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Helicity Induction in a Poly(phenylacetylene) Bearing Aza-18-crown-6 Ether Pendants with Optically Active Bis(amino acid)s and Its Chiral Stimuli-Responsive Gelation

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ABSTRACT: A stereoregular poly(phenylacetylene) bearing the aza-18-crown-6 ether as the pendant (poly-**1**) formed a predominantly one-handed helical conformation upon complexation with optically active bis(amino acid)s such as L-homocystine perchlorate (L-**2**) in acetonitrile, and the complex solution gradually gelled with time. The gel exhibited an induced circular dichroism (ICD) in the polymer backbone region, but the absolute value of the ICD intensity decreased with an increase in temperature and the gel gradually shrunk before melting at 55 °C. This gel−sol transition was irreversible, but once the solution was annealed at 60 °C and then rapidly cooled to 0 °C, the formation of the gel occurred again at ambient temperature. The poly-**1**−L-**2** gel shrunk in response to external stimuli such as the addition of a poor solvent. The effect of the enantiomeric excess (ee) of **2** on the helicity induction in the poly-**1** and its gelation was also investigated. In the presence of 60% ee of **2**, poly-**1** showed an intense CD like that of 100% ee. The gelation took place when the ee of **2** was greater than 60%. The helicity induction in poly-**1** and its gelation behavior were also investigated with other optically active bis(amino acid)s and achiral diamines.

Introduction

Crown ethers are the first artificial host molecules which can form complexes with a variety of metal cations and ammoniums through electrostatic ionic and dipole−dipole interactions as well as via hydrogen bonding when the cations fit the cavity inside the cyclic crown ether units.[1] This peculiar property has attracted great attention, and a number of chiral and achiral crown ethers have been prepared for use as synthetic receptors for target chiral or achiral guest molecules.[2] Polymers containing crown ethers as the pendant or main chain were also prepared, but because of the difficulty in the synthesis, only a few chiral crown ether-based polymers have been prepared.[3]

In earlier studies, we reported that optically inactive, stereoregular poly(phenylacetylene)s bearing various functional groups such as carboxy,[4] amino,[5] boronate,[6] and phosphonate groups[7] formed a predominantly one-handed helical conformation upon complexation with optically active compounds capable of interacting with the functional groups of the polymers. The complexes exhibited a characteristic induced circular dichroism (ICD) in the polyene backbone region.[8] This one-handed helicity induction concept in dynamic helical polyacetylenes allowed us to design and synthesize related stereoregular polyacetylenes with a high sensitivity to the amino acid chirality.[9] For instance, a poly(phenylacetylene) derivative bearing the aza-18-crown-6 ether pendants (poly-**1**) (Scheme 1) formed a one-handed helix upon complexation with free L-amino acids and various chiral amino alcohols in organic solvents[9a] as well as in water.[9b] The complex exhibited intense and characteristic ICDs. The Cotton effect signs corresponding to the helical sense of the polymer can be used as a sensitive probe for the chirality assignments of amino acids and amino alcohols, since all the common 19 L-amino acids produced the same Cotton effect sign in organic solvents.[9a] We anticipated that poly-**1** could also form a dynamically induced helix in the presence of chiral bis(amino acid)s with two amino groups such as homocystine (**2**), cystine (**3**), cystathionine (**4**), and glutathione disulfide (**5**) (Chart 1),[10] thus resulting in the formation of a supramolecular organogel through noncovalent bonding interactions between the pendant's crown ethers of the intermolecular polymer chains and the bis(amino acid)s (Scheme 1).

In this study, we prepared a gel of the single-handed helical poly-**1** with optically active bis(amino acid)s as the helix-inducer and cross-linker and investigated the property of the obtained gel using CD, UV−vis, and NMR spectroscopies. The effects of the structure and enantiomeric excess (ee) of the bis(amino acid)s and temperature on the helicity induction and gelation of poly-**1** were also investigated.

Experimental Section

Materials. Cis−transoidal, stereoregular poly-**1** was synthesized according to the previously reported method.[9a] The number-average molecular weight (M_n) and its distribution were 24.2×10^4 and 3.2, respectively, as determined by size exclusion chromatography (SEC) with tetrahydrofuran (THF) containing 0.1 wt % tetra-*n*-butylammonium bromide as the eluent. Dry CH_3CN (water content < 0.005 vol %), aqueous perchloric acid solution (60 wt %), and 1,6-diaminohexane (**8**) were purchased from Kanto Kagaku (Tokyo, Japan). L-Homocystine (L-**2**) and D-cystine (D-**3**) were purchased from Wako (Osaka, Japan). DL-Homocystine (*rac*-**2**), 1,2-bis(2-aminoethoxy)ethane (**7**), and diethylene glycol bis(3-aminopropyl)ether (**12**) were obtained from Tokyo Kasei (TCI, Tokyo, Japan). 1,8-Diaminooctane (**6**) and 1,10-diaminodecane (**11**) were from Acros Organics. Other chiral and achiral compounds including L-**3**, *rac*-**3**, L-**4**, L-**5**, and L-methionine (L-Met) were available from Aldrich (Milwaukee, WI). Cystamine (**9**) was prepared

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Scheme 1. Schematic Representation of the Macromolecular Helicity Induction on Poly-1 upon Complexation with Optically Active Bis(amino acid)s and the Gelation by Cross-Linking between the Crown Ether Pendants with Optically Active Bis(amino acid)s as a Noncovalent Cross-Linker

