# Helicity Induction of Poly(3-carboxyphenyl isocyanate) by Chiral Acid−Base Interaction

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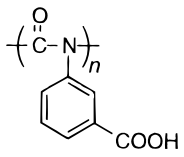
## Introduction

Polyisocyanates including aromatic types are known to have a prevailing one-handed helical structure when a chiral factor such as an optically active end group,[1,2] a side group,[3,4] or even a solvent[5] is introduced to the polymers. This is due to the fact that the polymers have a dynamic stiff helical structure in solution,[4,6] and a slight chiral factor can induce them into a prevailing one-handed helical conformation because all the monomer units between helix reversals must have the same helix sense and helix reversals are rare.

In the present study, we synthesized poly(3-carboxyphenyl isocyanate) (P3CPI) and investigated the possibility of the induction of a prevailing helicity through an acid−base interaction in the presence of chiral




P3CPI

amines. Helicity induction on a polymer through an acid−base interaction has been reported for polyacetylene,[7] polycarbodiimide,[8] and polyaniline,[9] but not for a polyisocyanate.

## Experimental Section

**3-(*tert*-Butoxycarbonyl)benzoic Acid.** To isophthaloyl dichloride (30 g, 0.15 mol) dissolved in THF (250 mL) was slowly added a mixture of *tert*-butyl alcohol (13.8 mL, 0.15 mol) and pyridine (26.3 mL, 0.33 mol). After the reaction mixture was refluxed for 6 h, water (100 mL) was added and the mixture was further refluxed for 6 h. The mixture was washed with 0.2 N HCl(aq) (180 mL) and water (150 mL × 2). The THF layer was stirred over anhydrous $MgSO_4$ for 1 h, and the solvent was removed with a rotary evaporator. After dicarboxylic acid was removed as the insoluble part in $CHCl_3$ (300 mL), 3-(*tert*-butoxycarbonyl)benzoic acid was isolated by recrystallization from benzene (16.0 g, 47%), mp 139 °C. $^1$H NMR ($CDCl_3$): $\delta$ 8.7 (s, 1H), 8.3−8.2 (m, 2H), 7.6−7.5 (t, 1H), 1.6 (s, 9H). IR ($CHCl_3$ solution on NaCl plate, cm$^{-1}$): 1720 (C═O of ester), 1700 (C═O of acid).

**3-(*tert*-Butoxycarbonyl)phenyl Isocyanate.** The isocyanate was synthesized by Curtius rearrangement starting from 3-(*tert*-butoxycarbonyl)benzoic acid. 3-(*tert*-Butoxycarbonyl)-benzoic acid (22.6 mL, 0.10 mol) was dissolved in acetone (200 mL), and the solution was cooled at 5−10 °C. $Et_3N$ (14.2 mL, 0.10 mol) and $ClCO_2Et$ (16.0 mL, 0.10 mol) were then added dropwise into the acid, and the mixture was stirred for 1.5 h. $NaN_3$ (13.2 g, 0.20 mol) dissolved in water (60 mL) was then added to the mixture, which was stirred for 1.5 h. The reaction mixture was poured into ice water (200 mL) and extracted with toluene (200 mL). Acetone was removed with a vacuum pump, and the remaining toluene solution was dried with $MgSO_4$ at a low temperature. After filtration, the toluene solution was gradually heated under nitrogen to 90 °C for 2.5 h to perform the Curtius rearrangement. Toluene was removed by evaporation under reduced pressure, and the residue was distilled under reduced pressure (104 °C/0.3 mmHg) to give a light yellow oil (15.7 g) in 70% yield. $^1$H NMR ($CDCl_3$): $\delta$ 7.8 (d, 1H), 7.7 (s, 1H), 7.4−7.3 (t, 1H), 7.3−7.2 (d, 1H), 1.6 (s, 9H). IR ($CHCl_3$ solution on NaCl plate, cm$^{-1}$): 2270 (N═C═O), 1720 (C═O of ester). Anal. Calcd for $C_{12}H_{13}NO_3$: N, 6.39; C, 65.74; H, 5.98. Found: N, 6.47; C, 65.65; H, 6.10.

**Preparation of Initiator Solution.** Piperidine was purified by distillation over $CaH_2$ under reduced pressure. The lithium amide of piperidine was prepared by adding an equimolar amount of *tert*-butyllithium to a solution of the amine in THF at room temperature.

