Helicity Induction on Poly(phenylacetylene)s Bearing Phosphonic Acid Pendants with Chiral Amines and Memory of the Macromolecular Helicity Assisted by Interaction with Achiral Amines in Dimethyl Sulfoxide

Hisanari Onouchi, Daisuke Kashiwagi, Kiichiro Hayashi, Katsuhiro Maeda, and Eiji Yashima*

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

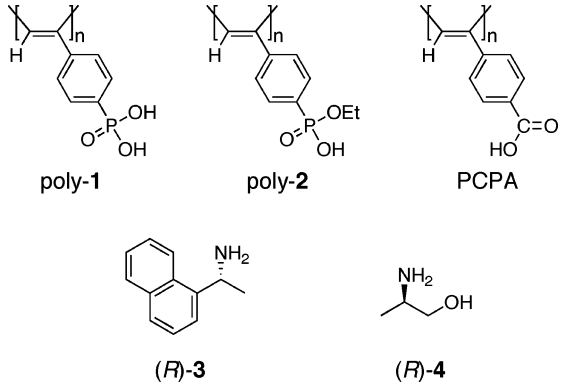
Received May 12, 2004; Revised Manuscript Received May 23, 2004

ABSTRACT: Two novel stereoregular poly(phenylacetylene)s bearing a phosphonic acid residue (poly-**1**) and its monoethyl ester (poly-**2**) as pendants were prepared by the polymerization of diethyl (4-ethynylphenyl)phosphonate followed by hydrolysis of the diethyl ester groups and polymerization of ethyl (4-ethynylphenyl)phosphonate, respectively. The polymers were found to form a predominantly one-handed helical conformation upon complexation with various chiral amines through noncovalent acid−base interactions in dimethyl sulfoxide (DMSO). The complexes exhibited an induced circular dichroism (ICD) in the UV−visible region of the polymer backbones. In particular, poly-**2** is an induced helical polymer more sensitive to the chirality of amines than poly-**1** and poly((4-carboxyphenyl)acetylene) and yields the same Cotton effect sign when complexed with chiral amines of the same absolute configuration. Moreover, the macromolecular helicity of poly-**1** and poly-**2** induced by chiral amines was "memorized" after the chiral amines were completely removed and replaced with various achiral diamines and oligoamines in DMSO. In sharp contrast to the same memory effect on the induced helical poly((4-carboxyphenyl)acetylene), the helical structures of poly-**1** and poly-**2** could not be efficiently maintained by achiral monoamines. The effect of the structure of the achiral diamines and oligoamines on the efficiency of the helicity retention and the stability of the memorized polymers were also investigated.

Introduction

The detection and amplification of chirality by helical polymers[1] and supramolecular helical assemblies[2] have attracted great interest in recent years, because these systems can be applied to developing novel chiroptical devices and chiral materials as enantioselective adsorbents and catalysts.[3] In a series of our studies, we reported the helicity induction on optically inactive, stereoregular cis−transoidal poly(phenylacetylene)s bearing functional groups, which can change their structures into the prevailing, dynamic one-handed helices upon complexation with specific chiral guests.[1e,4] For instance, the introduction of carboxy,[5] amino,[6] and boronate[7] groups as the pendant produced poly(phenylacetylene)s which can respond to the chirality of chiral amines, acids, and sugars, respectively, and their complexes show a characteristic induced circular dichroism (ICD) in the UV−visible region of the polymer backbones. The Cotton effect signs corresponding to the helical sense can be used as a novel probe for the chirality assignments of the guest molecules.[1,4] The macromolecular helicity induced on these poly(phenylacetylene)s is dynamic in nature. However, we recently found that such a dynamic macromolecular helicity of poly((4-carboxyphenyl)acetylene) (PCPA) induced by an optically active amine such as (*R*)-1-(1-naphthyl)ethylamine ((*R*)-**3**) (Chart 1) could be "memorized" even after the chiral amine was completely replaced by various achiral amines and amino alcohols in dimethyl sulfoxide (DMSO).[8] The mechanism of the helicity induction and the memory of the helical chirality of PCPA have been thoroughly investigated, and the following conclusions were drawn: (1) the ion pairing of PCPA with chiral amines is essential for the helicity induction, and (2) the electrostatic repulsion between the carboxylate groups of PCPA derived from the dissociation of the ion pairs plays a central role in the macromolecular helicity memory of PCPA in DMSO.[8b]

Chart 1. Structures of Poly-1, Poly-2, PCPA, and Chiral Amines



We expected that a similar macromolecular helicity memory could be possible for analogous stereoregular poly(phenylacetylene)s bearing other functional groups as pendants. We now report that novel stereoregular poly(phenylacetylene)s bearing a phosphonic acid residue (poly-**1**) or its monoethyl ester (poly-**2**) as pendants (Chart 1) can form a predominantly one-handed helical conformation in the presence of chiral amines and their induced helical chirality can be maintained when the

* To whom correspondence should be addressed. E-mail: yashima@apchem.nagoya-u.ac.jp.

10.1021/ma049066v CCC: $27.50
Published on Web 06/29/2004

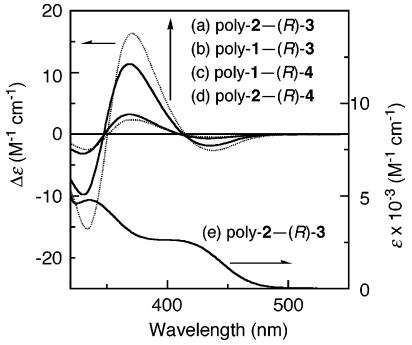


Figure 1. CD spectra of poly-**1** and poly-**2** with (*R*)-**3** and (*R*)-**4** ([**3** or **4**]/[polymer] = 2) in DMSO at ambient temperature (ca. 20−22 °C) with a polymer concentration of 1.0 mg/mL. The absorption spectrum of poly-**2** with (*R*)-**3** is also shown.

