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Macromolecular Helicity Induction for Novel Optically Inactive Poly(phenyl isocyanate) Bearing Crown Ether Based on the Host−Guest Complexation

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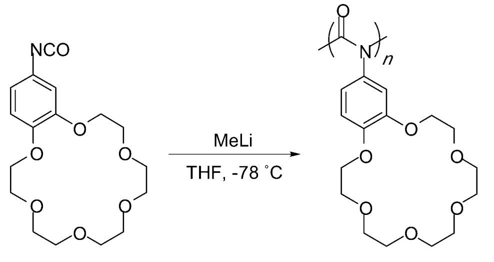
ABSTRACT: The macromolecular helicity induction of a novel optically inactive poly(phenyl isocyanate) bearing crown ether as a host group (**2**) based on host−guest complexation was discussed. 4′-Isocyanatobenzo-18-crown-6 (**1**) was polymerized with MeLi in THF at −78 °C to afford **2** with 71% yield. The circular dichroism (CD) spectrum of **2** in the presence of the perchloric acid salt of L-phenylalanine (L-Phe·$HClO_4$) showed a negative Cotton effect with the high intensity of -3.7×10^4 deg cm^2 dmol^{-1} in the range from 240 to 340 nm, corresponding to the absorption of the polymer backbone, while a positive Cotton effect was observed for D-Phe·$HClO_4$ and the CD spectrum pattern was the mirror image of that of **2** with L-Phe·$HClO_4$. On the other hand, a clear Cotton effect was not observed at all in the range from 230 to 290 nm for the unimer of **2**, 4′-(*N*,*N*-diacetylamino)benzo-18-crown-6 (**3**), with L-Phe·$HClO_4$, though the cation-binding property of **3** was almost the same as that of **2**, indicating that the induced CDs were based on not the inclusion of the chiral guest in the host group but the structure change in the main chain, i.e., the macromolecular helicity induction for **2** through the host−guest interaction. The helical structure of **2** was significantly affected by the molar ratio of the guest and host, the temperature change, and the type of guests.

Introduction

Synthetic helical polymers are of great interest in terms of their widespread applications and characteristic features such as molecular recognition.[1] Polyisocyanate is one class of helical polymers, which is known to have a prevailing one-handed helical structure in solution as well as in the solid state when the polymer is provided a chiral factor.[2,3] Green et al. reported, as an example, that only a small amount of chiral monomeric units incorporated into a polymer chain consisting mainly of achiral monomeric units induced the one-handed helical structure.[3c] Furthermore, these optically active polyisocyanates were switched between right- and left-handed helical conformations by changing the external conditions, such as temperature and solvent, and by irradiation of ultraviolet light and circularly polarized light.[3]

In addition, for an optically inactive polymer without a chiral factor, the one-handed helical structure can be induced by an external chiral stimulus after the preparation of a polymer, i.e., the macromolecular helicity induction. This has been interestingly reported for polyacetylene,[4] polycarbodiimide,[5] polyisocyanide,[6] and polyaniline[7] through an acid−base interaction. Recently, Yashima et al. revealed that macromolecular helicity was switched[8a] and induced[8b] through a host−guest interaction in the presence of guest molecules for the poly(phenylacetylene) with cyclodextrin and crown ether as the host group, respectively. These polymers may be applied as a probe for the assignment of the absolute configuration and for the determination of the optical purity. However, there have been few attempts to investigate the macromolecular helicity induction of polyisocyanate,[9] so that it is interesting to synthesize polyisocyanates capable of responsing to external stimuli, resulting in helicity induction in the polymers.

Scheme 1. Synthesis of Poly(phenyl isocyanate) Bearing Crown Ether



1

2

We now report the synthesis of a novel optically inactive poly(phenyl isocyanate) with a crown ether as the host group (**2**) by the anionic polymerization of 4′-isocyanatobenzo-18-crown-6 (**1**), as shown in Scheme 1. In addition, the macromolecular helicity induction for **2** is discussed for the host−guest complexation between **2** and the chiral guest, i.e., the perchloric acid salts of amino acids. To clarify the origin of the optical activity for the complex of **2** and the chiral guest, the chiroptical property of **2** is compared with that of 4′-(*N*,*N*-diacetylamino)benzo-18-crown-6 (**3**), which is identical with the unimer of **2**. Furthermore, we examine the effect of the molar ratio of the guest and the host, the temperature dependence, and the influence of the types of guests on

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the macromolecular helicity induction of **2**, because these factors are important for the conformational change, for example, switching of the macromolecular helicity, as previously reported for the synthetic helical polymers.