**Polymerization Procedure.** Polymerization was carried out in a glass ampule under an atmosphere of dry nitrogen. The monomer (0.5 g) was dissolved in THF (5 mL), and the solution was cooled to −98 °C. The initiator solution was then added with a syringe and the polymerization was continued at −98 °C for 0.5, 1, or 4 h. The polymerization was terminated with acetic anhydride (10 molar equiv to initiator).[10] The ampule containing the reaction mixture was kept for 1 h at −78 °C, and for 16 h at room temperature to allow acetylation at a chain end. The products were precipitated in a large amount of methanol, separated by centrifugation, and dried in vacuo at room temperature. The polymer was soluble in $CHCl_3$.

**Hydrolysis of *tert*-Butyl Ester Group.**[11] The above polymer was partly terminated with a proton to form an NH end group. This NH-terminated fraction is easily decomposed and accompanied by the formation of a cyclic trimer. To remove this fraction, the above polymer (100 mg) was dissolved in $CHCl_3$ (2 mL) and the solution was added to DMSO (10 mL) to promote the cyclization. The solution was stirred for 24 h at room temperature and then poured into a large amount of methanol. The acetyl-terminated polymer was separated by centrifugation and dried in vacuo. The resulting polymer was dissolved in $CHCl_3$ and precipitated in methanol to completely remove DMSO; the yield was 40 mg (40%).

The hydrolysis of the *tert*-butyl ester was carried out using trifluoroacetic acid (TFA). The polymer (40 mg) was stirred in TFA (2 mL). After the polymer was completely dissolved, the reaction mixture was poured into a large amount of $Et_2O$. The precipitated polymer was centrifuged and dried in vacuo; the yield was 24 mg. The polymer was soluble in MeOH, EtOH, and acetone.

**Measurements.** $^1$H NMR spectra were measured using a Varian Gemini-2000 (400 MHz) spectrometer with tetramethylsilane as the internal standard. IR spectra were measured using a JASCO FT/IR-7000 infrared spectrophotometer. Size exclusion chromatography (SEC) was performed with a JASCO 880-PU or a PU-980 chromatograph equipped with a JASCO 875-UV detector using TSK G5000H and Shodex AC-802.5 GPC columns connected in series with $CHCl_3$ as the eluent to determine the molecular weight relative to polystyrene standards. Determination of the absolute molecular weight by the light scattering method was performed with a Shodex GPC system-21 equipped with a Shodex RI-71S detector and a Wyatt Technology DAWN DSP-F multiangle light scattering detector using Shodex KF-803 and KF-806L GPC columns connected in series with THF as the eluent. UV spectra were measured with a JASCO Ubest-55 spectrometer. Circular dichroism (CD) spectra were taken on a JASCO J-720 spectrometer.

## Results and Discussion

Table 1 shows the results of the anionic polymerization of 3-(*tert*-butoxycarbonyl)phenyl isocyanate with Li-

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**Table 1. Polymerization of 3-(*tert*-Butoxycarbonyl)-phenyl Isocyanate in THF at −98 °C[a]**

| run | polymer | time (h) | yield[b] (%) | $(M_n \times 10^{-4})^c$ | $M_w/M_n$[c] |
|---|---|---|---|---|---|
| 1 | P-1 | 0.5 | 64 | 1.0[d] | 1.3[d] |
| 2 | P-2 | 1 | 60 | 1.0 | 1.3 |
| 3 | P-3 | 4 | 47 | 1.0 | 1.3 |
| 4 | P-4 | 0.5 | 66 | 1.0 | 1.3 |
| 5 | P-5 | 0.5 | 49 | 1.4 | 1.2 |

[a] Conditions: initiator, Li-piperidine; terminator, $Ac_2O$; [monomer]/[initiator] = 50; [terminator]/[initiator] = 10; (runs 1−4) monomer 0.5 g, THF 5 mL; (run 5) monomer 2.0 g, THF 20 mL. [b] MeOH insoluble part. [c] Determined by GPC with polystyrene standard. [d] $M_n$ and $M_w/M_n$ were estimated to be ca. $1.6 \times 10^4$ and 1.3 by the light scattering method, respectively.

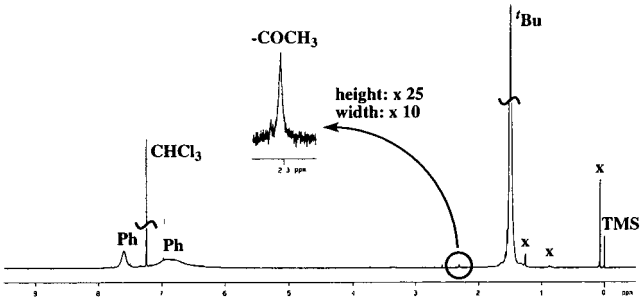


**Figure 1.** $^1$H NMR spectrum of poly(3-(*tert*-butoxycarbonyl)-phenyl isocyanate) (P-4) (run 4 in Table 1) terminated with acetic anhydride in $CDCl_3$ at 60 °C.

