Synthesis and Helicity Induction of Poly(phenylacetylene) Derivatives Bearing a Crown Cavity on the Main Chain

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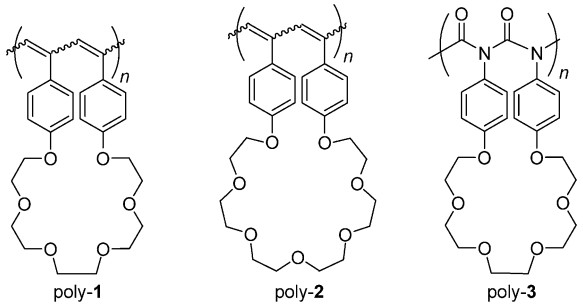
ABSTRACT: The cyclopolymerizations of α,ω-diacetylene monomers, 1,14-bis(4′-ethynylphenoxy)-3,6,9,-12-tetraoxatetradecane (**1**) and 1,17-bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane (**2**), were carried out in chloroform at a monomer concentration of 0.02 mol L^{-1} using $Rh(nbd)BPh_4$ as the catalyst to afford organic-solvent-soluble and gel-free polymers. The obtained polymers were assignable to poly(phenylacetylene) derivatives with crown ether on the main chain (poly-**1** and poly-**2**, respectively). In addition, the laser Raman spectra showed that both polymers possessed a highly cis−transoidal stereoregularity. The CD spectra of poly-**1** and poly-**2** in the presence of the perchloric acid salts of L-phenylglycine (L-Pgly·$HClO_4$) showed a characteristic induced CD (ICD) in the UV−vis absorption region of the polymer backbone from 290 to 530 nm, and the CD patterns of both polymers in the presence of D- and L-Pgly·$HClO_4$ were mirror images. Like other dynamic helical polymers, the amount of a guest, temperature, and solvent had significant influences on the induced helical structure.

Introduction

Most naturally occurring polymers such as a peptides,[1] polynucleotides,[2] and polysaccharides[3] are three-dimensionally controlled materials; in other words, these polymers consist of highly ordered structure motifs. External stimuli such as temperature, pH, and electronic potential make the bioactivity weak or sometimes inactive despite maintaining the primary structure. This means that the high-order structure control as well as the primary structure control of naturally occurring polymers is required for keeping the bioactivities, implying that the control of the highly ordered architecture is a key technique for controlling the properties of the polymer materials.

As one of the most commonly observed highly ordered structures, there exists the helical structure. The synthetic polymers with a well-defined helical conformation in the main chain, i.e., helical polymers, show characteristic features that are not observed in the usual optically active compounds, such as chiral small molecules and polymers with chiral side groups, and therefore a number of synthetic helical polymers have been designed and synthesized.[4] In particular, from the viewpoint of the synthesis of the helical polymers, macromolecular helicity induction driven by external stimuli provides us a facile strategy to artificially construct a helical structure.[4i,5] So far, for various types of polymers with specially designed binding sites, a one-handed screw sense was induced in the main chain through the interaction with small chiral molecules.

Chart 1. Structures of Poly-1, Poly-2, and Poly-3



These polymers exhibit a unique property on the basis of the kinds of the main chain structure and the kinds of the binding sites, e.g., the poly(phenylacetylene)s bearing crown ether pendants as the interaction site formed the one-handed helical structure that responded to the extremely small chirality of the guest molecule.[6] Hence, expanding the limit and scope of the macromolecular helicity induction system is always required. Recently, we developed a novel helicity induction system, that is, the helix formation for poly(phenyl isocyanate) bearing a crown cavity on the backbone (poly-**3** in Chart 1) driven by a host−guest complexation with a chiral guest.[7] In this system, the chiral structure of the guest was allowed to directly control the helical conformation in the macromolecular main chain through the asymmetric twist of the crown cavity based on the complex formation with the chiral guest. Except for this report, there has been no attempt to induce a one-handed helical structure into the polymer-bearing host on the backbone via host−guest complexation.

For crown ether chemistry, our continuous effort has led to the development of a synthetic strategy for producing the polymers with large-membered crown cavities as the cyclic repeating units via the cyclopolymerization of bifunctional monomers such as α,ω-divinyl ether,[8] α,ω-diepoxide,[9] α,ω-diepisulfide,[10] α,ω-