Experimental Section

Materials. 4′-Aminobenzo-18-crown-6 was synthesized by a previously reported method.[10] L- and D-phenylalanine (L- and D-Phe) and L-leucine (L-Leu) were purchased from the Peptide Institute Inc. (Osaka, Japan). L-Valine (L-Val) and L-methionine (L-Met) were obtained from the Kanto Chemical Co., Ltd. (Tokyo, Japan). The perchloric acid ($HClO_4$) salts of these amino acids were prepared according to a previous report.[11] THF was dried over sodium benzophenone ketyl and then vacuum-transferred from CaH_2. A solution of MeLi in diethyl ether was purchased from the Kanto Chemical Co., Ltd., and used without further purification. Dry acetonitrile, chloroform for the spectroscopy, all the metal hydroxides, and picric acid were obtained from Kanto Chemical Co., Ltd. Triphosgene and diisopropylethylamine were available from Aldrich Chemical Co., Inc.

Measurements. The ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-A400II instrument. Mass spectroscopy was recorded using a JEOL JMS-SX102A mass spectrometer (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). The static laser light scattering (SLS) measurement was performed in $CHCl_3$ at 25 °C using an Otsuka Electronics DLS-7000 light scattering spectrophotometer ($\lambda = 632.8$ nm; four-point measurements; $c = 1 \sim 5$ g L^{-1}). The refractive index increment (dn/dc) was measured in $CHCl_3$ at 25 °C using an Otsuka Electronics DRM-1021 double-beam differential refractometer ($\lambda = 632.8$ nm). IR spectra were recorded using a Perkin-Elmer Paragon 1000. Ultraviolet−visible (UV−vis) spectra were measured at 23 °C in a 1 mm path length using a Jasco V-550 spectrophotometer. Circular dichroism (CD) spectra were measured in a 1 mm path length using a Jasco J-720 spectropolarimeter. Melting points were measured using a Seiko, Inc., DSC 220 differential scanning calorimeter.

4′-Isocyanatobenzo-18-crown-6 (1). Since monomer **1** was extremely unstable toward moisture, the synthetic reaction, isolation, and storage of **1** should be carried out under an inert gas atmosphere. Although Toke et al. previously reported the synthesis of **1**,[12] it was quite difficult to synthesize pure **1** according to the procedure. Thus, we developed a specific procedure for synthesizing **1** from the carbonylation of 4′-aminobenzo-18-crown-6 using triphosgene, as follows. To a solution of triphosgene (5.3 g, 18 mmol) in dry CH_2Cl_2 (80 mL) was slowly added a mixture of 4′-aminobenzo-18-crown-6 (13 g, 41 mmol) and diisopropylethylamine (16 mL, 90 mmol) in dry CH_2Cl_2 (140 mL) over a period of 1 h under a dry nitrogen atmosphere. After stirring for an additional 30 min at room temperature, the reaction mixture was washed twice with a mixture of 1 N HCl (200 mL) and crushed ice (200 mL), and then the CH_2Cl_2 layer was dried with anhydrous $MgSO_4$. After the solvent was evaporated to dryness, the crude product was purified by short column chromatography on silica gel with stabilizer-free dry THF to give **1** as a white solid. Yield: 10 g (71%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.79 (d, $J = 8.5$ Hz, 1H, Ar), 6.64 (dd, $J = 2.5$, 8.5 Hz, 1H, Ar), 6.61 (d, $J = 2.5$ Hz, 1H, Ar), 4.14−3.65 (m, 20H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4 (Ar), 146.9 (Ar), 126.5 (Ar), 124.1 ($-NCO$), 117.1 (Ar), 114.5 (Ar), 110.7 (Ar), 71.0−69.0 ($-CH_2-$). IR (KBr, cm^{-1}): 2269 ($N{=}C{=}O$). Anal. Calcd for $C_{20}H_{29}NO_8$: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.53; H, 6.56; N, 3.94. MS (FD) (*m*/*e* and relative intensity): 353 (M^+, 100); 354 ($M-H^+$, 32). Mp: 60−62 °C.