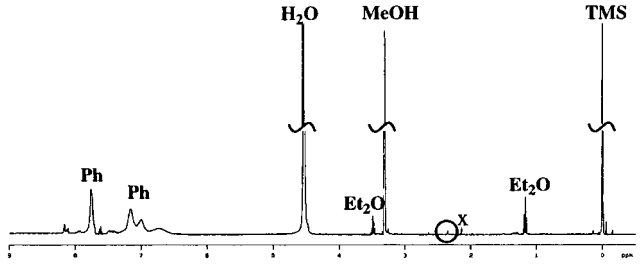


**Figure 2.** $^1$H NMR spectrum of poly(3-carboxyphenyl isocyanate) (P3CPI) in $CD_3OD$ at 60 °C.

piperidine in THF at −98 °C. The polymerization did not proceed quantitatively, and the polymer yield decreased as the polymerization time increased (runs 1−3). This must be due to the formation of a cyclic trimer through the back-biting reaction by a polymer chain end.[12]

Figure 1 shows the $^1$H NMR spectrum of the polymer (P-4) obtained in run 4 of Table 1. A small peak at 2.3 ppm can be assigned to the acetyl group introduced at the terminal end by acetylation, because the polymer terminated with HCl−$CH_3OH$ did not exhibit this peak. The degree of polymerization (DP) of this polymer estimated from the peak intensity ratio of the *tert*-butyl group (1.5 ppm) and acetyl group agreed well with the DP estimated by the GPC analysis. Another small peak at 2.5 ppm can be assigned to the $-NCH_2$ of the initiator residue.

The $^1$H NMR spectrum of poly(3-carboxyphenyl isocyanate) (P3CPI) derived from P-4 is shown in Figure 2. The peak due to the *tert*-butyl group disappears and the peak due to the terminal acetyl group at 2.3 ppm still exists.

The induced circular dichroism (ICD) spectrum of P3CPI was measured in the presence of a chiral amine (*S*)-4 (Figure 3), and the CD spectrum is shown in Figure 4. The spectrum was taken in $CH_3OH/C_2H_5OH$ = 3/1, because in pure $CH_3OH$, no ICD was observed,

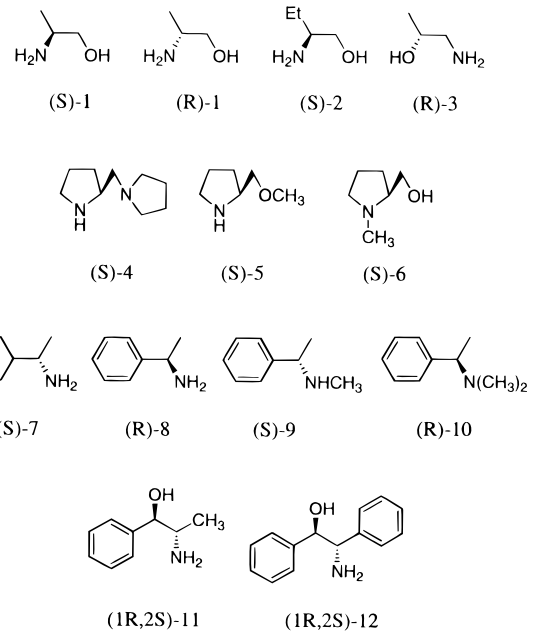


**Figure 3.** Chiral amine compounds.

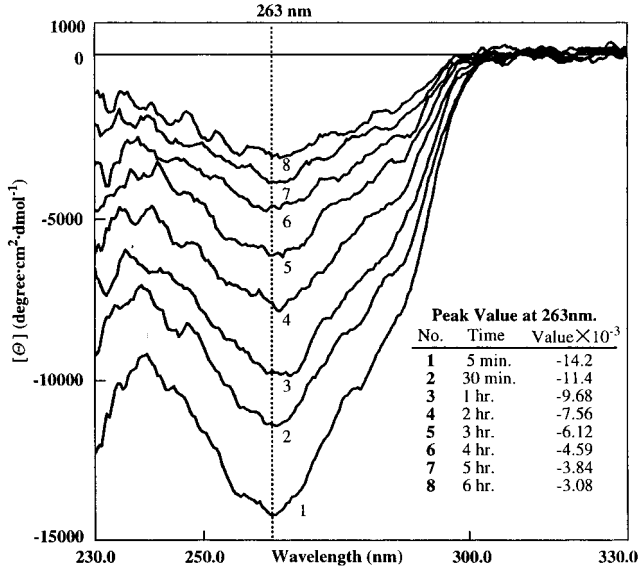


**Figure 4.** CD spectra of the P3CPI−(*S*)-4 system in MeOH/EtOH = 3/1 (concentration = 0.2 mg/mL, [(*S*)-4]/[P3CPI] = 1/1, cell length = 0.1 cm).

