Helicity Induction of Polyisocyanate with a Crown Cavity on the Main Chain Synthesized by Cyclopolymerization of α,ω-Diisocyanate

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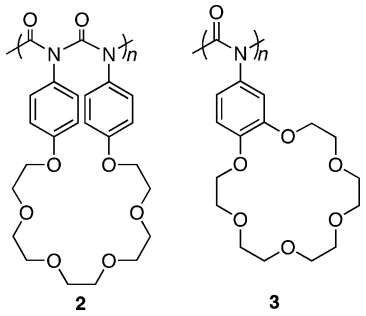
ABSTRACT: Polymerization of a novel α,ω-diisocyanate monomer, 1,14-bis(4-isocyanatophenoxy)-3,6,9,12-tetraoxatetradecane (**1**), was carried out in DMF using MeLi to afford a gel-free linear polymer according to a cyclopolymerization mechanism. The resulting polymer was assignable to poly(phenyl isocyanate) with a C_2 symmetrical crown cavity on the main chain (**2**). The circular dichroism (CD) spectrum of **2** in the presence of the perchloric acid salt of L-phenylglycine (L-Pgly·$HClO_4$) showed a negative Cotton effect with a high intensity of -3.2×10^4 deg cm^2 dmol^{-1} in the range from 245 to 330 nm, corresponding to the absorption of the polymer backbone, while a positive Cotton effect was observed for D-Pgly·$HClO_4$, and the CD spectrum pattern was a mirror image of that of **2** with L-Pgly·$HClO_4$. Thus, this suggested that the novel type of poly(phenyl isocyanate) with the crown cavity on the main chain (**2**) formed a one-handed helical structure driven by the host−guest complexation with the chiral guest molecules. Although the solvent significantly influenced the CD intensities of **2**, the CD intensities hardly changed at any temperature.

Introduction

The design, synthesis, and characterization of synthetic helical polymers should greatly contribute to a wide range of chemical fields such as biochemistry, analytical chemistry, and pharmaceutical chemistry.[1,2] The synthetic helical polymers show unusual or rather great interesting behavior in comparison with other chiral polymers, e.g., a helix-sense inversion by changing the external conditions,[3] a chiral amplification based on the cooperation of achiral monomeric units,[4] an arrangement of pendant groups in a helical array,[5] and the induction of a predominantly one-handed helical structure to an achiral helical polymer by an external chiral stimulus, i.e., macromolecular helicity induction. The induction of the helical structure through an acid−base interaction with chiral molecules has been reported for polyacetylene,[6] polycarbodiimide,[7] poly(organophosphazene),[8] polyisocyanide,[9] and polyaniline.[10] Recently, Yashima et al. have revealed that it was possible to form a one-handed helical structure in poly(phenylacetylene) with crown ether pendants using a host−guest interaction.[11] Although polyisocyanate is one class of helical polymers,[12] investigation of the helicity induction in polyisocyanate is still rare.[13] Very recently, we reported that one-handed macromolecular helicity was induced in the backbone of poly(phenyl isocyanate) with a crown ether (**3** in Chart 1) through host−guest complexation with amino acid derivatives.[14] For the studies on polymers with crown ethers, it has been found that the crown ether acted as a versatile interaction site for the helicity induction, i.e., the polymers with a crown ether on their side chain sensitively responded to chiral information on an extremely small amount of chiral compounds to form a one-handed helical structure.[11,14]

Chart 1. Structures of 2 and 3



2 **3**

Cyclopolymerization of a bifunctional monomer is one of the facile methods to produce a gel-free, linear polymer with cyclic repeating units, such as a crown ether. We have developed a synthetic strategy for producing polymers with a crown cavity via the cyclopolymerization of the bifunctional monomers. For example, α,ω-divinyl ether,[15] α,ω-diepoxide,[16] α,ω-diepisulfide,[17] and α,ω-diacetylene[18] bearing an oligooxyethylene chain were successfully polymerized to produce poly(crown ether), poly(thiacrown ether), and poly(azacrown ether), which exhibited the respective metal cation-binding properties depending on the size of the macrocyclic units and the kind of donor atoms.

However, there have been no attempts to cyclopolymerize diisocyanates capable of forming great large membered rings. So far, it has been known that the anionic polymerization of 1,2-diisocyanate derivatives proceeds according to the cyclopolymerization mechanism to afford gel-free, linear polyisocyanates with cyclic

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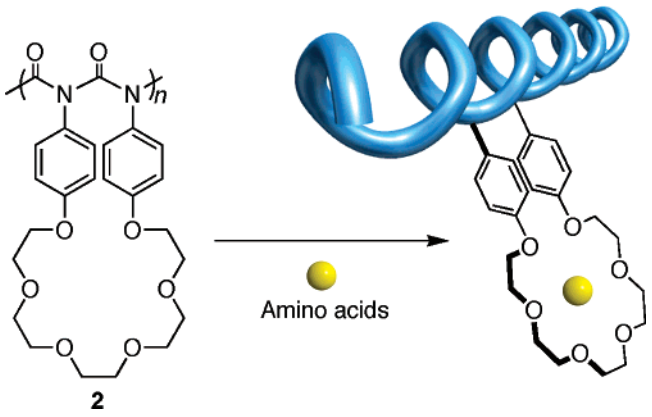


