain would be canceled.

Chiral Recognition Ability. To evaluate the chiral recognition ability of the polymers of **1**−**9**, ^{1}H NMR measurements of some racemates such as (±)-1,1′-bi-2-naphthol and (±)-mandelic acids were conducted in the presence of the polymers in $CDCl_3$ at ambient

Scheme 2



temperature (ca. 20 °C). However, a peak split caused by the enantiomers was not observed for the racemates, indicating that these polymers cannot discriminate the enantiomers in $CDCl_3$. These results are in contrast to those of the optically active poly(phenyl isocyanate)s bearing a carbamoyl group, which exhibited chiral recognition ability toward the racemates tested here under the same conditions.[10] This is probably because the ability of hydrogen bonding of the ester group is lower than that of the carbamoyl group, and the interaction between the racemates and the polymer is not sufficient to attain chiral discrimination.

Acknowledgment. One of us (K.M.) is grateful 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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MA981362I