chiral amines are removed and replaced with various achiral diamines and oligoamines in DMSO. The results are compared with the previously reported helicity induction and memory effect of PCPA. Poly-**1** and poly-**2** have a more acidic phosphonic acid group than the carboxy group of PCPA as the pendant, so that helicity induction may occur more efficiently in poly-**1** and poly-**2**, resulting in more intense ICDs in their polymer backbone regions. Poly-**1** was already reported to exhibit an induced helix upon complexation with various biomolecules such as amino acids and aminosugars in water,[9] but the helicity induction on poly-**1** and its memory in organic solvents have not yet been reported in detail.[10]

Results and Discussion

Synthesis and Helicity Induction of Poly-1 and Poly-2 with Chiral Amines. Cis−transoidal stereoregular poly-**1** and poly-**2** were prepared by a method similar to that previously reported as outlined in Schemes 1 and 2 (see Experimental Section), respectively.[9,11,12] The number average molecular weight (M_n) and its distribution (M_w/M_n) were estimated to be 14.8 × 10^4 and 1.9 (poly-**1**) and 1.9 × 10^4 and 3.5 (poly-**2**), respectively, as determined by size exclusion chromatography (SEC) with poly(ethylene oxide) and poly(ethylene glycol) standards in *N*,*N*-dimethylformamide (DMF) containing 10 mM lithium chloride as the eluent. The stereoregularity of the polymers was investigated by ^{1}H NMR and laser Raman spectroscopies. The ^{1}H NMR spectra of poly-**1** and poly-**2** in DMSO-d_6 showed sharp singlets centered at 5.86 and 5.83 ppm, respectively, due to the main chain protons, indicating that these polymers possess a highly cis−transoidal, stereoregular structure (see Figure S-1 in the Supporting Information).[13] The laser Raman spectra of the polymers also support this conclusion; poly-**1** and poly-**2** showed characteristic peaks at 1353 and 974 cm^{-1} due to the C−C and C−H bond vibrations in the *cis*-polyacetylenes, respectively,[14] while those in the *trans*-polyacetylene were scarcely observed (see Figure S-2 in the Supporting Information). The CD spectra of poly-**1** and poly-**2** in the presence of various chiral amines were then measured to investigate if the polymers could respond to the chirality of the chiral amines, thus showing characteristic ICDs.

The typical CD and absorption spectra of poly-**1** and poly-**2** in the presence of (*R*)-**3** and (*R*)-2-amino-1-propanol ((*R*)-**4**) (2 equiv to monomer units of the polymers) (Chart 1) in DMSO are shown in Figure 1.

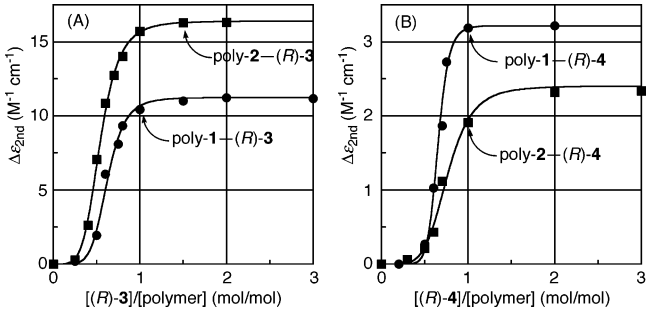


Figure 2. Titration curves of poly-**1** ($\Delta\epsilon_{second}$ of 365 nm) and poly-**2** ($\Delta\epsilon_{second}$ of 370 nm) with (*R*)-**3** (A) and (*R*)-**4** (B) in DMSO at ambient temperature (ca. 20−22 °C) with a polymer concentration of 1.0 mg/mL.

The complexes exhibited split-type ICDs in the UV−visible region of the polymer main chains due to the formation of a predominantly one-handed helical conformation of the polymers. The Cotton effect patterns were similar to each other, but the intensities were weak for the complexes with (*R*)-**4**. The CD titrations using (*R*)-**3** and (*R*)-**4** were then performed (Figure 2). The CD intensities increased with an increase in the concentration of (*R*)-**3** and (*R*)-**4** and reached a constant value in the presence of an almost equivalent amount of the chiral amine and amino alcohol. Particularly, the ICD magnitudes of the complexes dramatically changed at around the region where the molar ratio of the amine and amino alcohol to the polymers is from 0.5 to 1. These sudden onsets and rapid increases in the optical activity of poly-**1** and poly-**2** with a sigmoidal fashion suggest that the polymers form a slight excess of a one-handed helical structure at around the region ([amine]/[polymer] = 0−0.4 mol/mol) and further change in the population of the right- and left-handed helices of the polymer main chains into a one-handedness cooperatively occurred on the polymers with a further increase in the concentration of the amine and amino alcohol.[3b,8b,15]

The complexes with (*R*)-**3** showed more intense ICDs than those with (*R*)-**4**, and poly-**2** is more sensitive to the chirality of (*R*)-**3** than poly-**1**, thus exhibiting a more intense ICD, but for (*R*)-**4**, poly-**1** is slightly better based on the CD titration curves in Figure 2B. These results are in sharp contrast to the previously observed CD results using PCPA. During the complexation of PCPA with chiral amines, the magnitude of the ICD corresponding to an excess of a single-handed helix of PCPA increased with an increase in the bulkiness and basicity of the chiral amines, whereas chiral amino alcohols including (*R*)-**4** exhibited a very intense ICD irrespective of the bulkiness because the hydroxy group can participate in hydrogen bonding with the carboxy group of a neighboring monomer unit together with the acid−base ion-pairing interaction of the amino group.[5b] Therefore, the complexes of PCPA with (*R*)-**3** and (*R*)-**4** exhibited almost the same ICD intensities, although the ICD signs were opposite from those of the complexes with poly-**1** and poly-**2**; the second Cotton intensities ($\Delta\epsilon_{second}$) of the complexes of PCPA with (*R*)-**3** and (*R*)-**4** in DMSO were −9.27 and −9.73 ([amine]/[PCPA] = 50), respectively.[5b] The present results indicate that the hydroxy group of (*R*)-**4** may not be effective for hydrogen-bonding formation to poly-**1** and poly-**2** and that a change in the acidity of the pendant functional group significantly influences the acid−base complexation.