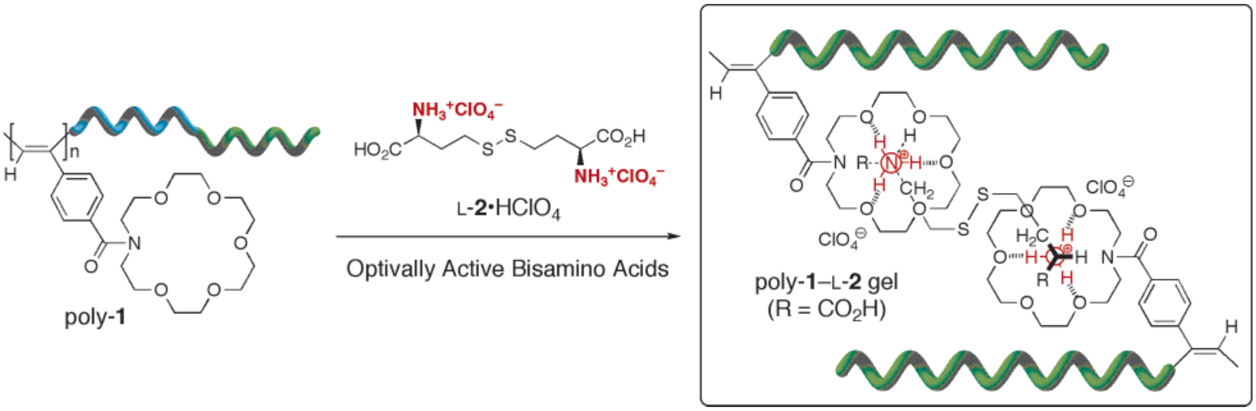
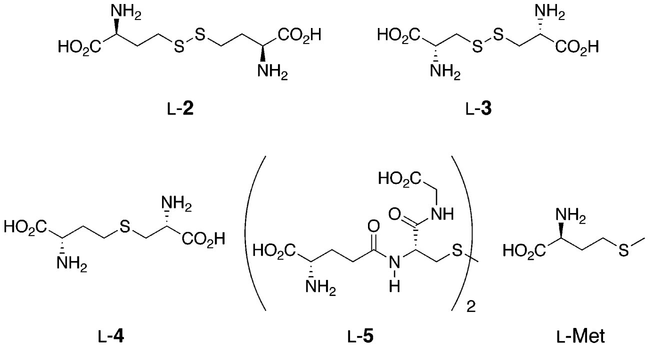


Chart 1. Structures of Optically Active Bis(amino acid)s and L-Methionine (L-Met)



by neutralization of cystamine dihydrochloride (Aldrich) with Na$_2$CO$_3$ in CHCl$_3$ containing a small amount of water.

Instruments. Absorption and CD spectra were measured in a 1.0 mm quartz cell on a Jasco V-570 spectrophotometer (Jasco, Hachioji, Japan) and a Jasco J-820 spectropolarimeter, respectively. The temperature was controlled with a Jasco PTC-423L apparatus. NMR spectra were measured on a Varian Mercury 300 (300 MHz for ^{1}H) spectrometer in CD$_3$CN (99 atom % D, Acros Organics) with a solvent residual peak as the internal standard. SEC measurements were performed with a Jasco PU-980 liquid chromatograph equipped with a UV (254 nm; Jasco UV-970) detector. A Tosoh (Tokyo, Japan) TSKgel Multipore H$_{XL}$-M SEC column (30 cm) was connected, and THF containing 0.1 wt % tetra-*n*-butylammonium bromide was used as the eluent at a flow rate of 0.5 mL/min. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh).

CD Measurements. A typical experimental procedure is described below. Dry CH$_3$CN was used through the course of absorption and CD measurements. Stock solutions of poly-**1** (2 mg/mL, 5.1 mM monomer units) in CH$_3$CN and L-**2** (10.2 mM) in CH$_3$CN containing 0.6 vol % aqueous HClO$_4$ ([HClO$_4$]/[L-**2**] = 2.2 (mol/mol)) were prepared. A 0.50 mL aliquot of the stock solution of poly-**1** was transferred to a vessel equipped with a screwcap using a micropipet (Sibata, Tokyo, Japan). To this was slowly added a 0.50 mL aliquot of the stock solution of L-**2** with stirring, and the CD and absorption spectra were then measured. In the same way, CD and absorption spectra of poly-**1** with other amino acids were measured.

CD Titrations. Stock solutions of L-**2** (0.051−12.8 mM) in CH$_3$CN containing 0.6 vol % aqueous HClO$_4$ ([HClO$_4$]/[L-**2**] = 2.2 (mol/mol)) were prepared in 13 1 mL flasks equipped with stopcocks. A stock solution of poly-**1** (10 mg/5 mL, 5.1 mM monomer units) in CH$_3$CN was also prepared in a 5 mL flask equipped with a stopcock. The 0.50 mL aliquots of the poly-**1** stock solution were transferred to 13 vessels equipped with screwcaps. To these vessels were slowly added 0.50 mL aliquots of the 13 stock solutions of L-**2** with stirring, so as to keep the poly-**1** concentration and the molar ratio of L-**2** to the monomer units of poly-**1** to be 1.0 mg/mL and 0.01, 0.02, 0.03, 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 2, and 2.5, respectively. The absorption and CD spectra were then taken for each sample immediately after the preparation of the solutions.

Nonlinear Effects. A stock solution of poly-**1** (10 mg/5 mL, 5.1 mM monomer units) in CH$_3$CN was prepared. Stock solutions of L-**2** (7.0 mg/mL, 26 mM) and *rac*-**2** (7.0 mg/mL, 26 mM) in CH$_3$CN containing 34 μL of 5 N HClO$_4$ ([HClO$_4$]/[**2**] = 2.2 (mol/mol)) were also prepared. Aliquots of the stock solutions of L- and *rac*-**2** were placed into five 1 mL flasks equipped with stopcocks so that the percent ee of **2** (L-rich) was 10, 20, 40, 60, and 80. The solutions were then diluted with water and CH$_3$CN to keep the concentration of **2** at 10.2 mM and the volumetric ratio of water to CH$_3$CN at 99.4/0.6 (v/v). The 0.50 mL aliquots of the poly-**1** stock solution were transferred to five vessels with screwcaps. To these vessels were slowly added 0.50 mL aliquots of the five stock solutions of **2** with different ee, and the absorption and CD spectra were then measured for each sample. The same procedure was performed in the experiments with **3**.