Figure 1. Schematic representation of the macromolecular helicity induction of **2** based on the host−guest complexation with amino acid derivatives.

repeating units.[19] In addition, several other diisocyanates such as 1,3- and 1,4-diisocyanate derivatives were shown to undergo anionic cyclopolymerization.[20] In a subsequent study, Patten and Novak reported that the 1,2-diisocyanate derivatives were successfully cyclopolymerized in an excellent yield using an organotitanium(IV) catalyst[21] that was used for the living polymerization of monoisocyanates.[22] A polymer synthesized by cyclopolymerization of a bifunctional monomer should be a novel type of polymer for helicity induction, because it has a crown cavity not on the side chain but on the main chain. Thus, of great interest is the synthesis of a polyisocyanate with a crown cavity via the cyclopolymerization method and the estimation of the helicity induction of the resulting polymer.

Here we present the synthesis of a novel optically inactive poly(phenyl isocyanate) with a crown cavity as the host (**2** in Chart 1) via the anionic cyclopolymerization of 1,14-bis(4-isocyanatophenoxy)-3,6,9,12-tetraoxatetradecane (**1**). The microstructure of the repeating units in the resulting polymer was assigned by means of ^{1}H, ^{13}C, and ^{15}N NMR spectroscopies. In addition, the macromolecular helicity induction of **2** is examined in the presence of chiral guest molecules, the perchloric acid salts of amino acids (Figure 1). The influence of the external conditions, such as solvent and temperature, on the macromolecular helicity induction of **2** was discussed in comparison with that of poly(phenyl isocyanate) with a crown ether on the side chain (**3**).

Results and Discussion

Synthesis and Characterization of Poly(phenyl isocyanate) with a Crown Cavity (2). For the polymerization of 1,14-bis(4-isocyanatophenoxy)-3,6,9,12-tetraoxatetradecane (**1**), MeLi was used as the initiator and acetyl chloride as the terminating agent. In addition, ethanol was finally added to the reaction mixture in order to confirm the residual isocyanate groups in the resulting polymers (Scheme 1). Table 1 lists the results for a series of polymerizations of **1**. For the polymerization with a monomer concentration of 0.1 M in DMF (run 1), the polymerization system gradually became heterogeneous after MeLi was added to the monomer solution, and the resulting product was insoluble in common organic solvents. On the other hand, for the monomer concentrations of 0.05 and 0.03 M (runs 2 and 3), the polymerizations afforded gel-free polymeric products along with the solvent insoluble parts. In particular, only the gel-free polymer was successfully

Scheme 1. Synthesis of Poly(phenyl isocyanate) with Crown Cavity on the Main Chain

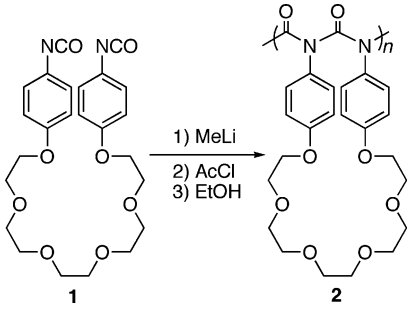


Table 1. Cyclopolymerization Results of α,ω-Diisocyanate 1 with MeLi[a]

run	solvent	[M] (mol L^{-1})	temp (°C)	yield[b] (%)	$M_n \times 10^{-4}$[c]	M_w/M_n[c]
1	DMF	0.1	−60	trace (78)		
2	DMF	0.05	−60	32 (16)	1.9	3.0
3	DMF	0.03	−60	43 (3)	1.7	1.7
4	DMF	0.02	−60	58 (0)	0.92	1.4
5	THF	0.02	−78	trace (86)		

[a] [M]/[I] = 50; time, 30 min. [b] The yield after purification using preparative SEC. The yield of solvent insoluble part is described in parentheses. [c] Determined by SEC in $CHCl_3$ using polystyrene standards.

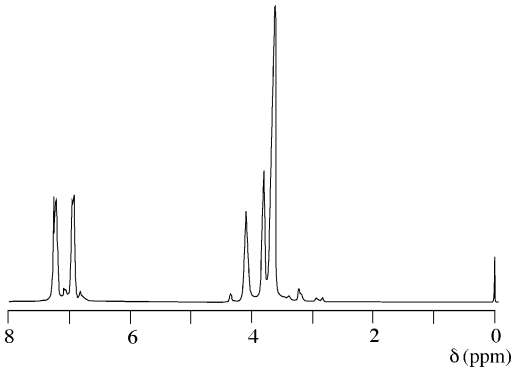


Figure 2. ^{1}H NMR spectrum of **2** in $CDCl_3$.

obtained for the monomer concentration of 0.02 M (run 4). However, the gel-free polymer was not at all obtained for a monomer concentration of 0.02 M in THF (run 5).