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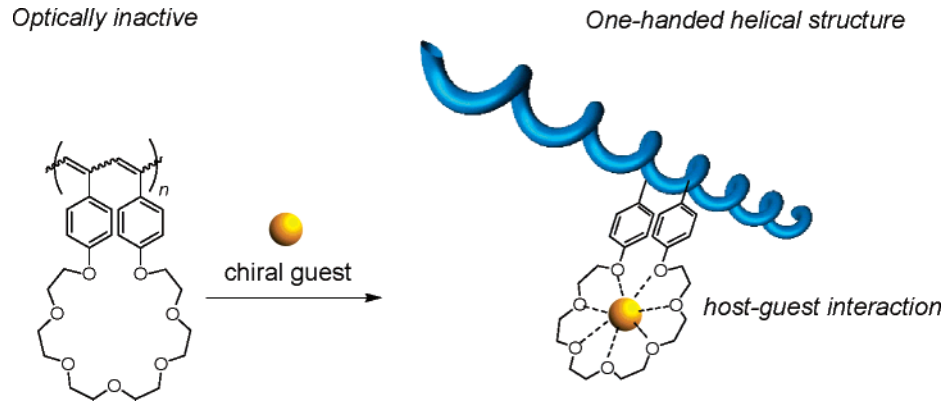


Figure 1. Schematic representation of macromolecular helicity induction.

Table 1. Cyclopolymerization Results of Monomer 1 and 2 with Rh(nbd)BPh$_4$[a]

run	monomer	[M] (mol L^{-1})	yield (%)	$M_n \times 10^{-4}$ [b]	M_w/M_n [b]
1	**1**	0.05	[c]		
2	**1**	0.04	86	2.7	7.6
3	**1**	0.02	87	6.3	3.7
4	**2**	0.02	73	1.7	3.0

[a] [M]/[I] = 100; time, 24 h; solvent, $CHCl_3$; temperature, 25 °C. [b] Determined by SEC in $CHCl_3$ using polystyrene standards. [c] Gelation occurred in 5 min.

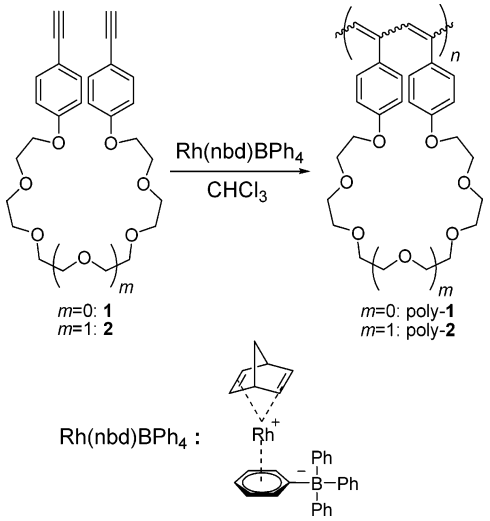
diisocyanate,[7] and α,ω-diacetylene,[11] which possess a guest-binding ability on the basis of the crown ether on the polymer backbone. Among these polymers, the poly(phenylacetylene)s with a crown cavity on the polymer backbone should be possible to be employed for the macromolecular helicity induction.

Therefore, we now present the design, synthesis, and helicity induction of poly(phenylacetylene)s with crown cavities on the polymer main chain (poly-**1** and poly-**2** in Chart 1), which possess a different crown cavity size (Figure 1). The poly(phenylacetylene) derivatives with a crown cavity on the polymer main chain (poly-**1** and poly-**2**) were synthesized via the cyclopolymerization of 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) and 1,17-bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane (**2**). Poly-**2** is a newly designed polymer for improving complexation ability, which is discussed in a later section. With respect to the microstructure of the resulting polymers, the extent of the cyclization and the stereoregularity were estimated by means of ^{1}H NMR and laser Raman analyses, respectively. Furthermore, the CD spectra of poly-**1** and poly-**2** in the presence of various perchloric acid salts of amino acids were measured under various conditions in order to investigate whether the one-handed helicity could be induced on the main chain.

Results and Discussion

Synthesis and Characterization of Poly(phenylacetylene) Derivatives Bearing a Crown Cavity on the Main Chain. The polymerizations of 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) and 1,17-bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane (**2**) were carried out in chloroform using Rh(nbd)BPh$_4$ as the catalyst (Scheme 1), and the polymerization results are listed in Table 1. The polymerization of **1** with the monomer concentration of 0.05 mol L^{-1} rapidly proceeded to give pale red gels (run 1). The polymerization of **1** with the monomer concentration of 0.04 mol

Scheme 1. Synthesis of Poly(phenylacetylene)s with Crown Cavity on the Main Chain



L^{-1} homogeneously proceeded to afford a gel-free polymer in high yield, while the polydispersity was relatively wide (run 2). For the monomer concentration of 0.02 mol L^{-1}, the polymerization of **1** was the most successfully accomplished to give a polymer with a relatively narrow molecular weight distribution and good solubility toward any organic solvents such as DMF, chloroform, and acetonitrile (run 3). Therefore, the polymerization of **2** was also carried out under this condition and proceeded without gelation to afford a polymer in high yield (run 4). Hence, bifunctional monomers **1** and **2** were successfully polymerized using Rh(nbd)BPh$_4$ as the catalyst.