Shrinking Ratio Measurements of Gels. The shrinking ratio of gels was calculated using the following equation: [shrinking ratio] = V/V_0, where V_0 and V represent the volumes of the gel before and after heating, respectively. A typical experimental procedure is described below. Stock solutions of poly-**1** (4 mg/2 mL, 5.1 mM monomer units) in CH$_3$CN and L-**2** (10.7 mM) in CH$_3$CN containing 0.6 vol % aqueous HClO$_4$ ([HClO$_4$]/[L-**2**] = 2.2 (mol/mol)) were prepared. A 0.50 mL aliquot of the stock solution of poly-**1** was transferred to a vessel equipped with a screwcap. To this was slowly added 0.50 mL of the L-**2** stock solution with stirring, and a 0.50 mL aliquot of the resulting solution of the poly-**1**−L-**2** complex ([poly-**1**] = 1.0 mg/mL, [L-**2**]/[poly-**1**] = 2.1) was immediately transferred to a 1.0 mm quartz cell. The gelation took place within 10 min. The gel was then heated at appropriate temperatures (25−55 °C), and the volume of the released solvent upon gel shrinkage was measured using a 250 μL Hamilton microsyringe to estimate the volume V. The shrinking ratio measurements were repeated three times under the same experimental conditions, and the mean and standard deviations were then calculated.

In a similar manner, the shrinking ratio measurements of the poly-**1**−L-**2** gel ([poly-**1**] = 1.0 mg/mL, [L-**2**]/[poly-**1**] = 2) in the presence of increasing volume of toluene were also performed, and the changes in the volume of the gel were estimated.

Scanning Electron Microscopy (SEM) Measurements. The poly-**1**−L-**2** gel ([poly-**1**] = 1.0 mg/mL, [L-**2**]/[poly-**1**] = 2) in CH$_3$CN containing 0.3 vol % aqueous HClO$_4$ ([HClO$_4$]/[L-**2**] = 2.2 (mol/mol)) was prepared in the same way, and to this was added toluene (CH$_3$CN/toluene = 50/50 (v/v)). The shrunken

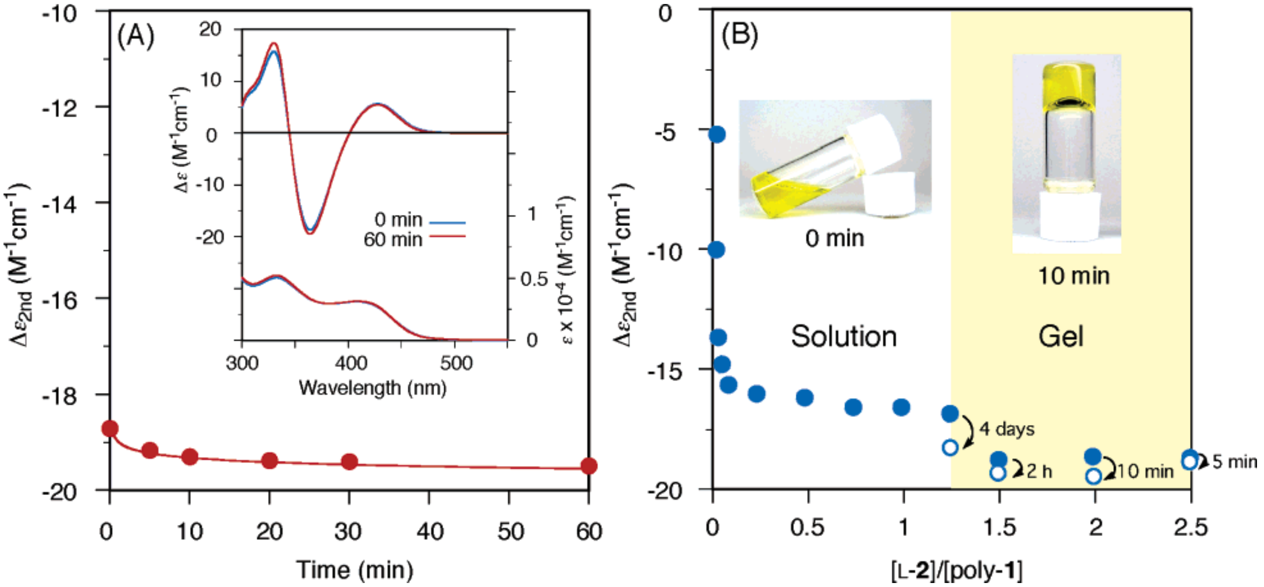


Figure 1. (A) Plots of ICD intensity of the second Cotton effect ($\Delta\epsilon_{2nd}$) in the complexation of poly-**1** (1.0 mg/mL) with L-**2** ([L-**2**]/[poly-**1**] = 2.0) against time in CH_3CN containing 0.3 vol % aqueous $HClO_4$ ([$HClO_4$]/[L-**2**] = 2.2) at 25 °C. Inset shows CD and absorption spectra of the poly-**1**−L-**2** complex after the sample had been allowed to stand for 0 and 60 min. (B) Plots of $\Delta\epsilon_{2nd}$ (blue ●) for poly-**1** (1.0 mg/mL) vs the concentration of L-**2** in CH_3CN containing 0.3 vol % aqueous $HClO_4$ ([$HClO_4$]/[L-**2**] = 2.2) at 25 °C. The changes of $\Delta\epsilon_{2nd}$ value with time after gelation are also shown (blue O). Inset shows the photographs of the poly-**1**−L-**2** complex ([L-**2**]/[poly-**1**] = 2.0) before (0 min) and after gelation (10 min).

gel was taken out and allowed to stand for 3 h under air and dried in vacuo for 12 h. The obtained dry gel was then sputter-coated with gold under an electric current of 20 mA at 8 Pa for 200 s before SEM measurements with a JEOL JSM-5600 instrument.