4′-(*N*,*N*-Diacetylamino)benzo-18-crown-6 (3). A solution of 4′-aminobenzo-18-crown-6 (1.3 g, 4.0 mmol) in acetic anhydride (20 mL) was refluxed for 4 h. After acetic anhydride was evaporated to dryness, the residue was purified by column chromatography on silica gel with ethyl acetate to give **3** as a white solid. Yield: 1.4 g (86%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, $J = 8.4$ Hz, 1H, Ar), 6.69 (dd, $J = 2.4$, 8.4 Hz, 1H, Ar), 6.64 (d, $J = 2.4$ Hz, 1H, Ar), 4.19−3.69 (m, 20H, $-CH_2-$), 2.29 (s, 6H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2 ($-CO-$), 149.6 (Ar), 146.3 (Ar), 132.3 (Ar), 121.2 (Ar), 114.2 (Ar), 113.9 (Ar), 70.9−69.1 ($-CH_2-$), 26.8 ($-CH_3$). IR (KBr, cm^{-1}): 1695 ($C{=}O$ of amide). Anal. Calcd for $C_{20}H_{29}NO_8$: C, 58.38; H, 7.10; N, 3.40. Found: C, 58.41; H, 7.12; N, 3.15. MS (FD) (*m*/*e* and relative intensity): 411 (M^+, 100); 412 ($M-H^+$, 25). Mp: 93−94 °C.

Polymerization. Polymerization was carried out in a dry Schlenk flask under an argon atmosphere. A solution of **1** (0.71 g, 2.0 mmol) in dry THF (4.0 mL) was cooled at −78 °C, and then a solution of MeLi in diethyl ether (1.04 mol L^{-1}, 97 μL, 0.10 mmol) was added using a microsyringe. After 30 min, the reaction was terminated by adding acetic anhydride (95 μL, 1.0 mmol), which was important for stabilizing the polymer chain end.[9a] The entire mixture was stirred for an additional 12 h at room temperature and then poured into a large amount of diethyl ether. The precipitate was purified by reprecipitation with $CHCl_3$/diethyl ether and then dried in vacuo to give **2**. Yield: 0.50 g (71%). $M_{w,SLS} = 2.6 \times 10^4$, $dn/dc = 0.1014$ mL g^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.29 (br, 1H, Ar), 5.75 (br, 2H, Ar), 4.14−3.68 (br, 20H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9 ($C{=}O$), 148.7, 148.1, 129.1, 118.0, 112.0, 110.4 (Ar), 70.9−68.6 ($-CH_2-$). IR ($CHCl_3$ solution on NaCl plate, cm^{-1}): 1709 ($C{=}O$ of amide).

Cation-Binding Property. The extraction of alkali metal picrates was carried out using a procedure similar to the one developed by Pedersen.[13] A solution of the polymer or model compound in CH_2Cl_2 (2 mL, [crown ether units] = 5.8×10^{-3} mol L^{-1}) was vigorously shaken in a centrifuged tube with an aqueous solution of alkali hydroxide and picric acid (2 mL, [picric acid] = 7.0×10^{-5} mol L^{-1}, [metal hydroxide] = 0.10 mol L^{-1}) at 20 °C. After separating into two clear phases by centrifugation, the alkali picrate extracted into the CH_2Cl_2 phase was indirectly determined by measuring the absorbance of the picrate in the aqueous phase at 380 nm using a UV−vis spectrophotometer.

For the case using L-Phe·$HClO_4$ as the guest, the relative concentrations of the guest to host (G/H) in the $CDCl_3$ layers were determined on the basis of a previous description.[14] A solution of the host in $CDCl_3$ (2 mL, [crown ether units] = 5.8×10^{-3} mol L^{-1}) was prepared in a centrifuged tube, and to the solution was then added a solution of in D_2O (2 mL, [L-Phe·$HClO_4$] = 2.0×10^{-2} mol L^{-1}). This two-phase system was vigorously shaken at 20 °C and centrifuged. The $CDCl_3$ layer was very carefully separated and then concentrated to an appropriate volume (ca. 0.5 mL). The G/H value was determined from the area ratio between the signals due to the aromatic protons of the benzo-18-crown-6 units (5.5−6.9 ppm) and those of phenylalanine (7.0−7.2 ppm) in the ^1H NMR spectra of the $CDCl_3$ layer.