The extent of the cyclization was an important factor for the host−guest complexation because only the cyclic monomeric units that were produced via a cyclopolymerization mechanism could be allowed to interact with the guest molecules; therefore, ^{1}H NMR measurements were performed on the obtained polymers. In the ^{1}H NMR spectra of both polymers, signals in the region from 5.6 to 5.9 ppm due to the main chain protons appeared (Figures 2 and 3). On the contrary, signals at 3.0 ppm due to the ethynyl protons completely disappeared. Thus, the polymerizations proceeded via the cyclopolymerization mechanism, and the extent of the cyclization was ca. 100%, i.e., the polymers synthesized from monomers **1** and **2** were assignable to the poly(phenylacetylene) derivatives bearing crown ether on the backbone (poly-**1** and poly-**2**, respectively). The ^{1}H NMR analyses also provide us with detailed information about the stereoreoregularity of polyacetylene deriva-

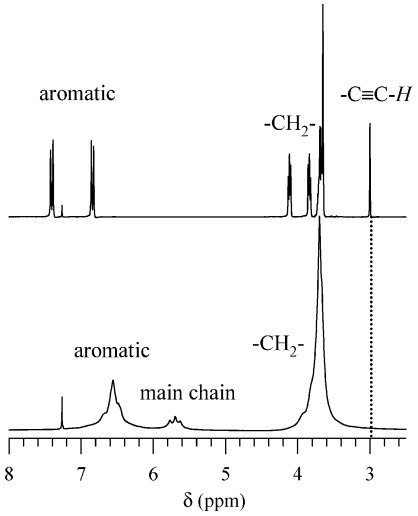


Figure 2. ^{1}H NMR spectra of **1** (upper) and poly-**1** (lower) in $CDCl_3$.

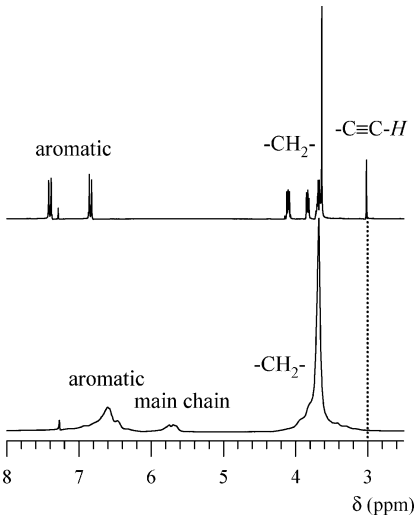


Figure 3. ^{1}H NMR spectra of **2** (upper) and poly-**2** (lower) in $CDCl_3$.

tives, which was an important element for the macromolecular helicity induction.[12] The ^{1}H NMR spectra of poly-**1** and poly-**2** showed broad signals due to the main chain protons observed in the range from 5.6 to 5.9 ppm corresponding to the cis structure.[13] However, no distinct signal due to the trans structure, which appeared at around 6.85 ppm, was observed.[14] To further clarify the stereoregurarity, we performed a laser Raman measurement, which was also utilized to determine the stereoregularity (Figure 4).[15] The laser Raman spectrum of poly-**1** showed characteristic peaks at 1543 cm^{-1}, 1338 cm^{-1}, and 963 cm^{-1} due to the cis structure, and at 1541 cm^{-1}, 1338 cm^{-1}, and 962 cm^{-1} for poly-**2**. In contrast, no clear peaks due to the trans structure were detected in both spectra. Therefore, it was confirmed that both poly-**1** and poly-**2** had highly cis−transoidal structures.

Macromolecular Helicity Induction. To investigate whether the one-handed helicity could be induced on the main chains of poly-**1** and poly-**2** via a host−guest interaction, CD measurements were carried out. The CD spectra of poly-**1** and poly-**2** were measured in the presence of the perchloric acid salt of L-phenylglycine (L-Pgly·$HClO_4$) and D-Pgly·$HClO_4$ as chiral guests (Figure 5). All CD spectra showed a clear induced CD (ICD) in the UV−vis absorption region of the polymer back-

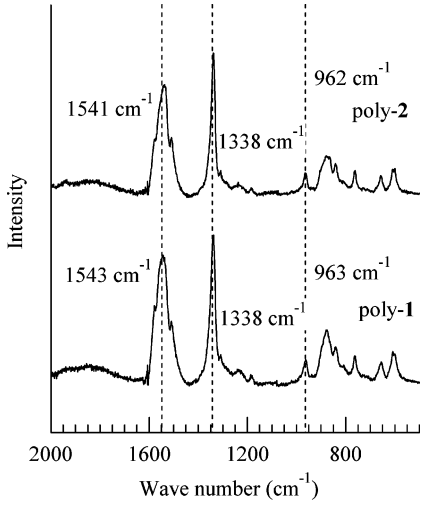


Figure 4. Laser Raman spectra of poly-**1** and poly-**2** in the solid state at room temperature.