The results of the ICD for the complexation with other primary chiral amines and amino alcohols (Chart 2) are

Chart 2. Structures of Chiral Amines and Amino Alcohols

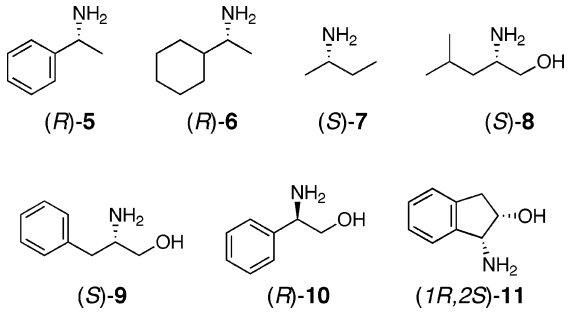


Table 1. Difference in Exciton Coefficient of the Second Cotton ($\Delta\epsilon_{second}$) for the Complexes of Poly-1, Poly-2, and PCPA with Chiral Amines and Amino Alcohols in DMSO[a]

	second Cotton [λ (nm) and $\Delta\epsilon_{second}$ (M^{-1} cm^{-1})]		
amine	poly-**1** $\Delta\epsilon$ (λ)	poly-**2** $\Delta\epsilon$ (λ)	PCPA[b] $\Delta\epsilon$ (λ)
(*R*)-**3**	+11.24 (365)	+16.92 (370)	−9.27 (375)
(*S*)-**3**	−11.03 (365)	−16.79 (370)	+8.67 (375)
(*R*)-**4**	+3.22 (365)[c]	+2.31 (370)[c]	−9.73 (373)
(*R*)-**5**	+9.55 (365)	+15.68 (369)	−3.82 (376)
(*R*)-**6**	+4.21 (365)	+8.43 (369)	
(*S*)-**7**	−7.48 (365)	−17.73 (370)	+0.42 (378)
(*S*)-**8**	+7.18 (366)	−17.84 (371)	+10.0 (371)[d]
(*S*)-**9**	−8.30 (366)	−18.63 (371)	+5.27 (374)
(*R*)-**10**	+8.52 (366)	+16.48 (372)	−6.58 (374)
(1*R*,2*S*)-**11**	+11.09 (366)	+18.71 (370)	−10.33 (374)

[a] The concentration of polymers is 1.0 mg/mL. [amine]/[poly-**1** or PCPA] = 50 and [amine]/[poly-**2**] = 10. [b] Cited from ref 5b. [c] [**4**]/[polymer] = 2. [d] [amine]/[PCPA] = 10.

summarized in Table 1. The ICD results for the complexes with PCPA[5b] are also shown for comparison. It is noteworthy that all of the primary amines (**3**, **5**−**7**) and amino alcohols (**4**, **8**−**11**) of the same configuration gave the same Cotton effect signs for poly-**2**. A similar tendency was observed for poly-**1**, but the complex with (*S*)-**8** exhibited the opposite Cotton effect sign. Moreover, the ICD intensities of the complexes of poly-**2** with the chiral amines were stronger than those of the poly-**1**−amine and PCPA−amine complexes except for **4** even in the presence of excess chiral amines ([amine]/[poly-**1** or PCPA] = 50), indicating that poly-**2** is the most sensitive induced helical polymer as a novel probe for sensing the chirality of amines and amino alcohols without derivatization, although the Cotton effect signs of the poly-**2** complexed with the chiral amine and amino alcohols tested are completely opposite to those of the corresponding PCPA complexes. The pendant phosphonic acid and its monoethyl ester are more acidic than the carboxylic acid of the PCPA, which must efficiently enhance the ion-pair formation, resulting in an excess of a single-handed helix, thus showing more intense ICDs.[16] The pK_a values of benzoic acid, phenylphosphonic acid, and the phenylphosphonic acid monomethyl ester, model compounds of PCPA, poly-**1**, and poly-**2**, are 4.19, 1.83 (pK_{a1}) and 7.07 (pK_{a2}),[17] and 2.97,[18] respectively. In other words, the helical conformation of the PCPA induced by chiral amines may still be imperfect.[8b,12b] The bulky phosphonic acid pendants also contribute to their high sensitivities of the amine chiralities.[19]

Previously, the interaction of PCPA with optically active amines in DMSO was systematically studied using NMR and CD spectroscopies, and a rational model was proposed to explain the relationship between the Cotton effect signs of PCPA and the absolute configuration of the chiral primary amines (Figure 3A).[5b] On the basis of this model together with the present ICD results of poly-**1** and poly-**2** in DMSO, a possible mechanism for the helicity induction of the poly-**1**− and poly-**2**−amine complexes in DMSO can be proposed as follows (Figure 3B). Amines may be favorably complexed with PCPA to form an ion pair as shown in Figure 3A, where the conformation of the amine is closer to the anti-staggered and the predominant helix-sense can be determined by the steric difference in the bulkiness of the smaller (S) and the bulky (L) substituents of the neighboring monomer units. The presumed molecular model of the PCPA−(*R*)-amine complexes suggests that the left-hand side monomer unit in Figure 3A is favorably positioned on the front side, while the right-hand side monomer unit is on backside, so that the PCPA backbone will possess a left-handed helix.[20] We note that the pendant groups of the PCPA in Figure 3A appear to arrange in a right-handed screw-sense from the side-view, but the main chain folds into a left-handed screw-sense.

A similar model can be possible for the complexes of poly-**1** and poly-**2** with (*R*)-amines (Figure 3B). However, the pendant phosphonate ions of the polymers are tetrahedral, whereas the carboxylate of PCPA is coplanar when complexed with amines, and, therefore, the predominant helix-sense of poly-**1** and poly-**2** may be controlled by the steric difference in the bulkiness between the S and L substituents of the neighboring monomer units, together with the S and the OH or OEt group of the neighboring monomer units. Consequently, the left-hand side monomer unit in Figure 3B could be favorably located on the backside and the right-hand side monomer unit on the front side, leading to an opposite, right-handed helix of poly-**1** and poly-**2** when compared with the model of the PCPA with (*R*)-amines (Figure 3A).