Results and Discussion

Figure 1A (inset) shows typical ICDs in the poly-**1** backbone region in the presence of 2.0 equiv of L-**2** in CH_3CN containing 0.3 vol % aqueous $HClO_4$. The absolute value of ICD intensity slightly increased with time and reached an almost constant value after 10 min at ambient temperature (22−25 °C) (Figure 1A). The absorption and ICD patterns are almost the same as those of the helical poly-**1** induced by free neutral L-amino acids such as L-alanine and L-methionine (L-Met) under the same conditions.[9a] Interestingly, the solution of the poly-**1**−L-**2** complex became a viscous liquid and subsequently gelled after 10 min (Figure 1B, inset). These results indicate that poly-**1** forms a predominantly one-handed helix upon complexation with the bis(amino acid) L-**2**, two ammonium groups of which also serve as a cross-linker between the intermolecular pendant crown ether units of poly-**1**s, resulting in the organogel. The CD titration using L-**2** showed that the absolute value of ICD intensity of the second Cotton effect ($\Delta\epsilon_{2nd}$) increased with the increasing concentration of L-**2** and reached an almost constant value at 0.3−1 equiv of L-**2** before gelation (Figure 1B). However, the absolute $\Delta\epsilon_{2nd}$ value further increased with an increase in the concentration of L-**2** ([L-**2**]/[poly-**1**] ≥ 1.5). The complex solution formed a gel in the presence of L-**2** greater than 1.25 equiv,[11] although the time required for the gelation (from 4 days to 5 min) was dependent on the concentration of L-**2** as shown in Figure 1B. During the gelation process, the intermolecular cross-linking through noncovalent bonding between the two ammonium groups of L-**2** and the crown ether pendants plays a crucial role. Intramolecular cross-linking contributes to the helicity induction in poly-**1** but cannot produce a gel. On the basis of these considerations, a further increase in the absolute $\Delta\epsilon_{2nd}$ value at [L-**2**]/[poly-**1**] ≥ 1.25 may be ascribed to the preferential formation of the intermolecular complexation (cross-linking), which may stabilize the helical conformation of poly-**1** induced by L-**2**.[12]

The thermal stability of the poly-**1**−L-**2** gel in CH_3CN containing 0.3 vol % aqueous $HClO_4$ was then measured by monitoring the decrease in the absolute $\Delta\epsilon_{2nd}$ value in the polymer backbone region at different temperatures, and the results were compared with those of the poly-**1**−L-Met complex (Figure 2A and Figure S-1 in the Supporting Information). Upon increasing the temperature, the absolute $\Delta\epsilon_{2nd}$ value of the gel ([L-**2**]/[poly-**1**] = 2.0) monotonically decreased, and the gel dissolved at 55 °C (a in Figure 2A). Cooling the solution, the absolute $\Delta\epsilon_{2nd}$ value increased but did not revert to the original value at 25 °C, and the solution did not gelate again. The first gel−sol transition was irreversible, but the further changes in the CD intensity of the solution of the poly-**1**−L-**2** complex reversibly occurred in the temperature range of 25−55 °C. Presumably, the intramolecular complexation preferentially took place rather than the intermolecular complexation (cross-linking) once the complete dissolution of the gel occurred at high temperature, as schematically illustrated in A and B in Figure 3. The ICD intensity changes in the poly-**1**−L-Met complex were then measured in the same solvent mixture (Figure S-1 in the Supporting Information). The poly-**1**−L-Met complex exhibited a smaller $\Delta\epsilon_{2nd}$ value at 25 °C than that of the poly-**1**−L-**2** gel even in the presence of the same amino acid residues, and the absolute value of ICD intensity decreased more steeply upon heating than the poly-**1**−L-**2** gel. These results also suggest that a helical conformation of poly-**1** induced by L-**2** may be stabilized by the inter- and intramolecular complexations (cross-linking).

The measurements of changes in the ^1H NMR spectra during the gelation of the poly-**1**−L-**2** complex ([L-**2**]/[poly-**1**] = 1.5) in CD_3CN containing 0.3 vol % aqueous $HClO_4$ with time and the subsequent gel−sol transition