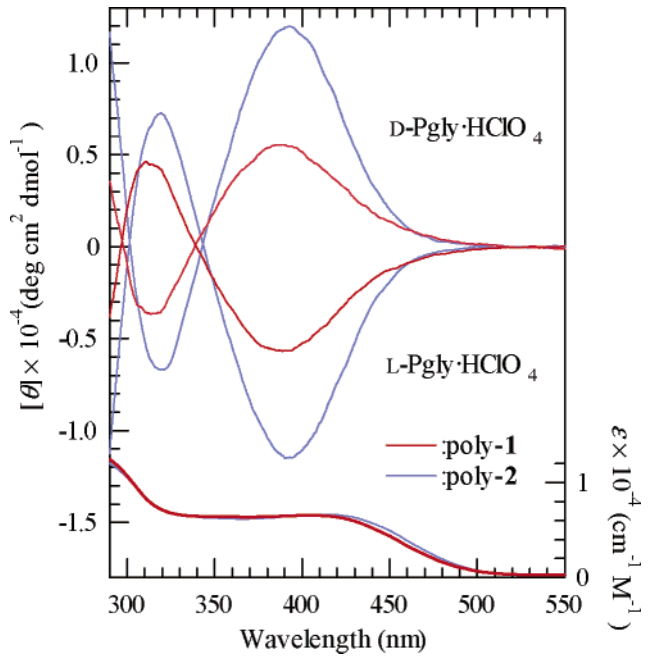


Figure 5. CD spectra of poly-**1** and poly-**2** in $CHCl_3$/acetonitrile = 1/1 at 25 °C ([monomeric units of poly-**1**] = 2.3 mmol L^{-1}, [monomeric units of poly-**2**] = 2.1 mmol L^{-1}, [D- and L-Pgly·$HClO_4$]/[monomeric units] = 15).

bones from 290 to 530 nm, and the CD spectra of both polymers with the D- and L-isomers were mirror images. These results indicated that both polymers formed a one-handed helical structure driven by the host−guest interaction with the chiral guest.

To investigate how the amount of a chiral guest affected the ICD intensity, CD titration experiments of poly-**1** and poly-**2** were performed with L-Pgly·$HClO_4$ as the chiral guest (Figure 6). The ICD intensities of poly-**1** and poly-**2** were saturated at 15 equiv of L-Pgly·$HClO_4$ relative to the monomeric units in the polymers. From our previous report, it was found that the ICD intensity of poly-**3** was saturated at 30 equiv of chiral guests. Thus, poly-**1** and poly-**2** had the ability to more tightly bind a guest molecule in comparison with that of poly-**3**.

For carrying out a detailed discussion about the binding property, we calculated the binding constants. On the basis of the Hill equation, the apparent binding

Table 2. Signs of Cotton Effects and [θ] Values of Poly-2 with Various Amino Acid Derivatives[a]

	first Cotton			second Cotton		
amino acid	sign	$[\theta]_{first} \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)	sign	$[\theta]_{second} \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)
L-phenylglycine	−	1.2	390	+	0.7	320
D-phenylglycine	+	1.2	393	−	0.7	319
L-leucine	−	1.5	390	+	1.2	320
D-leucine	+	1.5	387	−	1.2	320
L-phenylalanine	−	1.3	390	+	1.0	324
L-valine	−	0.9	387	+	0.7	321
L-methionine	−	1.4	389	+	1.1	319
D-4-hydroxyphenylglycine	+	1.4	393	−	0.9	318

[a] CD measurements of poly-**2** with various amino acids were performed in chloroform/acetonitrile (1/1, v/v) at 25 °C ([monomeric units of poly-**2**] = 2.1 mmol L^{-1} and [amino acids·$HClO_4$]/[monomeric units of poly-**2**] = 15).