Size exclusion chromatography (SEC) traces of the resulting gel-free polymers exhibited a main peak along with some peaks of an undesirable oligomer in the low molecular weight region. Thus, the original product was fractionated using a preparative SEC to give the main product with a unimodal peak in the SEC trace. The resulting main product was, of course, a gel-free, white powder, which was soluble in acetonitrile, $CHCl_3$, DMF, and DMSO but insoluble in water, methanol, THF, and toluene. The polymer yields and the number-average molecular weights (M_ns) of the main products tended to increase and to decrease with the decreasing monomer concentrations, respectively.

For the cyclopolymerization chemistry, the residual amount of isocyanate groups in the resulting polymers is generally important to determine the extent of cyclization. In the ^{1}H NMR spectrum of the main product (run 4), the signals at 7.27−6.83 ppm due to aromatic protons appeared along with those at 4.34−3.20 ppm due to methylene protons in the crown ether moiety (Figure 2). However, in the range around 1.30 ppm, there was no signal due to the ethyl carbamate

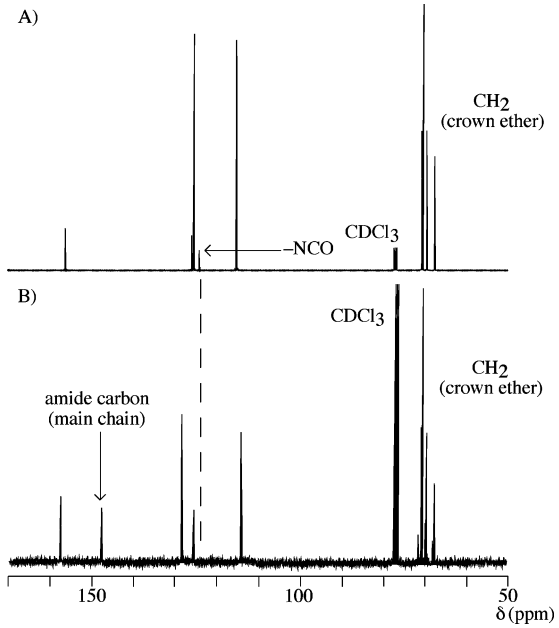


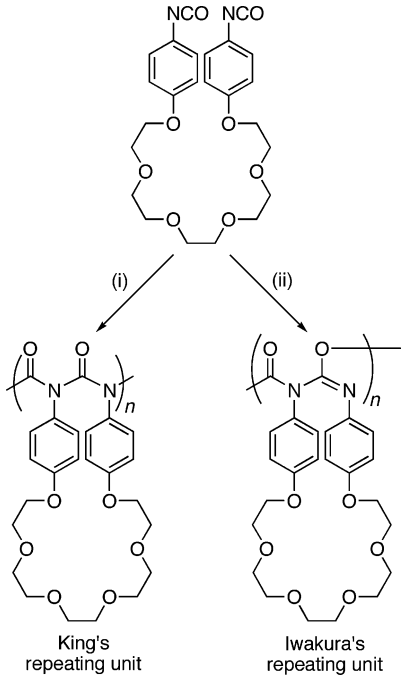
Figure 3. ^{13}C NMR spectra of (A) **1** and (B) **2** in $CDCl_3$.

groups derived from ethanol and the residual isocyanate groups (this was confirmed by a model termination reaction, see Experimental Section), indicating that all the isocyanate groups were consumed through the polymerization, i.e., the extent of cyclization was ca. 100%. In addition, the characteristic signal at 149.0 ppm due to the carbons of the amide groups in the main chain appeared, and that at 123.9 ppm due to the isocyanate carbons completely disappeared, as shown in the ^{13}C NMR spectrum of the main product (Figure 3B, run 4). There was no essential difference among the ^{1}H and ^{13}C NMR spectra of every main product. These results indicated that the polymerization of **1** proceeded through a cyclopolymerization mechanism to produce the polymer essentially consisting of cyclic constitutional units.

For the cyclopolymerization of diisocyanates, two types of cyclic repeating units have been proposed by King and Iwakura et al., i.e., the cyclic repeating unit produced by alternating intermolecular/intramolecular carbon−nitrogen double bond additions (King's repeating unit)[19a] and that produced by alternating carbon−nitrogen/carbon−oxygen double bond additions (Iwakura's repeating unit),[20a] as shown in Scheme 2. To clarify the cyclic repeating units of the main product, ^{15}N NMR analysis was performed. In the ^{15}N NMR spectrum of the main product (run 4), a sharp signal appeared at 148.5 ppm and no other signals were observed in all areas, as shown in Figure 4A. Additionally, a characteristic signal at 152.3 ppm due to amide nitrogen in the main chain appeared in the ^{15}N NMR spectrum of poly(*p*-methoxyphenyl isocyanate), suggesting that the signal observed in the ^{15}N NMR spectrum of the main product also corresponded with amide nitrogen in the cyclic repeating unit, King's unit. Therefore, the main product was assignable to poly(phenyl isocyanate) with a C_2 symmetrical crown cavity in the repeating units, polymer **2**.