Chiral Amplification (Nonlinear Effect). In a previous study, we reported that the complex formation of PCPA with partially resolved amines, such as **3** and **4**, displayed a unique, positive nonlinear relationship (chiral amplification or "majority rule")[3b,5b,21] between the enantiomeric excess (ee) of amines and the observed molar ellipticity of the Cotton effects; that is, the ICD intensities of PCPA, corresponding to the helical sense excesses, became out of proportion to the ee's of the amines, showing a convex deviation from linearity through a wide range of ee values of the chiral amines in DMSO.[5b] The departure from linearity was significant for the chiral amino alcohol **4**, and 60% ee of **4** was sufficiently enough to induce a full ICD for PCPA. However, for the chiral bulky amine **3**, the nonlinearity was very weak.

The changes in the ICD intensity of poly-**1** and poly-**2** against the ee's of **3** and **4** in DMSO were then measured (Figure 4). In sharp contrast to the nonlinear effects observed in PCPA, the CD intensities of poly-**1** and poly-**2** with **4** showed a linear effect, while strong positive nonlinear effects were observed for **3** in DMSO at ambient temperature. For example, when poly-**1** and poly-**2** were dissolved in DMSO with an excess of **3** of 40% ee (*R* rich), each complex exhibited ICDs as intense as those of 100% ee. The excess enantiomers bound to the polymers induce an excess of a single-handed helix despite its proportion, which results in a more intense ICD than that expected from the ee of **3**. As mentioned

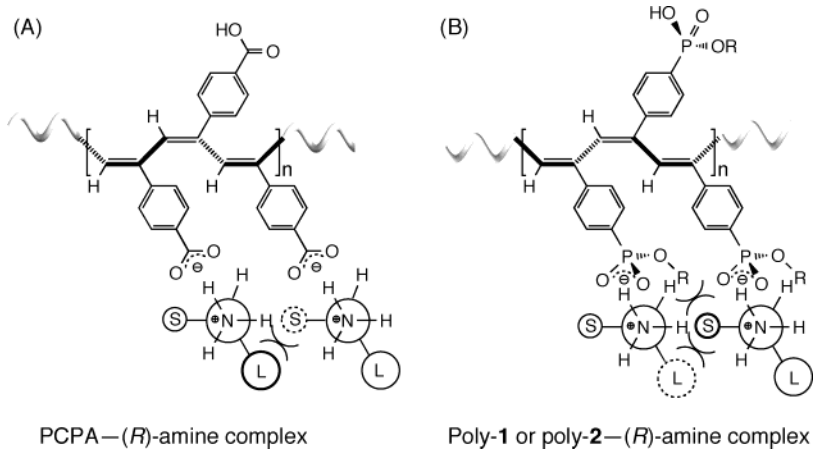


Figure 3. Possible structures for the PCPA−(*R*)-amine (A) and poly-**1** or poly-**2**−(*R*)-amine complexes (B).

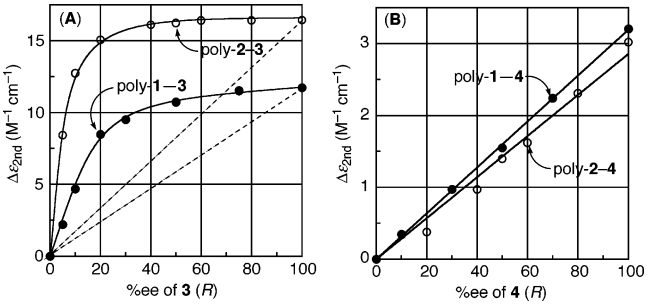


Figure 4. Changes in ICD intensity ($\Delta\epsilon_{second}$ (M^{-1} cm^{-1})) of poly-**1** and poly-**2** (1.0 mg/mL) versus the % ee of **3** (*R* rich) (A) and **4** (*R* rich) (B) ([amine]/[poly-**1**] = 50 and [amine]/[poly-**2**] = 10) in DMSO at ambient temperature (ca. 20−22 °C).

above, poly-**1** and poly-**2** showed weak ICDs upon complexation with optically pure **4** (Figure 1 and Table 1), and this weak helicity inducing ability might be closely correlated with the nonchiral amplification phenomena of these polymers with **4**.

Memory of the Macromolecular Helicity of Poly-1 and Poly-2. As described above, the macromolecular helicity of PCPA induced by (*R*)-**3** can be "memorized" after complete replacement of the (*R*)-**3** by various achiral amines in DMSO.[8] We then investigated if a similar macromolecular helicity memory could be possible for analogous stereoregular poly-**1** and poly-**2** bearing a phosphonic acid or its ethyl ester as the pendant instead of the carboxy group.

2-Aminoethanol (**12**) and *n*-butylamine (**13**) were first selected as achiral amines for the memory experiments, because these achiral amines were good chaperoning molecules to assist in the memory of the macromolecular helicity of PCPA induced by (*R*)-**3**.[8] The memory experiments were carried out in the same way as was previously reported.[8] Typically, the complexes of poly-**1** and poly-**2** with 2 equiv of (*R*)-**3** were prepared in DMSO; the complexes showed an almost full ICD. Each complex solution was then injected into an SEC system using a DMSO solution of **12** or **13** (0.8 and 0.08 M, respectively) as the mobile phase to isolate the poly-**1** and poly-**2**. Rather surprisingly, the fractionated polymer solutions showed no ICD for the isolated poly-**1** and a very weak ICD for the poly-**2** after replacement of the (*R*)-**3** by **12** and **13** during the SEC fractionation (Table 2). A possible explanation for these no and weak memory effects will be described later. We note that, under the same conditions, the PCPA fractions containing an excess of achiral **12** or **13** exhibited intense ICDs