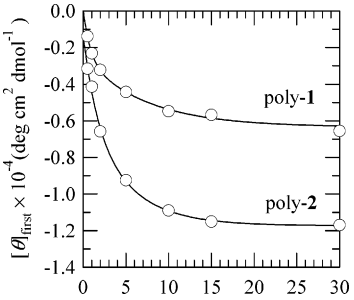


Figure 6. Titration curve of molar elipticity values for the first Cotton effect at 390 nm. CD measurements of poly-**1** and poly-**2** in the presence of L-Pgly·$HClO_4$ were performed in chloroform/acetonitrile (1/1, v/v) at 25 °C ([monomeric units in poly-**1**] = 2.3 mmol L^{-1}, [monomeric units in poly-**2**] = 2.1 mmol L^{-1}, and [L-Pgly·$HClO_4$]/[monomeric units] = 0.5 to ~30).

constants of poly-**1**, poly-**2**, and poly-**3** with L-Pgly·$HClO_4$ were calculated to be 2.2×10^2, 3.5×10^2, and 0.9×10^2, respectively.[16] In crown ether chemistry, the structure of the crown ether has an influence on the guest-binding ability.[17] In fact, the crown cavity on the main chain of poly-**1** had a stronger binding property than that of poly-**3**, though the monomeric units in both poly-**1** and poly-**3** had the same number of donating atoms, six oxygen atoms, and the same size of the cyclic structure, a 27-membered ring. Hence, the cyclic constitutional units in poly-**1** should orient in a suitable conformation for complexation with guest molecules more flexibly than that in poly-**3**. Furthermore, on the basis of the binding constants, it was found that poly-**2** bound L-Pgly·$HClO_4$ more tightly than poly-**1** due to the difference in the number of oxygen atoms, six for poly-**1** and seven for poly-**2**, which has also been known to affect the guest-binding property and guest selectivity.[17] Thus, the number of oxygen atoms and structure of the cyclic repeating units played an important role in the guest-encapsulation ability and the sensitivity in the helicity induction.

Hereafter, as further investigations on the macromolecular helicity induction, we focused on that for poly-**2**, which had the advantages of a higher ICD intensity and stronger guest-binding property over those of poly-**1**. First, we measured the CD spectra of poly-**2** with various guests, and the values of the first and second Cotton effects ($[\theta]_{first}$, $[\theta]_{second}$) are summarized in Table 2. Although the ICD intensity in the presence of every chiral guest was significantly different from each other, poly-**2** showed an intense Cotton effect in the range from 290 to 530 nm. Moreover, the signs of the Cotton effects were, as expected, dependent on the absolute configuration of the employed chiral guest molecules, i.e., minus for the L-isomer and plus for the D-isomer.

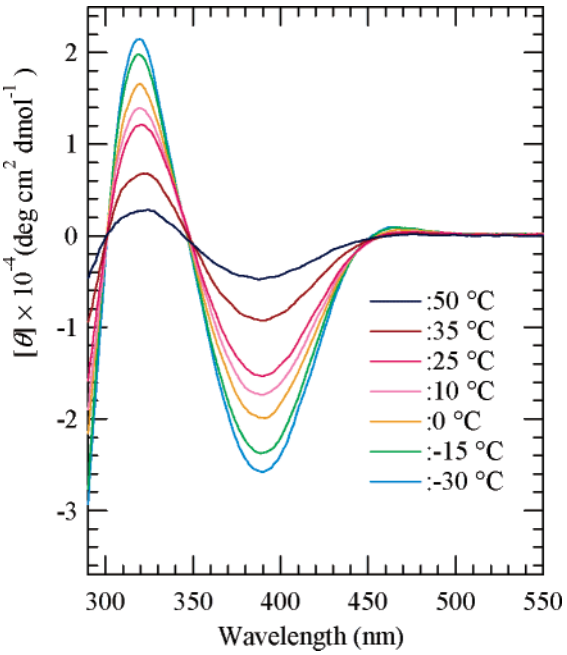


Figure 7. CD spectra of poly-**2** in $CHCl_3$/acetonitrile (1/1, v/v) in the temperature range from −30 to 50 °C ([monomeric units of poly-**2**] = 2.1 mmol L^{-1}, [L-Leu·$HClO_4$]/[monomeric units of poly-**2**] = 15).

We also investigated the effect of temperature, which is known to significantly affect the complexation ability and the formation of the helical structure.[18] The CD spectra of poly-**2** in the presence of L-Leu·$HClO_4$ were measured in the temperature range from −30 to 50 °C, as shown in Figure 7. It has been revealed that poly-**3** having a crown cavity on the main chain likewise scarcely changed in this temperature range. However, the ICD intensity of poly-**2** increased in accordance with the decreasing temperature like common dynamic helical polymers, suggesting that the macromolecular main chain in poly-**2** is more flexible than that in poly-**3**.