Macromolecular Helicity Induction. To elucidate the complexation ability of **2** toward cationic guests, the metal cation-binding property of **2** was compared with that of poly(phenyl isocyanate) with a crown ether on the side chain (**3**), which is an architectural analogue

Scheme 2. Possible Structures of the Cyclic Repeating Units in 2[a]



[a] Key: (i) Intermolecular/intramolecular carbon−nitrogen double bond additions to produce King's repeating unit; (ii) carbon−nitrogen/carbon−oxygen double bond additions to produce Iwakura's repeating unit.

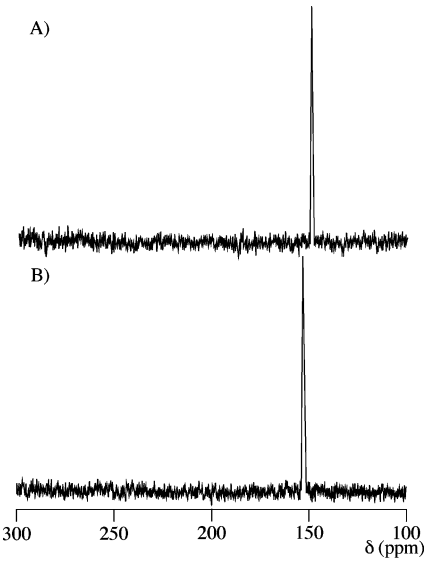


Figure 4. ^{15}N NMR spectra of (A) **2** and (B) poly(*p*-methoxyphenyl isocyanate) in $CDCl_3$.

of **2**.[14] Figure 5 shows the results of the extraction of lithium, sodium, potassium, rubidium, and cesium picrates using **2** and **3**. Previously, we reported that **3** exhibited a high extraction yield toward metal cations, particularly K^+, whose diameter agreed with the benzo-18-crown-6 cavity. On the other hand, the yields of the metal cations for **2** were extremely smaller than those for **3**, and no selectivity was observed in the kind of the metal cations using **2**. Although **2** has six oxygen atoms as donors as does **3**, the size of the cyclic structure of **2** is larger than that of **3**, i.e., a 27-membered ring for **2** and a 18-membered ring for **3**. Hence, **2** should be difficult to orient in a suitable conformation for complexation with cationic guests, resulting in the low

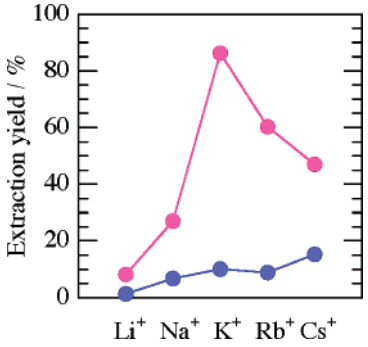


Figure 5. Extraction yields (%) of alkali-metal picrates by polymer **2** (blue circle) and polymer **3** (red circle): [monomeric units] = 5.8×10^{-3} mol L^{-1} in CH_2Cl_2 phase; [picric acid] = 7.0×10^{-5} mol L^{-1}; [metal hydroxide] = 0.10 mol L^{-1} in the aqueous phase.

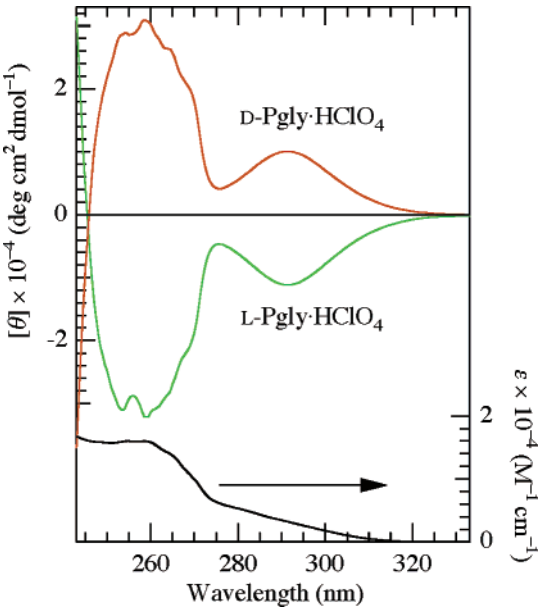


Figure 6. CD and UV spectra of **2** in chloroform/acetonitrile (1/1, v/v) at 25 °C containing L- and D-Pgly·$HClO_4$ ([monomeric units in **2**] = 2.1 mmol L^{-1} and [Pgly·$HClO_4$]/[monomeric units in **2**] = 30).

metal-cation-binding property of **2**. However, **2** clearly showed complexation ability toward cationic guests, indicating that the cyclic repeating units in **2** certainly acted as the host in the host−guest complexation.