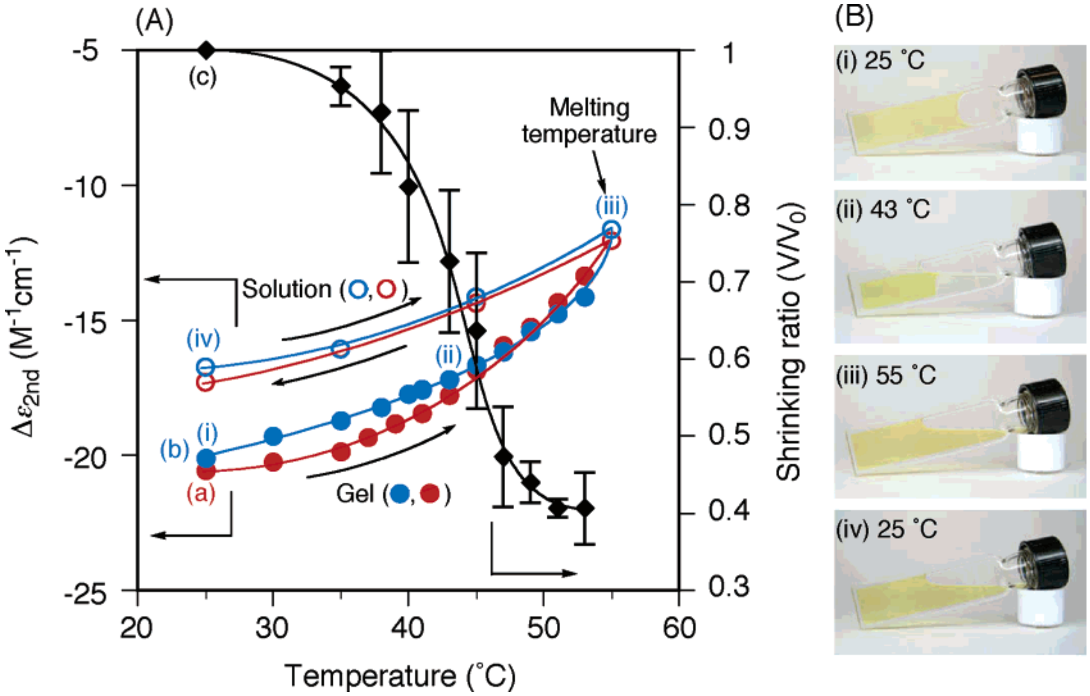


Figure 2. (A) Temperature dependence of the $\Delta\epsilon_{2nd}$ value ([L-**2**]/[poly-**1**] = 2.0 (a, red ● and ○) and 2.1 (b, blue ● and ○), [poly-**1**] = 1.0 mg/mL) and shrinking ratio (c, ◆) of the poly-**1**−L-**2** gel ([L-**2**]/[poly-**1**] = 2.1) in CH_3CN containing 0.3 vol % aqueous $HClO_4$ ([$HClO_4$]/[L-**2**] = 2.2). The error bars represent the standard deviation estimated by three measurements of shrinking ratio. (B) Photographs of a gel ([L-**2**]/[poly-**1**] = 2.1) after heating at 25 (i), 43 (ii), and 55 °C (iii) and then cooling to 25 °C (iv).

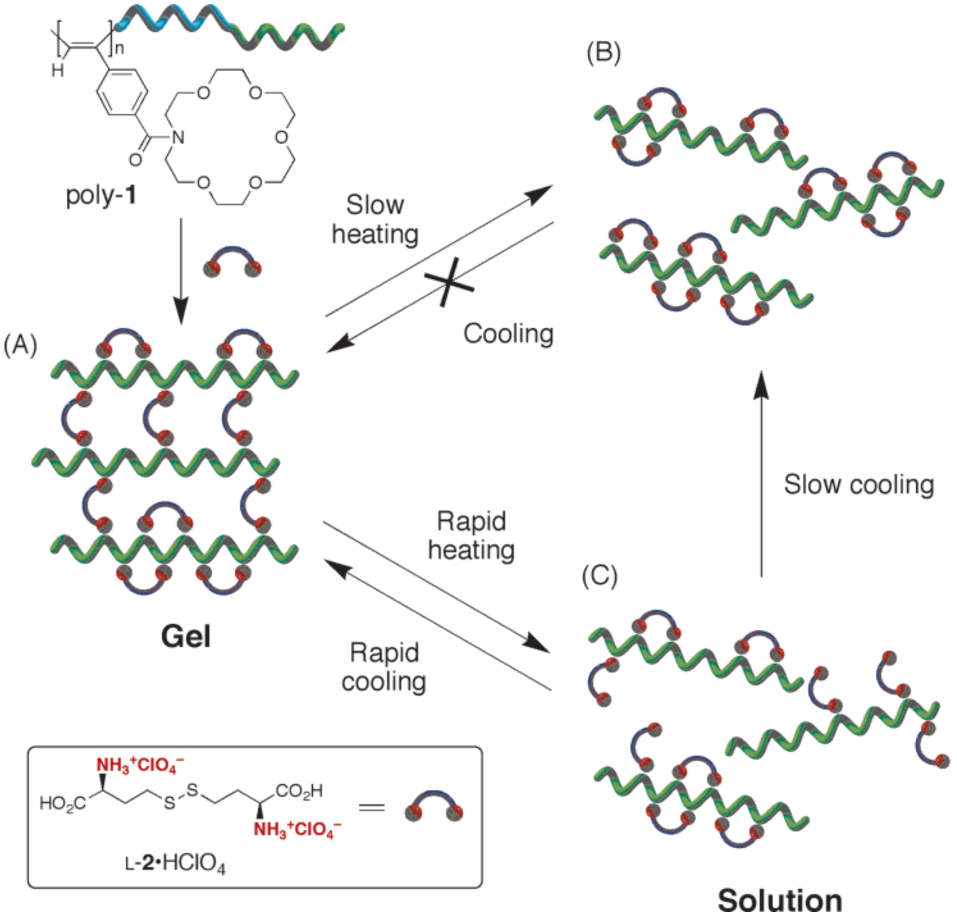


Figure 3. Schematic illustrations of a one-handed helicity induction and gelation of poly-**1** upon complexation with L-**2**·$HClO_4$ (A) and the mechanism of irreversible (A and B) and reversible (A and C) gel−sol transition upon slow heating and cooling and rapid heating and cooling cycles, respectively.

upon heating of the gel also support the above speculation (Figure S-2 in the Supporting Information). The changes in the $\Delta\epsilon_{2nd}$ value of the same sample were also followed with time and upon heating, and we observed