Moreover, the effect of solvent, whose polarity was also an important factor for the host−guest complexation[17] and the helical structure,[19] was investigated. The CD measurements were performed in chloroform/acetonitrile (1/1, v/v), acetonitrile, chloroform/methanol (1/1, v/v), and DMF with L-Leu·$HClO_4$ as the chiral guest (Figure 8). The intensity of the ICD increased in the order of DMF < chloroform/methanol (1/1, v/v) < acetonitrile < chloroform/acetonitrile (1/1, v/v), i.e., the intensity of the ICD increased according to the decreasing solvent polarity. In particular, no clear Cotton effect was observed for the measurement in DMF, in which the solvation of the guest molecules predominantly took

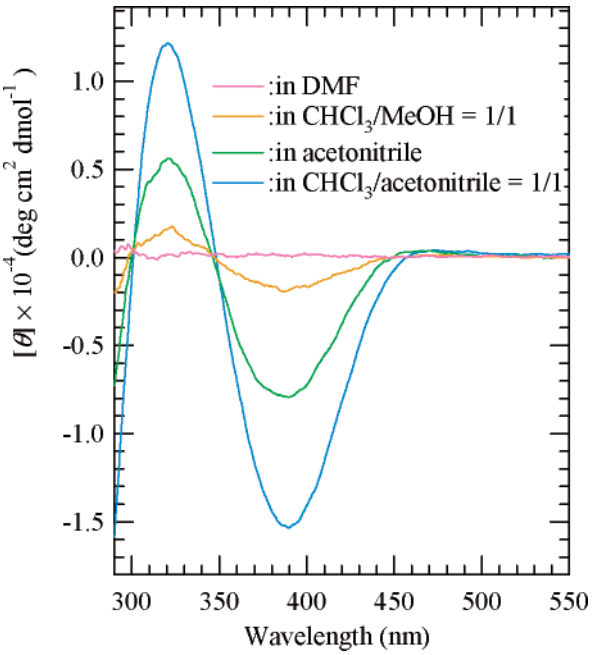


Figure 8. CD spectra of poly-**2** at 25 °C in DMF, $CHCl_3$/MeOH (1/1, v/v), CH_3CN, and $CHCl_3$/CH_3CN (1/1, v/v) ([monomeric units of poly-**2**] = 2.1 mmol L^{-1}, [L-Leu·$HClO_4$]/[monomeric of poly-**2**] = 15).

place in comparison with the host−guest interaction. Therefore, it was confirmed that the crown cavity on the main chain of poly(phenylacetylene) acted as a binding site and one-handed helicity was induced on the backbone triggered by the host−guest interaction.

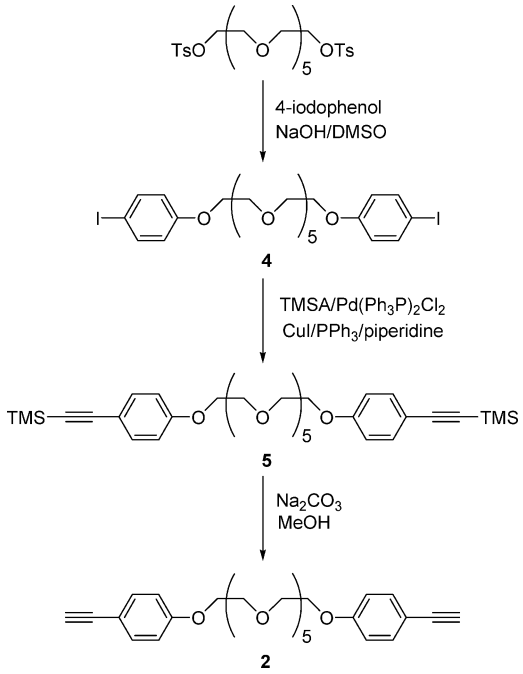
Conclusions

The cyclopolymerizations of 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) and 1,17-bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane (**2**) homogeneously proceeded to afford solvent-soluble and gel-free polymers in high yield. The obtained polymers perfectly consisted of large-membered crown ethers as repeating units, and they were therefore assigned as poly-**1** and poly-**2**, respectively. The stereoregularity of both polymers was determined to be highly cis−transoidal by means of the laser Raman analysis. The CD spectra of poly-**1** and poly-**2** in the presence of chiral guests showed characteristic ICDs, and the sign of the CD spectra depended on the absolute configuration of the guests, indicating that a one-handed helicity was induced on the main chain through the host−guest interaction of the polymers with chiral guests. This report is the first demonstration of a macromolecular helicity induction in poly(phenylacetylene) triggered by the host−guest interaction of the crown cavity on the polymer main chain with a chiral guest. Thus, crown ether on the polymer main chain as well as that on the polymer pendant generally acts as the facile binding site for macromolecular helicity induction, having nothing to do with the kind of polymer main chain or crown ether structure.

Experimental Section

Materials. L-Phenylalanine (L-Phe, >99.9% ee), L-leucine (L-Leu, >99.9% ee), and D-leucine (D-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 Chemicals Co., Ltd. (Tokyo, Japan).