We examined the potential of the macromolecular helicity induction in polymer **2** driven by the host−guest interaction with chiral guests. Figure 6 shows the circular dichroism (CD) and ultraviolet (UV) spectra of **2** (run 4) in the presence of the L- and D-Pgly·$HClO_4$ as the chiral guest. The CD spectrum of the **2** and L-Pgly·$HClO_4$ system showed a characteristic induced CD (ICD), i.e., a negative Cotton effect with a high intensity of -3.2×10^4 deg cm^2 $dmol^{-1}$ in the range from 245 to 330 nm corresponding to the absorption of the polymer backbone.[23] On the contrary, in the CD spectrum of **2** with D-Pgly·$HClO_4$, a positive Cotton effect was observed and the CD spectrum pattern was a mirror image of that of **2** with L-Pgly·$HClO_4$. These results suggested that a one-handed helical structure in the main chain of **2** was predominantly formed through the host−guest complexation with Pgly·$HClO_4$.

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 2 lists the results of the Cotton effect signs and the molar ellipticity ([θ]) values for the ICD of **2** with RHC(COOH)NH_2·$HClO_4$. Polymer **2** exhibited an ICD with a high intensity through the formation of a complex with the $HClO_4$ salts of every amino acid. As we expected, 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-form.

To clarify the effect of the amount of L-Pgly·$HClO_4$ on **2**, a titration experiment was carried out. Figure 7 shows the titration curve of the molar ellipticity value for the second Cotton effect ($[\theta]_{second}$) in the CD spectra of **2** with L-Pgly·$HClO_4$ in chloroform/acetonitrile (1/1, v/v) at 25 °C. The intensity of the ICD linearly increased with the increasing concentration of L-Pgly·$HClO_4$, and no less than 30 equiv of L-Pgly·$HClO_4$ toward **2** were needed for saturation of the ICD magnitude, i.e., -3.2×10^4 deg cm^2 $dmol^{-1}$. In general, the crown ether is one of the most sensitive interaction sites for the helicity induction system, i.e., polymers with the crown ether very sensitively responded to the chiral stimulus to form the one-handed helical structure. In fact, poly(phenylacetylene)s with a crown ether and **3** indicated a chiral amplification with cooperative interaction in the crown ether pendants,[11,14] whereas no chiral amplification was observed in the titration experiment of **2**, which should be caused by the low complexation ability of **2**. Thus, the type of the interaction site might dramatically influence the sensitivity of the helicity induction system.

The effects of solvent and temperature on the complex formation of **2** with L-Pgly·$HClO_4$ and on the helical structure of **2** were investigated in various solvents, such as chloroform/methanol (1/1, v/v), acetonitrile/methanol (2/1, v/v), acetonitrile, and chloroform/acetonitrile (1/1, v/v), in the temperature range from −30 to +50 °C, as shown in Figure 8. At 25 °C, the intensity of the ICD increased with the decreasing polarity of the solvent, i.e., in the order of chloroform/methanol (1/1, v/v) < acetonitrile/methanol (2/1, v/v) < acetonitrile < chloroform/acetonitrile (1/1, v/v), because the nonpolar solvent had a great advantage with respect to the host−guest complexation and the formation of the one-handed helical structure. For the dynamic helical polymer, it has been revealed that the temperature as well as the solvent significantly influenced the helical structure.[3b−k] In fact, the ICD intensity of **3** in the presence of L-Phe·$HClO_4$ depended on the temperature change; that is, the ICD intensity increased with decreasing temperature in every solvent, and this change was reversible. However, the ICD intensity of **2** in the presence of L-Pgly·$HClO_4$ hardly changed at any temperature. This result suggested that the conformational change in the main chain of **2** was significantly restricted when the chiral guest was encapsulated into the crown cavity on the main chain of **2**, as shown in Figure 9. This phenomenon should be characteristic in polymers with the interaction site on their main chain, i.e., polymers synthesized by the cyclopolymerization of bifunctional monomers. Therefore, **2** should be a novel probe for the assignment of the absolute configuration and for the determination of the optical purity, over a wide range of temperature.

Conclusions

A novel α,ω-diisocyanate monomer, 1,14-bis(4-isocyanatophenoxy)-3,6,9,12-tetraoxatetradecane (**1**), was successfully cyclopolymerized under the dilute conditions

Table 2. Signs of Cotton Effects and [θ] Values for the ICD of 2 with RHC(COOH)NH_2·$HClO_4$[a]

	first Cotton			second Cotton		
amino acid	sign	$[\theta] \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)	sign	$[\theta] \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)
L-phenylglycine	−	1.1	292	−	3.2	260
D-phenylglycine	+	1.0	291	+	3.1	259
L-phenylalanine	−	0.2	293	−	0.1	252
L-leucine	−	0.8	291	−	1.9	245
L-valine	−	0.7	291	−	1.5	246
L-methionine	−	0.7	291	−	1.4	247
D-4-hydroxyphenylglycine	+	1.0	295		n.d.	

[a] CD measurements of **2** with RHC(COOH)NH_2·$HClO_4$ were performed in chloroform/acetonitrile (1/1, v/v) at 25 °C ([monomeric units in **2**] = 2.1 mmol L^{-1} and [RHC(COOH)NH_2·$HClO_4$]/[monomeric units in **2**] = 30).