CD Measurements. The concentration of **2**, which was calculated on the basis of monomeric units, was 2.8 mmol L^{-1} for all measurements. The G/H value was 5.0 except for the titration experiment in Figure 5. A typical procedure is described below. A stock solution of **2** (5.7 mmol L^{-1}) in acetonitrile was prepared in a 5 mL flask, and a 1 mL aliquot of the solution was transferred to a 2 mL flask. L-Phe·$HClO_4$ (7.52 mg, 28.3 mmol) was added to the 2 mL flask. The solution was then diluted with acetonitrile to 2 mL and was vigorously shaken. After 10 min, the CD and UV spectra were measured in a 1 mm quartz cell using spectropolarimeter with thermostat.

Results and Discussion

Synthesis of Poly(4′-isocyanatobenzo-18-crown-6) (2). The polymerization of 4′-isocyanatobenzo-18-crown-6 (**1**) with MeLi in THF at −78 °C heterogeneously proceeded to afford a polymeric product in 71% yield, which was soluble in water, methanol, DMSO, DMF, acetonitrile, and $CHCl_3$ but insoluble in diethyl ether, THF, and toluene. In the ^{13}C NMR spectrum of

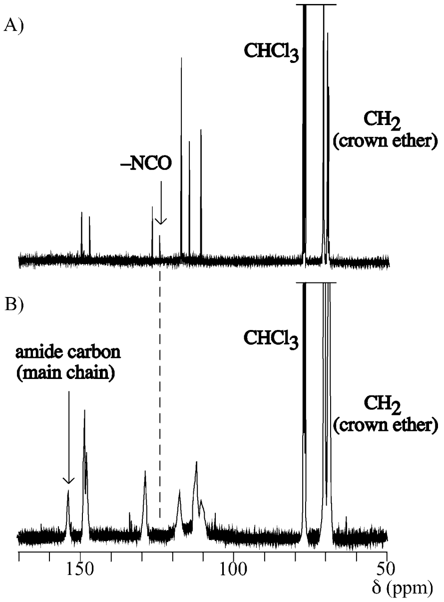

Figure 1. ^{13}C NMR spectra of (A) **1** and (B) **2** in $CDCl_3$.

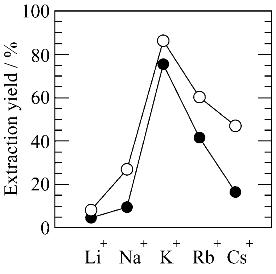

Figure 2. Extraction yields (%) of alkali-metal picrates by polymer **2** (open circle) and unimer **3** (closed circle): [benzo-18-crown-6 units] = 5.8×10^{-3} mol L^{-1} in CH_2Cl_2 phase; [picric acid] = 7.0×10^{-5} mol L^{-1} and [metal hydroxide] = 0.10 mol L^{-1} in the aqueous phase.

the product, the signals due to the methylene carbons in the crown ether moiety appeared at 70.9−68.6 ppm along with those due to the carbons of the amide groups in the main chain at 153.9 ppm, as shown in Figure 1. In addition, the peak due to the amide group appeared at 1709 cm^{-1} in the IR spectrum, while no peak due to the isocyanate group was observed at 2269 cm^{-1}. Unfortunately, the SEC trace of the product showed no peak using $CHCl_3$ as the eluent. Thus, the SLS measurement was carried out for determining the molecular weight of the product. The resulting absolute weight-average molecular weight ($M_{w,SLS}$) was 2.6×10^4. These results indicated that the obtained polymer was assignable to poly(phenyl isocyanate) with crown ether moieties, polymer **2**.