Table 2. Memory Efficiencies of the Macromolecular Helicity of Poly-1 and Poly-2 Induced by (*R*)-3 Using a Series of Achiral Amines

		memory efficiency (%)[b]	
run	achiral amine[a] (M)	poly-**1**	poly-**2**
1	**12** (0.8)	ca. 0	4.0
2	**13** (0.08)	ca. 0	16.2
3	**14** (0.8)	68.2	93.2
4	**14** (0.08)	59.8	83.4
5	**14** (0.008)	59.7	80.3
6	**15** (0.8)	67.1	86.7
7	**16** (0.8)	70.0	86.9
8	**17** (0.8)	71.0	93.4
9	**18** (0.08)	78.2	*c*

[a] The parentheses indicate the concentration in DMSO as the mobile phase. [b] Memory efficiencies (%) were estimated on the basis of the ICD values at $\Delta\epsilon_{second}$ just after the SEC fractionation of the polymer−(*R*)-**3** complex solution ([polymer] = 1.0 mg/mL, [(*R*)-**3**]/[polymer] = 2) using various achiral amines in DMSO as the mobile phase. [c] Not eluted because of precipitation.

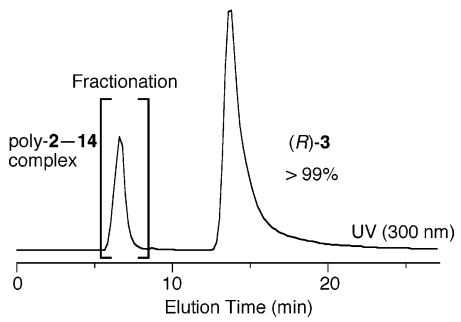


Figure 5. Chromatogram for the separation of the poly-**2**−(*R*)-**3** complex. SEC fractionation was performed using a UV−vis detector (300 nm) with 0.8 M **14** in DMSO as the eluent at a flow rate of 1.0 mL/min.

comparable to those measured before the SEC fractionations.[8] Other achiral bulky amines including *t*-butylamine and 1-aminoadamantane also showed no memory effect for poly-**1** in DMSO. However, we have found that achiral diamines such as ethylenediamine (**14**) very effectively maintain the induced macromolecular helicity of the phosphonic acid-bound poly(phenylacetylene)s in DMSO.

A typical SEC chromatogram for the separation of the poly-**2**−(*R*)-**3** complex using a DMSO solution containing 0.8 M **14** is shown in Figure 5. The poly-**2** eluted first, followed by the *(R)*-**3**, and both were completely separated. Each fraction was collected and subjected to CD and absorption measurements. On the basis of the UV

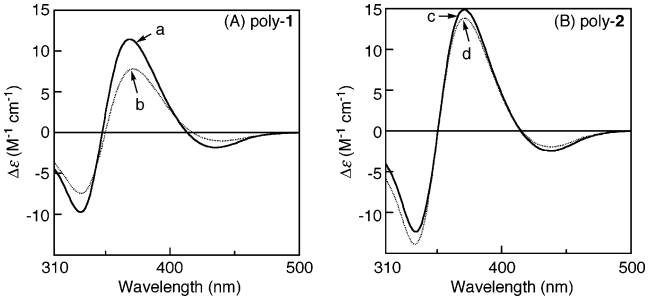
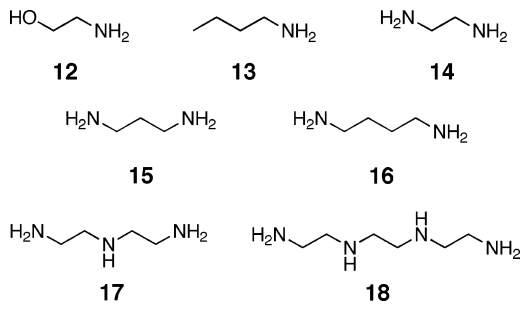


Figure 6. CD spectra of poly-**1** (A) and poly-**2** (B) (1 mg/mL) with (*R*)-**3** (a, c) ([(*R*)-**3**]/[poly-**1** or poly-**2**] = 2) and the isolated poly-**1** and poly-**2** (b, d) by SEC fractionation using a DMSO solution of **14** (0.8 M) as the mobile phase, in DMSO at ambient temperature (ca. 20−22 °C).

Chart 3. Structures of Achiral Amines



spectrum of the (*R*)-**3** fraction, more than 99% of the (*R*)-**3** was recovered. On the basis of the ratio of the ICD intensities of the second Cotton ($\Delta\epsilon_{second}$) of the poly-**1** (Figure 6A) and poly-**2** (Figure 6B) before (a and c) and after (b and d) the SEC fractionation, the memory efficiencies were estimated to be 68.2% and 92.1%, respectively. Unfortunately, PCPA precipitated upon complexation with the diamine **14** under the same conditions, and, therefore, we could not determine whether the induced helical chirality of PCPA by (*R*)-**3** would be maintained by the diamine.

We further investigated the macromolecular helicity memory of the poly-**1** and poly-**2** induced by (*R*)-**3** using a series of achiral diamines (**15**, **16**) and tri- and tetraamines (**17**, **18**) (Chart 3). The experiments were performed in the same manner, and the results of the memory efficiency experiments are summarized in Table 2. The effect of the concentration of a typical achiral diamine **14** in the mobile phase (0.8−0.008 M) on the memory efficiency was also investigated. The memory efficiency tended to slightly decrease with the decreasing concentration of **14** (Table 2). The magnitudes of the ICDs of the memorized poly-**1** and poly-**2** are dependent on the structures of the achiral amines used as well as the pendant functionality of the polymers. All achiral amines exhibited a rather high memory efficiency for poly-**2** (80−93%) except for **18**, which caused precipitation of the polymer upon complexation in DMSO, while they showed moderate helicity memory effects on poly-**1** (60−78%) (Table 2). Among the achiral amines tested, a diamine **16** and tri- or tetraamine (**17** or **18**) worked most efficiently as achiral chaperoning molecules to assist in the memory of the macromolecular helicity of poly-**1**, while **14** and **17** showed a good memory effect for poly-**2**. As for a series of achiral diamines (**14**−**16**), the number of methylene groups influenced the memory efficiency, but the effect was not significant. On the basis of these observations, one may think that chiral diamines such as (1*R*,2*R*)-1,2-diaminocyclohexane could more efficiently induce a one-handed helicity on poly-**1** and poly-**2**. However, upon complexation with 0.1 equiv of the chiral diamine, the polymers precipitated in DMSO, and further experiments were difficult.