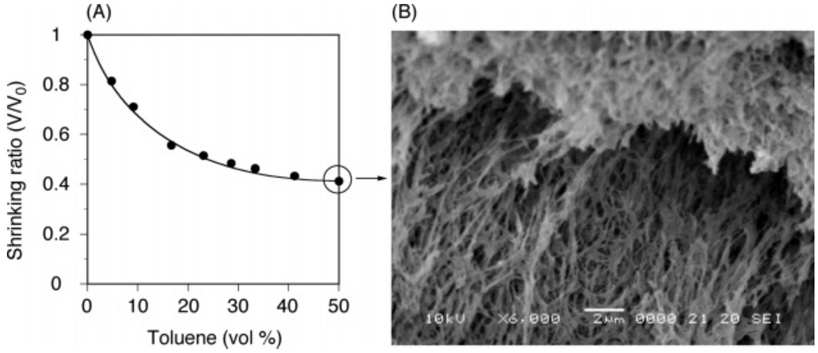


Figure 4. (A) Plots of shrinking ratio of the poly-**1**−L-**2** gel (V/V_0) vs toluene contents (vol %) in CH_3CN−toluene mixtures containing a small amount of aqueous $HClO_4$ ([$HClO_4$]/[L-**2**] = 2.2). The molar ratio of L-**2** to poly-**1** is 2.0. (B) SEM image of the dried xerogel obtained from the poly-**1**−L-**2** gel in CH_3CN/toluene (50/50, v/v).

changes similar to those in Figures 1A and 2A, respectively. The ^1H NMR spectra of the poly-**1**−L-**2** complex showed rather broad resonances, and the main chain and aromatic proton resonances of poly-**1** were too broad to detect in the presence of L-**2**. The poly-**1**−L-**2** complex solution formed a gel after the sample had been allowed to stand for 2 h. During this gelation process, the broad peak at 3.6 ppm assigned to the protons of the crown ether moiety of poly-**1** was further broadened (see Figure S-2B in the Supporting Information), probably because the local mobility of the polymer backbone as well as the pendants is highly restricted due to binding with L-**2**. The gel was then gradually heated in order to follow the changes in its ^1H NMR spectrum. The proton resonances of the crown ether pendants at 3.6 ppm became sharp with an increase in temperature from 25 to 55 °C. After the dissolution of the gel at 55 °C, the sharpness of the peak was significant. The other proton resonances derived from L-**2** also showed the same tendency (see Figure S-2D in the Supporting Information). By cooling the solution to 25 °C, the peaks became broadened again, but they were not as broad as those of the gel before heating. These results also support the mechanism of the gel−sol transition illustrated in Figure 3A,B.

As described above, the poly-**1**−L-**2** gel showed an irreversible gel−sol transition as a function of temperature for the slow heating-slow cooling cycle (25−55 °C). Moreover, the solution of the poly-**1**−L-**2** complex after dissolution of the gel did not form a gel even after rapid cooling at −20 °C for 17 h. However, we found that the poly-**1**−L-**2** complex solution re-formed as a gel again by rapid cooling at 0 °C for 2 h after the gel had dissolved by rapid heating at 60 °C for 10 s. This cycle can be reversibly repeated. A possible mechanism for this reversible gel−sol transition of the poly-**1**−L-**2** gel can be proposed as follows (Figure 3). The poly-**1**−L-**2** gel was formed by intermolecular complexation between the two ammonium groups of L-**2** and the crown ether pendants of poly-**1** (Figure 3A) and dissolved by slow heating accompanied by the transformation from an intermolecular to intramolecular complexation (Figure 3B), resulting in the irreversibility of the sol−gel transition upon cooling. On the other hand, the dissolution of the gel by rapid heating may not cause the instant transformation from an intermolecular to intramolecular complexation (Figure 3C). Therefore, the solution produced by rapid heating may re-form a gel by rapid cooling. Consequently, the cycle of gelation and dissolution can be reversibly repeated by rapid heating and cooling.

The poly-**1**−L-**2** gels prepared at [L-**2**]/[poly-**1**] = 1.5 and 2.0 transform into a solution at 55 °C. However, we found that a poly-**1** gel formed in the presence of a slight excess L-**2** ([L-**2**]/[poly-**1**] = 2.1−2.5) in CH_3CN containing 0.3 vol % aqueous $HClO_4$ gradually shrunk upon heating before melting. Figure 2A shows the changes in the $\Delta\epsilon_{2nd}$ value (b in Figure 2A) and volume of the poly-**1**−L-**2** gel ([L-**2**]/[poly-**1**] = 2.1, c in Figure 2A) at different temperatures. The gel exhibited a decrease in the absolute value of CD intensity upon heating, similar to the gels prepared at [L-**2**]/[poly-**1**] = 1.5 and 2.0 (Figure S-2C in the Supporting Information and a in Figure 2A). However, the poly-**1**−L-**2** gel at [L-**2**]/[poly-**1**] = 2.1 gradually shrunk by increasing the temperature before melting at 55 °C (Figure 2B), and the shrinking ratio reached 0.4 at 50 °C (c in Figure 2A). The volume change remarkably occurred around the region where the temperature was from 35 to 50 °C, and the gel dissolved at 55 °C. This shrinking process was irreversible; the shrunken gel did not swell again while cooling back to 25 °C. The reason for this shrinkage of the poly-**1**−L-**2** gel at [L-**2**]/[poly-**1**] = 2.1 is not clear at present, but a delicate balance between the interchain complexation with L-**2** and dissolution of L-**2** may play a role in the thermally induced shrinkage and melting of the gel. Hamachi and co-workers recently reported supramolecular hydrogels of glycosylated amino acid derivatives which can trap and release water-soluble drugs in a reversible, thermally controlled swelling-shrinking process.[13] Therefore, the present poly-**1**−L-**2** gel may also be used as a novel gel for the catch-and-release of various molecules with molecular recognition.

The poly-**1**−L-**2** gel also shrunk by adding a poor solvent as well as upon heating. The volume of the poly-**1**−L-**2** gel ([L-**2**]/[poly-**1**] = 2.0) decreased with the increasing volumes of toluene and the shrinking ratio (V/V_0) of the gel reached 0.4 in 50 vol % of toluene (Figure 4A).