To elucidate the complexation ability of **2** toward cationic guests, the metal cation-binding property of **2** was compared with that of 4′-(*N*,*N*-diacetylamino)benzo-18-crown-6 (**3**), which is exactly identical with the unimer of **2**. Figure 2 shows the results of the extraction of the lithium, sodium, potassium, rubidium, and cesium picrates using polymer **2** and unimer **3**. The yield of K^+, whose diameter agreed with the benzo-18-crown-6 cavity, for **2** was almost the same as that for **3**, whereas the yields of Rb^+ and Cs^+ for **2** were larger than those for **3**, though the diameters of Rb^+ and Cs^+ were greater than the benzo-18-crown-6 cavity in **2**. This result can be explained by cooperative coordination effects, i.e., two neighboring crown ethers associate with a single cation, as previously reported for the polymeric crown ethers.[15] However, the cooperative coordination effect for **2** was relatively smaller than that for poly(4′-vinylbenzo-18-crown-6), indicating that the main chain of **2** was more rigid than that of poly(4′-vinylbenzo-18-crown-6). Thus, the rigidity for **2** should be favorable to the formation of the helical structure.

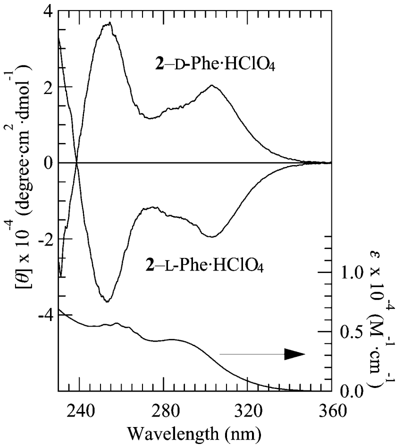

Figure 3. CD and UV spectra of **2** in acetonitrile at 25 °C containing L- and D-Phe·$HClO_4$ ([monomeric units in **2**] = 2.8 mmol L^{-1} and [Phe·$HClO_4$]/[monomeric units in **2**] = 5.0).

Macromolecular Helicity Induction. We examined the potential of the macromolecular helicity induction in polymer **2** driven by a host−guest interaction using amino acids. Figure 3 shows the CD and UV spectra of **2** in the presence of the L-Phe•$HClO_4$ or D-Phe•$HClO_4$ as the chiral guest. The CD spectrum of **2** and the L-Phe•$HClO_4$ system showed a negative Cotton effect with the high intensity of -3.7×10^4 deg cm^2 $dmol^{-1}$ in the range from 240 to 340 nm, corresponding to the absorption of the polymer backbone.[16] On the contrary, in the CD spectrum with D-Phe•$HClO_4$, a positive Cotton effect was observed, and the CD spectrum pattern was the mirror image of that of **2** with L-Phe•$HClO_4$. On the other hand, a clear Cotton effect was not observed in the range from 230 to 290 nm for unimer **3** in the presence of L-Phe•$HClO_4$.

For the complexes for **2** and **3** with L-Phe•$HClO_4$, the relative concentration of the guest to host (G/H) in the $CDCl_3$ layer was determined after the extraction experiment. The G/H values were 0.37 for **2** and 0.28 for **3**, suggesting that polymer **2** and unimer **3** had a similar cation-binding property for L-Phe•$HClO_4$. Therefore, the induced CDs were based on not the complexation of the chiral guest in the host group but the structure change of the main chain; i.e., the response of the chiral information transmitted from the amino acids through the host−guest interaction produced the one-handed helical structure of **2** (Figure 4).

To clarify the effect of the molar ratio of L-Phe•$HClO_4$ and **2**, a titration experiment was carried out. Figure 5 shows the titration curve of the molar ellipticity value for the second Cotton effect ($[\theta]_{second}$) at 254 nm in the CD spectra of **2** with L-Phe•$HClO_4$ in acetonitrile at 25 °C. The intensity of the induced CD increased with the increasing concentration of L-Phe•$HClO_4$ and then reached a constant value of -3.7×10^4 deg cm^2 $dmol^{-1}$ when the molar ratio of L-Phe•$HClO_4$ and the monomeric units in **2** was 5.0. The induced CD spectrum could be detected even with 0.05 equiv of L-Phe•$HClO_4$ on the basis of the monomeric units in **2**. In addition, a nonlinear effect was observed below 1.0 equiv of L-Phe•