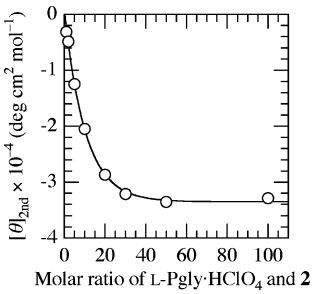


Figure 7. Titration curve of $[\theta]_{second}$ values. CD measurements of **2** with L-Pgly·$HClO_4$ were performed in chloroform/acetonitrile (1/1, v/v) at 25 °C ([monomeric units in **2**] = 2.1 mmol L^{-1} and [L-Pgly·$HClO_4$]/[monomeric units in **2**] = 1.0−100).

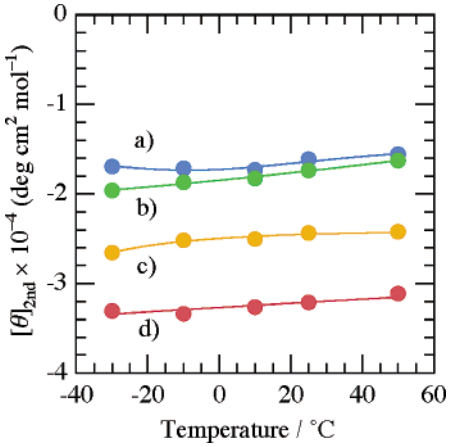


Figure 8. Temperature dependence of $[\theta]_{second}$ values in (a) chloroform/methanol (1/1, v/v), (b) acetonitrile/methanol (2/1, v/v), (c) acetonitrile, and (d) chloroform/acetonitrile (1/1, v/v). Concentrations of monomeric units in **2** and of L-Pgly·$HClO_4$ are 2.1 and 63 mmol L^{-1}, respectively.

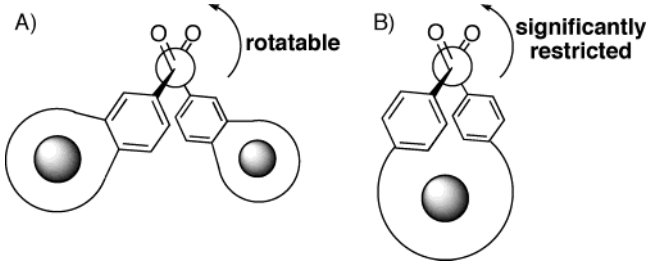


Figure 9. Schematic representation of conformational change in the main chain for (A) **3** and (B) **2** when the chiral guest is encapsulated into the crown cavity.

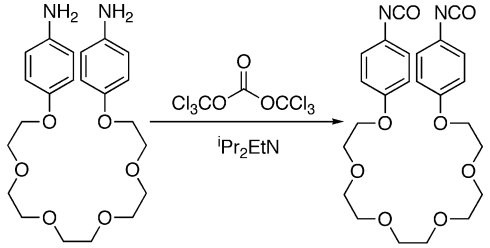
in DMF using MeLi though the resulting cyclic repeating unit had to form a very large-membered ring. The resulting polymer was assignable to poly(phenyl isocyanate) with the crown cavity on the main chain (**2**). In the CD spectra of polymer **2** in the presence of various chiral guests, the perchloric acid salts of amino acids, large Cotton effects were observed in the range from 245 to 330 nm corresponding to the absorption of the polymer backbone, indicating that the novel type of poly(phenyl isocyanate) with the crown cavity on the main chain (**2**) as well as that on the side chain formed the one-handed helical structure driven by the host−guest complexation with the chiral guest molecules. For the dynamic helical polymer, the temperature change generally influenced the induced helical structure, whereas the induced helical structure of **2** hardly changed at any temperature. This phenomenon should be characteristic in polymers with the interaction site on their main chain, i.e., the polymers synthesized by the cyclopolymerization of bifunctional monomers. To our knowledge, the present study is the first report describing macromolecular helicity induction in the polymers with the host on their main chain.