Very recently, we found that PCPA and chiral amines could be complexed more efficiently through ion pairing in the presence of the common salts of the chiral amines, and the memory efficiency significantly improved when the replacement of the chiral amine with achiral amines was performed in the presence of the common salts of the chiral amines.[8b] To examine if a similar enhancement of the memory efficiency or appearance of memory effect could be possible for poly-**1** and poly-**2**, we carried out the same memory experiments using the hydrochloride or *para*-toluenesulfonic acid salt of (*R*)-**3** ((*R*)-**3**·HCl or (*R*)-**3**·Tos). The poly-**1**−(*R*)-**3** and poly-**2**−(*R*)-**3** complexes ([(*R*)-**3**]/[polymer] = 2) containing various amount of the salts in DMSO (0.5−2.0 equiv to monomer units of polymers) were prepared, all of which showed a full ICD regardless of the amount of the salts. Each sample was then injected into the SEC system using a DMSO solution containing **12** (0.8 M) or **13** (0.08 M) as the mobile phase to simultaneously remove (*R*)-**3** and its salt. In the absence of the chiral salts, the helicity of poly-**1** induced by (*R*)-**3** could not be maintained at all by **12** and **13** as shown in Table 2. However, in the presence of the salts, the isolated poly-**1** showed a weak, but apparent ICD; the memory efficiency improved from ca. 0% to 4.7% and 23.5% for **12** and to 5.4% and 10.7% for **13** when (*R*)-**3**·HCl and (*R*)-**3**·Tos were used as the common salts during the helicity induction process, respectively, whereas a significant effect of the chiral salts was not observed for the memory of an induced helical poly-**2**.

The macromolecular helicity memory of poly-**1** and poly-**2** assisted by the interactions with achiral amines lasted for a long time of over 3 months as did that of PCPA.[8b] Macromolecular helicity amplification (repair) of the memorized poly-**1** and poly-**2** was not observed in these systems, but the memory gradually declined at ambient temperature (20−25 °C) and the ICD intensities showed a decrease with time (see Figure S-3 in the Supporting Information). The stability of the memory was almost independent of the structures of the achiral amines used, but highly dependent on the concentration of the achiral amines. The ICD intensities of the poly-**1**−**14** and poly-**2**−**14** solutions fractionated by SEC decreased with time, and the decreasing rate was accelerated with the increasing concentration of **14** (see Figure S-4 in the Supporting Information).

As for the mechanism of the memory effect, we recently reported the detailed studies for PCPA with achiral amines and concluded that the intramolecular electrostatic repulsions between the carboxylate groups play a central role in the maintenance of the helical chirality of PCPA to prevent the atropisomerization of the PCPA main chain.[8b] On the basis of the previous results together with the present ones, a possible mechanism of the helicity induction and memory of the helical chirality of poly-**1** and poly-**2** can be proposed.

The differences in the helicity induction and memory effect observed between PCPA and poly-**1** and poly-**2** might be correlated to the differences in the chemical and physical properties of the pendant groups, because all of the polymers consisted of the same repeating units of the π-conjugated diene structure. The phenylphos-

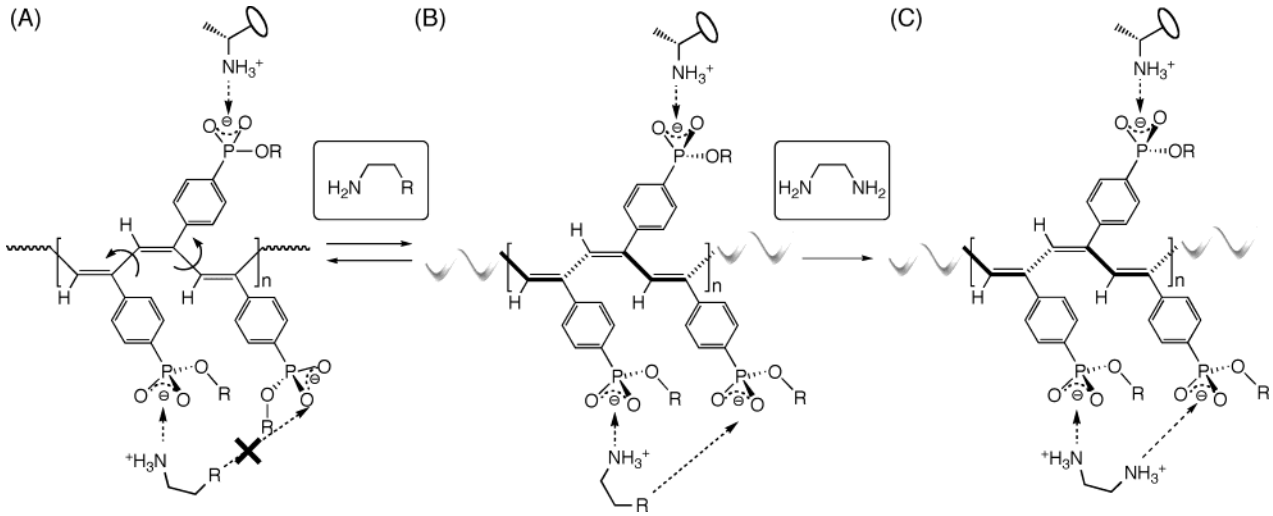


Figure 7. Schematic illustration of the mechanism of weak (A) and effective (C) macromolecular helicity memory of poly-**1** and poly-**2** with achiral monoamines (A) and diamines (C).