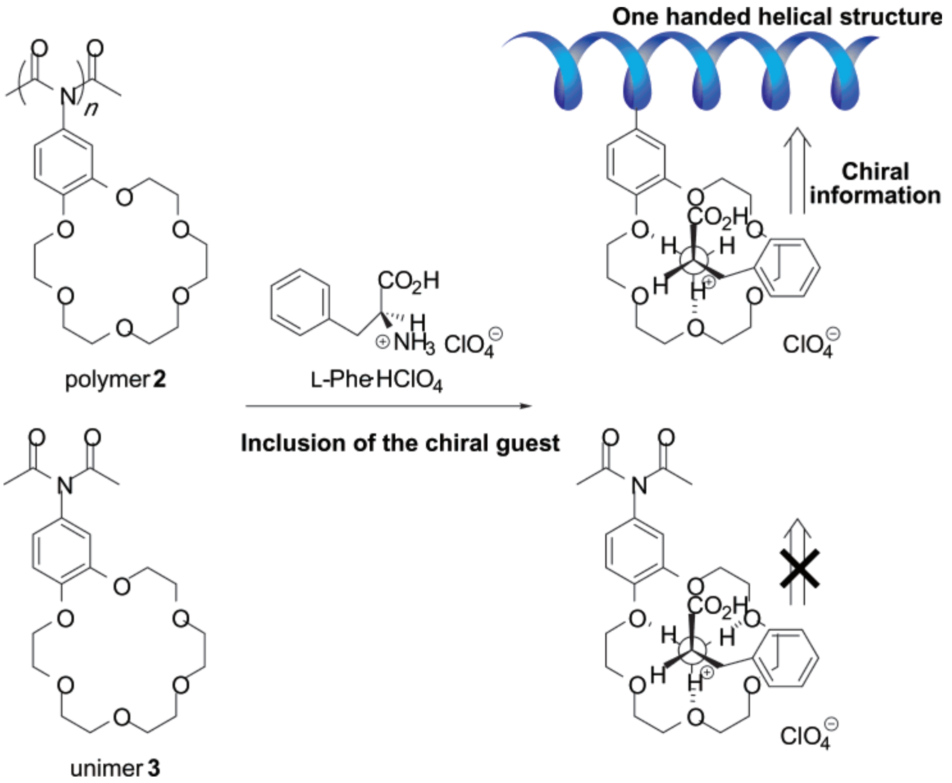

Figure 4. Schematic representation of the macromolecular helicity induction in **2** with L-Phe·$HClO_4$ based on the host–guest complexation.

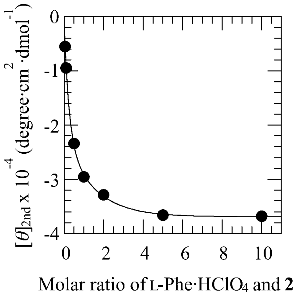

Figure 5. Titration curve of the molar ellipticity values for the second Cotton effect at 254 nm. CD measurements of **2** with L-Phe·$HClO_4$ were performed in acetonitrile at 25 °C ([monomeric units in **2**] = 2.8 mmol L^{-1} and [L-Phe·$HClO_4$]/[monomeric units in **2**] = 0.05–10).

$HClO_4$ in the titration curve, suggesting that the achiral units in **2** cooperated with the chiral units on the formation of the one-handed helical structure, i.e., the chiral amplification. However, the amplification effect was smaller than those for the other polymer systems.[3a,c,8b]

The effects of solvent and temperature on the complex formation of **2** with L-Phe·$HClO_4$ were investigated in various solvents, such as water, methanol, acetonitrile, and chloroform/acetonitrile (3/1, v/v) in the temperature range from −30 to 50 °C, as shown in Figure 6. At 25 °C, the intensity of the induced CD in acetonitrile and chloroform/acetonitrile (3/1, v/v) were considerably higher than those in water and methanol; in other words, the intensity of the induced CD increased with the decreasing polarity of the solvent. In addition, the intensity of the induced CD significantly increased in the negative direction with the decreasing temperature in every solvent, and this change was also reversible. A similar observation has been reported by Green et al. and Okamoto et al.[3a,f] These dependences indicated that the nonpolar solvent and the low temperature were great advantages with respect to the host–guest complexation and the formation of the one-handed helical structure.