The shrunken gel was suitable for SEM to observe the morphology of the gel. We then performed SEM observations of the dried poly-**1**−L-**2** gel obtained from the poly-**1**−L-**2** gel in CH_3CN/toluene (50/50, v/v). As shown in Figure 4B, well-developed fibrous network assemblies with a diameter of about 100−200 nm were observed by SEM, although helically twisted fibers could not be clearly observed.

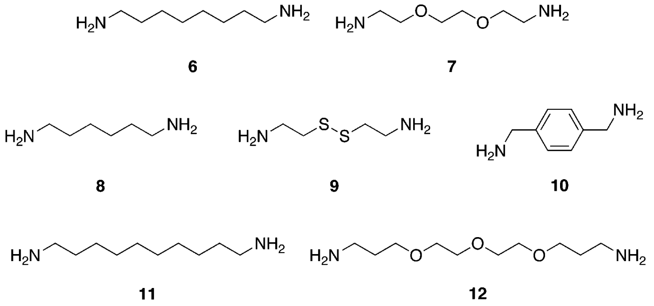
We next investigated the helicity induction and gelation ability of poly-**1** using a series of optically active bis(amino acid)s (Chart 1) as a cross-linker and a helicity inducer. These results are summarized in Table

Table 1. CD Data and Gelation Ability of Poly-1 Complexed with Various Bis(amino acid)s

run	bis(amino acid)	[bis(amino acid)]/[poly-**1**]	$\Delta\epsilon_{2nd}$ (λ)[a]	appearance	T_m (°C)[b]
1	L-**2**	2	−19.4 (364)	gel	55
2	*rac*-**2**	2	0	solution	
3	L-**3**	2.5	−18.8 (366)	gel	61
4	D-**3**	2.5	18.4 (363)	gel	61
5	*rac*-**3**	2.5	0	solution	
6[c]	L-**4**	5	−13.4 (368)	solution	
7[c]		5.5		precipitation	
8	L-**5**	2	−15.2 (369)	solution	
9		2.5		precipitation	

[a] CD spectra were measured in CH_3CN containing 0.3 vol % aqueous $HClO_4$ ($[HClO_4]/[\text{bis(amino acid)}] = 2.2$) at 25 °C with poly-**1** (1.0 mg/mL); $\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1}) and λ (nm). [b] Melting temperature of gel. [c] In CH_3CN containing 0.4 vol % aqueous $HClO_4$ ($[HClO_4]/[\text{bis(amino acid)}] = 2.2$).

Chart 2. Structures of Achiral Diamines



1. The poly-**1**−L-**3** complex ([L-**3**]/[poly-**1**] = 2.5) also formed a gel within 1 h, and the gel exhibited an optical activity due to a predominantly one-handed helix formation during the gelation (run 3 in Table 1). The enantiomer D-**3** exhibited the ICD of the mirror images in the poly-**1** chromophore region, and the complex with poly-**1** formed a gel. Heating of both the gels (poly-**1**−L-**3** and -D-**3** gels) to 61 °C results in dissolution without shrinking. This gel−sol transition was also irreversible. On the other hand, poly-**1** did not form a gel in the presence of increasing the amounts of other optically active bis(amino acid)s (L-**4** and L-**5**) in CH_3CN containing a small amount of aqueous $HClO_4$, and the complexes finally precipitated (runs 6−9 in Table 1), although these bis(amino acid)s could effectively induce a helicity in poly-**1**. The differences in these bis(amino acid) structures are the distance involving the number of bonds between the two ammonium groups; L-**2** and L-**3** showing the interchain cross-linking ability have two ammonium groups separated from nine and seven bonds, respectively, whereas L-**5** has greater than 17 bonds between the two ammonium groups. Surprisingly, L-**4** showed no gelation ability despite its analogous structure to L-**3**; only the difference between them is the disulfide (L-**3**) and sulfide bonds (L-**4**).

To gain further insight into the gelation mechanism of poly-**1**, various achiral diamines, such as 1,8-diaminooctane (**6**), 1,2-bis(2-aminoethoxy)ethane (**7**), 1,6-diaminohexane (**8**), cystamine (**9**), *p*-xylylenediamine (**10**), 1,10-diaminodecane (**11**), and diethylene glycol bis(3-aminopropyl ether) (**12**), were used as a cross-linker (Chart 2). However, none of these diamines formed a gel upon complexation with poly-**1** in CH_3CN containing 0.3 vol % aqueous $HClO_4$ despite the facts that **6** and **7** (nine bonds) and **8** and **9** (seven bonds) have the same number of bonds between the two ammonium groups as L-**2** and L-**3**, respectively, and **9** has the disulfide bond similar to L-**3**. These results indicate that the gelation of poly-**1** is highly sensitive to the structure and chirality of the bis(ammonium)s with a different distance between the separated charges. We presume that a predominantly one-handed helical conformation of poly-**1** may also be necessary for the gelation because achiral diamines used in the present study showed no gelation, and L-**4** and L-**5**, which could not induce a full ICD in poly-**1**, did not gelate poly-**1** (Table 1). If this is the case, the gelation of poly-**1** assisted by **2** and **3** might be highly influenced by their optical purities (enantiomeric excess (ee)).