and in pure $C_2H_5OH$, the polymer was not dissolved. A rather intense CD peak was observed at 263 nm. This must be assigned to the ICD on the polyisocyanate because (*S*)-4 has no absorption above 250 nm.

The CD pattern is similar to those of the optically active poly(phenyl isocyanate)s with a one-handed helical conformation, suggesting that a prevailing one-handed helical structure is induced on P3CPI through an acid−base interaction. A similar observation has been reported by Green et al., who observed a prevailing one-handed helical conformation of poly(*n*-hexyl isocyanate) driven by a minute chiral solvation energy.[5] However, its peak intensity was smaller than the CD intensity of P3CPI induced through the acid−base interaction.

The peak intensity, however, gradually decreased with time. This is due to the decomposition of the polymer through the formation of a cyclic trimer. When other chiral amines were used, analogous CD patterns

**Table 2. Signs of CD Spectra and Molar Ellipticities ([θ]) for P3CPI−Amine Complexes[a]**

| amine | original polym | polym conc (mg/mL) | [amine]/ [P3CPI] | peak value | | |
|---|---|---|---|---|---|---|
| | | | | wave-number | sign | $[\theta] \times 10^{-4}$ |
| *S*-1 | P-4 | 2 | 1 | 261.0 | − | 1.3 |
| *R*-1 | P-4 | 2 | 1 | 263.0 | + | 1.4 |
| *S*-2 | P-4 | 2 | 1 | 264.0 | − | 0.3 |
| *R*-3 | P-4 | 2 | 1 | 263.0 | + | 1.2 |
| *S*-4 | P-4 | 2 | 1 | 262.0 | − | 1.3 |
| *S*-5 | P-4 | 2 | 1 | 260.0 | − | 1.4 |
| *S*-6 | P-5 | 1 | 2 | 255.5 | − | 1.2 |
| *S*-7 | P-5 | 1 | 1 | 262.5 | + | 0.6 |
| *R*-8 | P-5 | 1 | 1 | 262.0 | + | 0.3 |
| *S*-9 | P-5 | 1 | 1 | 261.0 | + | 0.4 |
| *R*-10 | P-5 | 1 | 4 | 257.5 | + | 0.3 |
| 1*R*,2*S*-11 | P-5 | 1 | 1 | 261.5 | + | 2.3 |
| 1*R*,2*S*-12 | P-5 | 1 | 1 | 259.0 | + | 0.8 |

[a] Each datum was collected at 10 min after addition of amines.

were observed at 240−300 nm. This indicates that the induced helical structures of P3CPI with the chiral amines are similar.

The results of the CD measurements in the presence of various amines as shown in Figure 3 are summarized in Table 2. These spectra were also taken in $CH_3OH/C_2H_5OH$ = 3/1. However, the polymer was deposited when a small amount of an amine was added to the monomeric units of P3CPI. Therefore, in most cases, 1 equiv of a primary or secondary amine was added to a solution. For *tert*-amines, (*S*)-6 and (*R*)-10, 2−4 equiv must be used to dissolve the polymer. The complex formation between the polymer and the *tert*-amines may be more difficult due to steric hindrance. The CD patterns for the enantiomeric amines, (*S*)-1 and (*R*)-1, were mirror images of each other and showed opposite signs of the Cotton effects. The ICDs for structurally similar aliphatic amines 1−3 and 4−6 and aromatic amines 11−12 were the same in the sign, if the absolute configuration of the asymmetric carbon attached to the amino group is the same. For (*S*)-1−6, a negative Cotton effect was observed at 260 nm and for (*S*)-11 and -12, a positive one.

Three 1-phenylethylamines 8−10 did not show the same ICD. Although these results are not well explained at the present time, the polymer may be used to predict the absolute configuration of chiral amines with an analogous structure. Similar observations have been reported for poly(phenylacetylene)s with a functional group.[7]

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