Experimental Section

Materials. 1,14-Bis(4-aminophenoxy)-3,6,9,12-tetraoxatetradecane was synthesized by a previously reported method.[24] L-Phenylalanine (L-Phe) and L-leucine (L-Leu) (>99.9% ee) were purchased from the Peptide Institute, Inc. (Osaka, Japan). L-Phenylglycine (L-Pgly, >99%), D-phenylglycine (D-Pgly, >98%), L-valine (L-Val, >99%), and L-methionine (L-Met, >99%) were obtained from the Kanto Chemical Co., Ltd. (Tokyo, Japan). D-4-Hydroxyphenylglycine (>98%) was purchased from the Acros Organics (Geel, Belgium). The perchloric acid ($HClO_4$) salts of these amino acids were prepared according to a previous report.[25] THF was dried over sodium benzophenone ketyl and then vacuum transferred from CaH_2. DMF was distilled over CaH_2 under reduced pressure. A solution of MeLi in diethyl ether (1.04 mol L^{-1}), dry acetonitrile (purity > 99.5%, water content < 0.005 vol %), dry dichloromethane (CH_2Cl_2, purity > 99.5%, water content < 0.003 vol %), dry ethanol (purity > 99.5%, water content < 0.005 vol %), chloroform for the spectroscopy (>99.0%), methanol for the spectroscopy (>99.7%), acetyl chloride (>95%), all the metal hydroxides, and picric acid were obtained from Kanto Chemical and used without further purification. Triphosgene (> 98%) and diisopropylethylamine (> 99.5%) were available from the Aldrich Chemical Co., Inc. (Milwaukee, WI), and no further purification was used. Phenyl isocyanate (>98%) was obtained from Aldrich and distilled over CaH_2 just prior to use. *p*-Methoxyphenyl isocyanate (>98%) was available from Tokyo Kasei (TCI, Tokyo, Japan) and distilled over CaH_2 just prior to use.

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-A400II instrument. The ^{15}N NMR spectrum was recorded using a BRUKER MSL400 instrument. In the ^{15}N NMR measurement, formamide was used as the reference (112.4 ppm). Mass spectroscopy (MS) was recorded using a JEOL JMS−SX102A mass spectrometer. The size exclusion chromatography (SEC) was performed at 40 °C in chloroform (0.8 mL min^{-1}) using a Jasco GPC-900 system

Scheme 3. Synthesis of α,ω-Diisocyanate with Oligooxyethylene Chain (1)



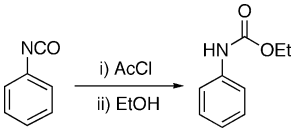
1

equipped with a TOSOH TSKgel GMH_{HR}-M column (linear, 7.8 mm × 300 mm) and a Shodex KF-804L column (linear, 8 mm × 300 mm). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. The preparative SEC was performed at 23 °C in chloroform (3.8 mL min^{-1}) using a JAI LC-908 system equipped with two JAI JAIGEL-3H (20 mm × 600 mm) and a JAI JAIGEL-5H (20 mm × 600 mm) polystyrene columns and JAI UV-310 and JAI RI-5HC detectors. IR spectra were recorded using a Perkin-Elmer Paragon 1000. Ultraviolet−visible (UV−vis) spectra were measured at 23 °C in a 10 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. Preparation of the polymerization solution was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) under dry argon atmosphere (H_2O, O_2 < 1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively.

1,14-Bis(4-isocyanatophenoxy)-3,6,9,12-tetraoxatetradecane (1). A α,ω-diisocyanate monomer was synthesized via carbonylation of the corresponding diamine using triphosgene, as shown in Scheme 3. To a solution of triphosgene (5.8 g, 20 mmol) in dry CH_2Cl_2 (90 mL) was slowly added a mixture of 1,14-bis(4-aminophenoxy)-3,6,9,12-tetraoxatetradecane (9.5 g, 23 mmol) and diisopropylethylamine (17 mL, 0.10 mol) in dry CH_2Cl_2 (150 mL) over a period of 2 h under a dry nitrogen atmosphere. After being stirred 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 CH_2Cl_2/THF (9/1, v/v) to give **1** as a white solid. Yield: 7.4 g (69%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (m, 4H, Ar), 6.83 (m, 4H, Ar), 4.07 (t, J = 4.8 Hz, 4H, $ArOCH_2CH_2O-$), 3.83 (t, J = 4.8 Hz, 4H, $ArOCH_2CH_2O-$), 3.72−3.65 (m, 12H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4 (Ar), 125.7 (Ar), 125.3 (Ar), 123.9 (−NCO), 115.2 (Ar), 70.6−67.5 ($-CH_2-$). IR (KBr, cm^{-1}): 2276 (N=C=O). Anal. Calcd for $C_{24}H_{28}N_2O_8$: C, 61.01; H, 5.97; N, 5.93. Found: C, 60.40; H, 5.94; N, 6.02. MS (FD) (*m/e* and relative intensity): 472 (M^+, 100); 473 ($M-H^+$, 29). Mp: 51−53 °C.