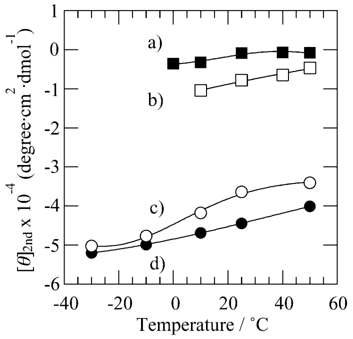

Figure 6. Temperature dependence of the molar ellipticity values for the second Cotton effect at 254 nm in (a) water, (b) methanol, (c) acetonitrile, and (d) chloroform/acetonitrile (3/1, v/v). Concentrations of monomeric units in **2** and of L-Phe·$HClO_4$ are 2.8 and 14 mmol L^{-1}, respectively.

Table 1. Signs of Cotton Effects and $[\theta]_{2nd}$ Values for Induced CD of 2 with RHC(COOH)NH_2·$HClO_4$[a]

amino acid	sign	$[\theta]_{2nd} \times 10^{-4}$ (deg cm^2 dmol^{-1})	wavelength (nm)
L-Phe	−	3.7	254
D-Phe	+	3.7	254
L-Leu	−	1.3	251
L-Val	−	2.8	253
L-Met	−	1.2	251

[a] [Monomeric units in **2**] = 2.8 mmol L^{-1}; [RHC(COOH)NH_2·$HClO_4$]/[monomeric units in **2**] = 5.0.

We further examined the helicity induction of **2** in the presence of various $HClO_4$ salts of amino acids (RHC(COOH)NH_2·$HClO_4$). Table 1 lists the results of the Cotton effect signs and the $[\theta]_{second}$ intensities for the induced CD of **2** with RHC(COOH)NH_2·$HClO_4$. Polymer

2 exhibited an induced CD with a high intensity through the formation of a complex with the $HClO_4$ salts of the every amino acid. The sign of the Cotton effect was reflected in the absolute configuration of the amino acid, i.e., minus for the L-amino acid and plus for the D-one. Furthermore, the intensities of the induced CD using L-Phe·$HClO_4$ and L-Val·$HClO_4$ as the chiral guest were relatively higher than those using L-Leu·$HClO_4$ and L-Met·$HClO_4$, suggesting that the bulkiness of the side chain in the guest significantly affected the macromolecular helicity induction for **2**.

Conclusions

A novel poly(phenyl isocyanate) derivative bearing a crown ether (**2**) was synthesized by the anionic polymerization of 4′-isocyanatobenzo-18-crown-6 (**1**) using MeLi in THF at −78 °C. In the CD spectra of polymer **2** in the presence of various chiral guests, i.e., the perchloric acid salts of amino acids, large Cotton effects were observed in the range from 240 to 340 nm, corresponding to the absorption of the polymer backbone, though 4′-(*N*,*N*-diacetylamino)benzo-18-crown-6 (**3**), which was identical with the unimer of **2**, did not show any Cotton effect. Therefore, it was concluded that the induced CDs were based on the structure of the main chain; that is, polymer **2** formed the one-handed helical structure driven by the host−guest interaction with the perchloric acid salts of the amino acids. Additionally, the intensity of the Cotton effect was relatively large, though the chiral guest was only donated to the host group in the polymer. To our knowledge, the present study is the first report describing the macromolecular helicity induction in polyisocyanate with the host group, crown ether in this study, through the host−guest complexation.

Supporting Information Available: Extraction yields (%) of alkali-metal picrates by polymer **2** and unimer **3**, CD spectra of **2** with L-Phe·$HClO_4$ for the titration experiment, CD spectra of **2** with L-Phe·$HClO_4$ in water, methanol, acetonitrile, and chloroform/acetonitrile (3/1, v/v), temperature dependence for the CD spectra of **2** with L-Phe·$HClO_4$ in chloroform/acetonitrile (3/1, v/v), and CD spectra of **2** in the presence of various perchloric acid salts of amino acids. This material is available free of charge via the Internet at https://pubs.acs.org.

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