phonic acid and its monoesters are more acidic than benzoic acid, and, therefore, the former can form more stable ion-paired complexes with chiral amines in polar DMSO,[22] whereas the less acidic benzoic acid residues of PCPA may not be completely ionized, leading to weaker ion-paired interactions.[23] In fact, the binding affinities (binding constants) of phenylphosphonic acid derivatives to primary amines are 1-order greater than those of the benzoic acid derivatives in polar solvents.[8,22,23] This high ionic complexation ability of the pendant's phophonic acid residues of poly-**1** and poly-**2** with amines might result in an efficient induction of a predominantly one-handed helical conformation of the polymers upon complexation with chiral amines in DMSO as well as in water. The steric effect of the bulky phosphonic acid residues at the para position on the phenyl group might also contribute to the effective helicity induction on poly-**1** and poly-**2**,[12b,19] because, as we already reported, copolymers of an optically active phenylacetylene with an achiral phenylacetylene bearing a bulky substituent at the para position showed an intense ICD, while a copolymer of the same optically active phenylacetylene with a less bulky phenylacetylene exhibited a weak ICD in the copolymer backbone regions.[19]

Although the induced helical conformation of PCPA with chiral amines can be memorized by achiral amines such as **12** and **13**, these achiral monoamines were not effective for the memory of the induced helical structures of poly-**1** and poly-**2**; achiral diamines or oligoamines are necessary for the memory effect by the polymers. This indicates that the bidentate or multi-ion-paired electrostatic interactions between the neighboring phosphonate groups of the polymers and the di- or multi-ammonium moieties are essential for the memory (Figure 7C). Moreover, this also suggests that the intramolecular electrostatic repulsions between the neighboring phosphonates complexed with a monoamine were not efficient enough to prevent the atropisomerization of the main chains of poly-**1** and poly-**2**, which is in contrast to the memory effect of the PCPA (Figure 7A). This might be ascribed to the difference in the structures of the pendants; the benzoate groups are almost coplanar,[24] while the phenylphosphonate groups are tetrahedral,[25] which may serve to lower the barrier to the atropisomerization of the polymer backbones of poly-**1** and poly-**2** (Figure 7), probably because the negative charge of the phosphonate groups may be localized in two of the three P−O bonds upon complexation with the amines (Figure 7), so that the atropisomerization may smoothly occur between the adjacent monomer units, in which the less charged substituents (OH or OEt) are favorably positioned close to each other (Figure 7A). The longer bond lengths between the aromatic carbon and the phosphorus (1.74−1.79) and of the three P−O bonds (1.48−1.56) in the phosphonate group[25] as compared with the bond lengths between the aromatic carbon and the carboxyl carbon (1.48) and of the two C−O bonds (1.24−1.29) in the benzoate group[24] should be also taken into consideration for the ready inversion of the helicity of poly-**1** and poly-**2** with achiral monoamines.

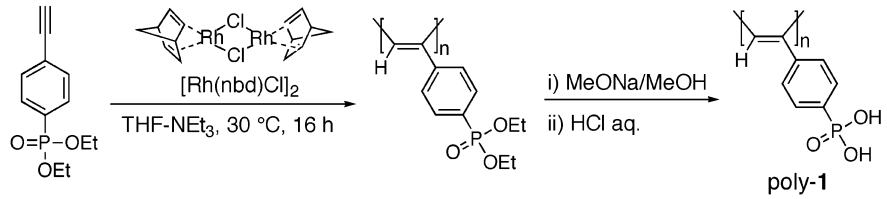
Conclusions

In summary, we found that novel poly(phenylacetylene)s with the phosphonic acid and its monoethyl ester as the pendants formed a predominantly one-handed helical conformation induced by a noncovalent interaction with various chiral amines in DMSO. The complexes exhibited characteristic and more intense ICDs than PCPA. In particular, poly-**2** was highly sensitive to the chirality of amines and showed the same Cotton effect signs if the configurations of the chiral amines were the same. The macromolecular helicity of poly-**1** and poly-**2** induced by chiral amines could be successfully memorized by achiral diamines or oligoamines with a rather high memory efficiency. Consequently, the present results demonstrate that analogous helical polyacetylenes[6,7] and other dynamic helical polymers[26] bearing rationally designed functional pendants induced by chiral compounds may be further memorized by achiral compounds with multiple functional groups.[27]

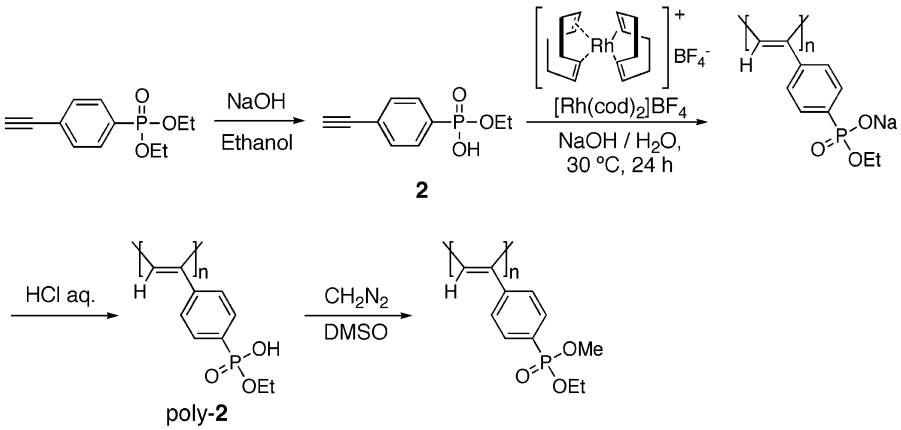
Experimental Section

Materials. Anhydrous DMSO (water content < 0.005%) and methanol (water content < 0.002%) were purchased from Aldrich and stored under nitrogen. THF was dried over sodium benzophenone ketyl, distilled onto $LiAlH_4$ under nitrogen, and distilled under high vacuum just before use. Sodium methoxide was obtained from Kishida (Osaka, Japan). Ethylenediamine (**14**) was

Scheme 1



Scheme 2



obtained from Tokyo Kasei (TCI, Tokyo, Japan), dried over potassium hydroxide, and distilled under nitrogen. 2-Aminoethanol (**12**) was dried over calcium oxide and distilled under reduced pressure. These amines were stored under nitrogen. (*R*)-(+)- and (*S*)-(−)-1-(1-Naphthyl)ethylamine ((*R*)-**3** and (*S*)-**3**) and (*R*)-1-phenylethylamine ((*R*)-**5**) were kindly supplied from Yamakawa Chemical (Tokyo, Japan), distilled under reduced pressure, and stored under nitrogen. Other optically active amines and achiral amines were available from Aldrich or TCI.