Polymerization. The polymerizations of **1** were carried out in a dry Schlenk flask under an argon atmosphere. An example of the procedure is described for the preparation of polymer **2** (run 4). In a glovebox (under moisture- and oxygen-free argon atmosphere, H_2O, O_2 < 1 ppm), **1** (0.72 g, 1.5 mmol) was weighed into a dry Schlenk flask and dissolved in dry DMF (76 mL). The flask was then removed from the glovebox and cooled at −60 °C. A solution of MeLi in diethyl ether (1.04 mol L^{-1}, 29 μL, 30 μmol) was added to the solution using a microsyringe. After 30 min, the reaction was terminated by adding acetyl chloride (22 μL, 0.30 mmol), which was important for stabilizing the polymer chain end.[26] After the entire mixture was stirred for an additional 12 h at room temperature, dry ethanol (8.9 mL, 0.15 mol) was added to the mixture at 0 °C in order to convert the unreacted isocyanate groups into ethyl carbamates. The mixture was stirred for an additional 4 h at room temperature and then poured into a large amount of diethyl ether. The precipitate was filtered off and dried in vacuo to give the original product as a white powder. The original product was fractionated into two parts, i.e., a main part and some oligomer, using preparative SEC. The fractionated main product was redissolved in a small amount of chloroform, and then poured into large amount of diethyl ether. The precipitate was filtered off and dried in vacuo to give polymer **2** as a white powder. Yield: 0.41 g (58%). M_n = 9.2 × 10^3, M_w/M_n = 1.4. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (br, 4H, Ar), 6.96 (br, 4H, Ar), 4.20−3.64 (br, 20H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0 (C=O), 159.0, 129.4, 126.3, 115.2 (Ar), 71.5−67.6 ($-CH_2-$). ^{15}N NMR (41 MHz, $CDCl_3$): δ 148.5 (amide nitrogen). IR (film on NaCl plate, cm^{-1}): 1709 (C=O of amide).

Scheme 4. Model Termination Reaction for the Polymerization of 1



Synthesis of Poly(*p*-methoxyphenyl isocyanate). The polymerization of *p*-methoxyphenyl isocyanate was carried out in a dry Schlenk flask under an argon atmosphere. In a glovebox, *p*-methoxyphenyl isocyanate (1.0 g, 6.7 mmol) was weighed into a dry Schlenk flask and dissolved in dry THF (13 mL). The flask was then removed from the glovebox and cooled at −78 °C. A solution of MeLi in diethyl ether (1.04 mol L^{-1}, 0.13 mL, 0.13 mmol) was added to the solution. After 30 min, the polymerization was terminated by adding acetyl chloride (95 μL, 1.3 mmol). The mixture was stirred for an additional 12 h at room temperature and then poured into a large amount of methanol. The precipitate was filtered off and purified by reprecipitation with chloroform-methanol and dried in vacuo to give poly(*p*-methoxyphenyl isocyanate) as a white powder. Yield: 0.86 g (86%). M_n = 7.2 × 10^3, M_w/M_n = 1.2. ^1H NMR (400 MHz, $CDCl_3$): δ 6.53−6.15 (br, 4H, Ar), 3.64 (s, 3H, $-OCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5 (C=O), 158.5, 129.1, 127.0, 113.6 (Ar), 55.3 ($-OCH_3$). ^{15}N NMR (41 MHz, $CDCl_3$): δ 152.3 (amide nitrogen). IR (film on NaCl plate, cm^{-1}): 1716 (C=O of amide).

Model Termination Reaction. A model termination reaction for the polymerization of **1** was performed using phenyl isocyanate, as shown in Scheme 4. To a solution of phenyl isocyanate (1.0 mL, 9.2 mmol) in dry DMF (92 mL) was added acetyl chloride (6.5 mL, 92 mmol) at −60 °C. After this mixture was stirred at room temperature for 12 h, dry ethanol (54 mL, 0.92 mol) was added to the solution at 0 °C. The mixture was stirred at room temperature for 4 h and then evaporated to dryness to give a pale yellow solid. From the ^1H and ^{13}C NMR measurements, the solid was assignable to ethyl *N*-phenylcarbamate. Yield: 1.4 g (95%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 2H, Ar), 7.28 (t, J = 8.0 Hz, 2H, Ar), 7.02 (t, J = 7.6 Hz, 1H, Ar), 6.78 (s, 1H, −NH−), 4.20 (q, J = 7.1 Hz, 2H, $-OCH_2-$), 1.30 (t, J = 7.1 Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7 (C=O), 138.0, 129.0, 123.3, 118.6 (Ar), 61.2 ($-OCH_2-$), 14.5 ($-CH_3$). IR (KBr, cm^{-1}): 1704 (C=O of urethane).

Cation-Binding Property. The extraction of alkali metal picrates was carried out using a procedure similar to that developed by Pedersen.[27] A solution of the polymer in CH_2Cl_2 (2 mL, [crown ether units] = 5.8 × 10^{-3} mol L^{-1}) was vigorously shaken in a centrifuge 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 the reaction was separated 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 using a UV−vis spectrophotometer.

CD Measurements. The concentration of **2**, which was calculated on the basis of monomeric units, was 2.1 mmol L^{-1} for all measurements. The molar ratio of the chiral guest and the monomeric units in **2** was 30 except for the titration experiment in Figure 7. A typical procedure is described below; A stock solution of **2** (4.2 mmol L^{-1}) in chloroform/acetonitrile (1/1, v/v) was prepared in a 5 mL flask, and a 1 mL aliquot of the solution was transferred to a 2 mL flask. L-Pgly·$HClO_4$ (31.7 mg, 0.126 mmol) was added to the 2 mL flask. The solution was then diluted with chloroform/acetonitrile (1/1, v/v) to 2 mL and was vigorously shaken. After 10 min, the CD and UV spectra were measured in a 1 mm quartz cell using a spectropolarimeter with a thermostat.

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

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