Scheme 2. Synthesis of Monomer 2



The perchloric acid ($HClO_4$) salts of these amino acids were prepared according to a previous report.[20] Dry chloroform (purity >99.5%, water content <0.005 vol %), dry acetonitrile (purity >99.5%, water content <0.005 vol %), chloroform for the spectroscopy (>99.0%), *N*,*N*-dimethylformamide for the spectroscopy (purity >99.7%, water content <0.1%), and methanol for the spectroscopy (>99.7%) were obtained from the Kanto Chemicals Co., Ltd., and used without further purification. Piperidine (>98.0%) was purchased from the Kanto Chemicals Co., Ltd. and used after distillation over CaH_2. Triphenylphosphine was available from Kanto Chemicals Co., Ltd. and used after recrystallization from dichloromethane/diethyl ether. (Trimethylsilyl)acetylene was kindly supplied from the Shinetsu Chemical Co., Ltd. (Tokyo, Japan). 4-Iodophenol was obtained from the Junsei Chemicals Co., Ltd. (Tokyo, Japan) and was used without any further purification. Hexaethylene glycol di(*p*-toluenesulfonate) was synthesized by a previously reported method.[21] Bis(triphenylphosphine)paradium (II) dichloride was purchased from the Aldrich Chemicals Co., Inc. (Milwaukee, WI) and used as received. Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh_4) was prepared in accordance with a previous report.[22] 1,14-Bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane (**1**) was synthesized by a previously reported method.[11a]

Instruments. The ^1H and ^{13}C NMR spectra were recorded using JEOL JNM-EX270 and JEOL JNM-A400II instruments. The laser Raman spectra were recorded using a JASCO NRS-1000. The size exclusion chromatography (SEC) was performed at 40 °C in chloroform (0.8 mL min^{-1}) using a Jasco GPC-900 system 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. Circular dichroism (CD) spectra were measured in a 1 mm path length using a JASCO J-720 spectropolarimeter. 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.

Synthesis of 1,17-Bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane (2). The syntheses of the diacetylene monomer **2** and intermediary compounds are outlined in Scheme 2. The detailed procedure is as follows.

Synthesis of 1,17-Bis(4′-iodophenoxy)-3,6,9,12,15-pentaoxaheptadecane (4). To a stirred mixture of 4-iodophenol (40 g, 0.18 mol) and sodium hydroxide (8.9 g, 0.22 mol) in DMSO (100 mL) was added a saturated solution of hexaethylene glycol di(*p*-toluenesulfonate) (49 g, 83 mmol) in DMSO, and the reaction mixture was kept at 90 °C for 8 h. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (1000 mL), and the solution was washed with a 2 N NaOH aqueous solution (3 × 500 mL) and water (3 × 500 mL) until the organic layer became neutral. The extracts were dried using anhydrous Na_2SO_4, filtered, and evaporated. The residue was recrystallized from toluene−ether (1/9, v/v) to give **4** as a pale yellow solid. Yield: 48 g (84%). ^{1}H NMR ($CDCl_3$): δ 3.64−3.71 (m, 16H, $-CH_2-$), 3.82−3.85 (m, 4H, Ar−OCH_2CH_2-), 4.06−4.10 (m, 4H, Ar−OCH_2CH_2-), 6.69 (d, J = 8.91 Hz, 4H, aromatic), 7.54 (d, J = 8.91, 4H, aromatic). ^{13}C NMR ($CDCl_3$): δ 67.50 ($-CH_2-$), 69.57 ($-CH_2-$), 70.56 ($-CH_2-$), 70.60 ($-CH_2-$), 70.82 ($-CH_2-$), 82.90 (aromatic), 117.01 (aromatic), 138.14 (aromatic), 158.64 (aromatic). Anal. Calcd for $C_{24}H_{32}I_2O_7$ (686.32): C, 42.00; H, 4.70; I, 36.98. Found: C, 42.05; H, 4.73; I, 37.07. Mp: 59−61 °C.