Interestingly, we found that the racemic **2** and **3** (*rac*-**2** and *rac*-**3**) could not gelate poly-**1** under the same experimental conditions as those for the optically pure L-**2** and L-**3** (runs 2 and 5 in Table 1). We then performed the same helicity induction and gelation experiments for poly-**1** using **2** and **3** with different enantiomeric excesses, and the changes in the $\Delta\epsilon_{2nd}$ values of poly-**1**

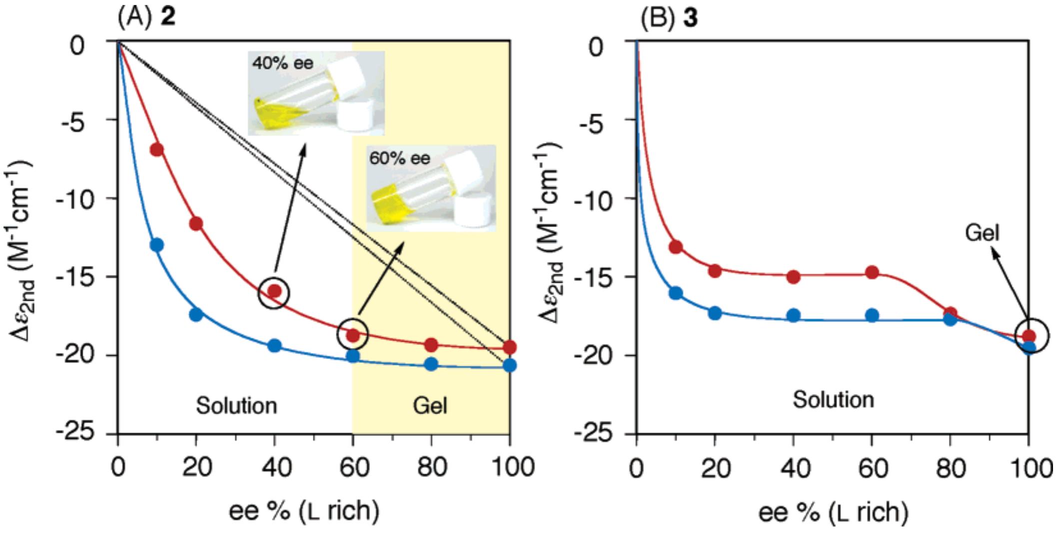


Figure 5. Nonlinear effects between the $\Delta\epsilon_{2nd}$ value and percent ee of **2** (A) and **3** (B) (L rich) in the complexation with poly-**1** (1.0 mg/mL) in CH_3CN containing 0.3 vol % aqueous $HClO_4$ ($[HClO_4]/[\text{bis(amino acid)}] = 2.2$) at 25 °C (red ●) and −10 °C (blue ●); the molar ratio of **2** and **3** to monomeric unit of poly-**1** is 2.0 and 2.5, respectively. The ICD intensities of poly-**1**−**2** and poly-**1**−**3** complexes were measured after the samples had been allowed to stand for 1.5 and 8 h at ambient temperature, respectively. Photographs of poly-**1** complexed with 40 and 60% ee of **2** are also shown in (A).

are plotted vs the percent ee of **2** and **3** (L rich) (A and B in Figure 5, respectively).

The ICD intensities of poly-**1**, corresponding to the helical sense excess of poly-**1**, were out of proportion to the ee's of **2**, showing a convex deviation from linearity through a wide range of ee values of **2** (Figure 5A). The extent of the departure from linearity was greater at −10 °C than 25 °C, and the complexes of poly-**1** with 60 and 40% ee of **2** exhibited ICDs as intense as that of 100% ee at 25 and −10 °C, respectively (Figure 5A). This is a typical example of chiral amplification (nonlinear effect or majority rule) observed in helical polymers and originated from the dynamic nature of the helical conformations of the polymer backbones.[8,9a,14] More interestingly, the solution of the poly-**1**−**2** complex formed a gel only when the ee of **2** was greater than 60% ee at which the poly-**1** might have an almost perfect one-handed helix based on the ICD intensity, although a rather longer time (1 and 6 h) was required for the gelation of poly-**1** with 80 and 60% ee of **2**, respectively (Figure 5A). To the best of our knowledge, this is the first observation of a helical gel induced and assisted by noncovalent chiral interactions in an enantioselective fashion.[15] However, when nonracemic **3** was used as a gelator, gelation was not attained even with the 80% ee of **3**, although **3** exhibited a noticeable positive nonlinear effect (Figure 5B).

Poly-**1** is a dynamically racemic helical polymer composed of interconverting right- and left-handed helical segments.[8,9a] Achiral bis(ammonium) compounds may not be able to complex with the pendant crown ether residues of interchain racemic helical segments of poly-**1**. However, the geometrically favorable, chiral bis(amino acid)s can induce a one-handed helix in poly-**1**, which may further assist in the interchain complexation of poly-**1** with the same helical sense, resulting in the novel thermoresponsive organogel formation. This speculation is supported by the chiral stimuli-responsive gelation of poly-**1** with nonracemic **2** and **3**.

Conclusions

In summary, we have found that poly(phenylacetylene) bearing the aza-18-crown-6 ether pendants formed a predominantly one-handed helical conformation upon complexation with optically active bis(amino acid)s, resulting in an organogel due to the noncovalent intermolecular cross-linking between the crown ether pendants of poly-**1** and the two ammonium groups of the bis(amino acid)s. The gelation of poly-**1** is highly sensitive to the structure and chirality of the bis(ammonium) compounds, and a one-handed helical structure of poly-**1** induced by chiral bis(amino acid)s seems to be essential for the gelation. The gel−sol transition by slow heating−cooling cycles was irreversible, but the process can be reversibly repeated by rapid heating and cooling of the gel. Although a number of stimuli-responsive gels have been prepared in response to external physical and chemical stimuli, such as temperature, pH, and solvent compositions,[16] stimuli-responsive helical gels are rare.[12,15] We expect that the present strategy will be applicable for designing and synthesizing other various helical gels consisting of dynamic helical polymers with chiral and achiral functional pendants.[17]

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Supporting Information Available: Temperature dependence of the $\Delta\epsilon_{2nd}$ values of the poly-**1**−L-**2** gel and poly-**1**−L-Met complex, changes in the $\Delta\epsilon_{2nd}$ value and ^{1}H NMR spectra of the complex of poly-**1** with L-**2** with time, and temperature-dependent changes in the $\Delta\epsilon_{2nd}$ value and ^{1}H NMR spectra of the poly-**1**−L-**2** gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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