Synthesis of 1,17-Bis[4′-((trimethylsilyl)ethynyl)phenoxy]-3,6,9,12,15-pentaoxaheptadecane (5). To a mixture of **4** (4.5 g, 6.1 mmol), triphenylphosphine (0.17 g, 0.66 mmol), bis(triphenylphosphine)paradium (II) dichloride (0.19 g, 0.27 mmol), and copper (I) iodide (0.039 g, 0.20 mmol) in piperidine (50 mL) was added (trimethylsilyl)acetylene (5 mL) under a nitrogen atmosphere. After stirring at 50 °C for 16 h, the reaction mixture was filtered and evaporated. The residue was treated with water (100 mL) and extracted with chloroform (3 × 100 mL). After the extract was dried over anhydrous $MgSO_4$, the solvent was evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (8/2, v/v) to give **5** as a pale yellow syrup. Yield: 2.1 g (56%). ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 18H, $-SiCH_3$), 3.64−3.69 (m, 16H, $-CH_2-$), 3.81−3.85 (m, 4H, Ar−OCH_2CH_2-), 4.09−4.12 (m, 4H, Ar−OCH_2CH_2-), 6.82 (d, J = 8.58 Hz, 4H, aromatic), 7.39 (d, J = 8.58, 4H, aromatic). ^{13}C NMR ($CDCl_3$): δ −0.01 ($-SiCH_3$), 67.32 ($-CH_2-$), 69.51 ($-CH_2-$), 70.49 ($-CH_2-$), 70.52 ($-CH_2-$), 70.76 ($-CH_2-$), 92.37 (−Ar−C≡*C*−), 105.08 (−Ar−*C*≡C−), 114.34 (aromatic), 115.28 (aromatic), 133.33 (aromatic), 158.85 (aromatic). Anal. Calcd for $C_{34}H_{50}Si_2O_7$ (626.93): C, 65.14; H, 8.04. Found: C, 65.29; H, 8.01.

Synthesis of 2. To a solution of **5** (2.1 g, 3.3 mmol) in methanol (25 mL) and tetrahydrofuran (25 mL) was added Na_2CO_3 (1.3 g, 12 mmol). After stirring at room temperature for 3.5 h, the reaction mixture was filtered, and the solvent was removed under vacuum. The residue was treated with water (50 mL) and extracted with chloroform (3 × 50 mL), and the extracts were dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (8/2, v/v) to give **2** as a viscous liquid. Yield: 1.4 g (88%). ^{1}H NMR ($CDCl_3$): δ 3.02 (s, C≡C−H), 3.64−3.73 (m, 16H, $-CH_2-$), 3.81−3.85 (m, 4H, Ar−OCH_2CH_2-), 4.07−4.15 (m, 4H, Ar−OCH_2CH_2-), 6.84 (d, J = 8.91 Hz, 4H, aromatic), 7.42 (d, J = 8.82 Hz, 4H, aromatic). ^{13}C NMR ($CDCl_3$): δ 67.26 ($-CH_2-$), 69.41 ($-CH_2-$), 70.40 ($-CH_2-$), 70.43 ($-CH_2-$), 70.67 ($-CH_2-$), 75.83 (−Ar−C≡*C*−H), 83.46 (−Ar−*C*≡C−H), 114.11 (aromatic), 114.40 (aromatic), 133.78 (aromatic), 158.96 (aromatic). Anal. Calcd for $C_{28}H_{34}O_7$ (482.57): C, 69.69; H, 7.10. Found: C, 69.52; H, 7.15.

Polymerization. The polymerizations of **1** and **2** were carried out in a dry flask under an argon atmosphere. An example of the procedure is described. In a glovebox (under moisture- and oxygen-free argon atmosphere, H_2O, O_2 <1 ppm), Rh(nbd)BPh_4 (3.2 mg, 6.2 μmol) was weighed into a flask and dissolved in dry chloroform (29 mL). To the solution was added a solution of **2** in dry chloroform (0.29 mmol L^{-1}, 2.1 mL). After stirring at 25 °C for 24 h, to the reaction mixture was added triphenylphosphine (9.8 mg, 37μmol). The solution was filtered and then poured into a large amount of diethyl ether. The precipitate was purified by reprecipitation with chloroform/diethyl ether and then dried under reduced pressure to give poly-**2** as a yellow powder. Yield: 0.22 g (73%). $M_n = 1.8 \times 10^4$, $M_w/M_n = 3.0$. ^{1}H NMR ($CDCl_3$): δ 3.36−4.02 (br, 24H, $-CH_2-$), 5.62−5.80 (br, 2H, vinyl), 6.37−7.00 (br, 8H, Ar). ^{13}C NMR ($CDCl_3$): δ 66.91−71.36 (m, $-CH_2-$), 113.65, 126.20−142.04, 157.80.

CD Measurements. The concentrations of poly-**1** and poly-**2** were 2.3 mmol L^{-1} and 2.1 mmol L^{-1}, respectively, for all measurements, which were calculated on the basis of the monomeric units. The molar ratio of the chiral guests to the monomeric units in poly-**1** and poly-**2** was 15 except for the titration experiment. A typical procedure is described below: A stock solution of poly-**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·$HClO_4$ (16 mg, 0.06 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.

Determination of Binding Constants (K_s) on the Basis of Hill Analysis. For calculating the apparent binding constant (K_s), we used the Hill equation, $\log(Y/(1-Y)) = n\log[G] + n\log(K_s)$, where Y, n, and [G] are the fractional saturation, the Hill coefficient, and the concentration of the guest, respectively.[16]

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