Cis−transoidal poly-**1** was prepared by polymerization of diethyl (4-ethynylphenyl)phosphonate with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene), followed by hydrolysis of the ester groups (86% yield) according to the previously reported method (Scheme 1).[9,11] The stereoregularity of the obtained polymer was examined by measuring the ^{1}H NMR spectrum and was found to be almost complete cis−transoid.[13] The molecular weight (M_n) and its distribution (M_w/M_n) of poly(diethyl (4-ethynylphenyl)phosphonate) were estimated to be 1.48 $\times$ 10^5 and 1.9, respectively, by SEC with poly(ethylene oxide) and poly(ethylene glycol) standards in DMF containing 10 mM lithium chloride. Poly(ethyl (4-ethynylphenyl)phosphonate) (poly-**2**) was prepared by the polymerization of the corresponding monomer (**2**) in water with a water-soluble rhodium catalyst in the presence of NaOH.[12]

Ethyl (4-ethynylphenyl)phosphonate (**2**) was prepared according to Scheme 2.

Ethyl (4-Ethynylphenyl)phosphonate (2). To a solution of diethyl (4-ethynylphenyl)phosphonate (4.1 g, 17 mmol) in ethanol (50 mL) was added aqueous NaOH (13.6 N, 63 mL), and the solution was stirred at room temperature. After 5 h, the solution was acidified with concentrated HCl (80 mL). After filtration, the filtrate was extracted with chloroform (800 mL) and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed by evaporation to give 3.7 g of **2** as a slightly brown solid (100% yield); no further purification was necessary. Mp 62.7−64.6 °C. IR (KBr, cm^{-1}): 3278 ($\nu_{\equiv C-H}$), 1215 ($\nu_{P=O}$). ^{1}H NMR (DMSO-d_6): δ 1.13−1.18 (t, CH_3, 3H), 3.82−3.91 (m, CH_2, 2H), 4.38 (s, ≡CH, 1H), 7.56−7.60 (m, aromatic, 2H), 7.65−7.72 (m, aromatic, 2H). ^{13}C NMR (DMSO-d_6): δ 16.3 (d, J = 6.2 Hz), 60.8 (d, J = 5.1 Hz), 82.7 (d, J = 1.1 Hz), 82.9, 124.6 (d, J = 3.4 Hz), 131.2 (d, J = 23.9 Hz), 131.3 (d, J = 28.5 Hz), 131.9 (d, J = 181.3 Hz). ^{31}P NMR (DMSO-d_6): δ 14.0. Anal. Calcd for $C_{10}H_{11}O_3P\cdot{}^1/_5H_2O$: C, 56.19; H, 5.38. Found: C, 56.09; H, 5.25.

Polymerization of 2. Polymerization of **2** was carried out in water using $[Rh(cod)_2]BF_4$ as a catalyst in a way similar to that reported previously (Scheme 2).[12]

Monomer **2** (1.0 g, 4.8 mmol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation−flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and the appropriate amounts ion-exchanged, distilled water and aqueous NaOH (1.0 N) ([NaOH]/[**2**] = 1.5) were added with a syringe. To this was added a solution of $[Rh(cod)_2]BF_4$ (0.025 M) in water at 30 °C. The color of the mixture changed instantly to dark red. The concentrations of the monomer and the rhodium complex were 0.5 and 0.0025 M, respectively. After 24 h, the resulting polymer (the sodium salt of poly-**2**) was precipitated into a large amount of ethanol, collected by filtration, and dried in vacuo at room temperature overnight (1.1 g, 100% yield). The sodium salt of poly-**2** (1.0 g, 4.5 mmol) was dissolved in a small amount of distilled water. The aqueous solution was acidified with aqueous HCl (5 N), and the precipitated poly(ethyl (4-ethynylphenyl)phosphonate) (poly-**2**) was collected by centrifugation and dried in vacuo at room temperature overnight (0.89 g, 94% yield). A part of poly-**2** was quantitatively converted to its methyl esters by reaction with CH_2N_2 in diethyl ether. The M_n and M_w/M_n were estimated by SEC with poly(ethylene oxide) and poly(ethylene glycol) standards using DMF containing 10 mM lithium chloride as the eluent (M_n = 1.9 $\times$ 10^4, M_w/M_n = 3.5).

Spectroscopic data of poly-**2**. IR (KBr, cm^{-1}): 1200 ($\nu_{P=O}$). ^{1}H NMR (DMSO-d_6, 80 °C): δ 1.06−1.10 (m,

CH_3, 3H), 3.71−3.75 (m, CH_2, 2H), 5.83 (s, =CH, 1H), 6.71 (s, aromatic, 2H), 7.41 (s, aromatic, 2H). ^{31}P NMR (DMSO-d_6, 80 °C): δ 15.4. Anal. Calcd for $(C_{10}H_{11}O_3P \cdot {}^1/_3H_2O)_n$: C, 55.56; H, 5.44. Found: C, 55.52; H, 5.30.

Instruments. The melting point was measured on a Büchi melting point apparatus and is uncorrected. NMR spectra were taken on a Varian Mercury 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.5 MHz for ^{31}P) or a Varian VXR-500S spectrometer (500 MHz for ^{1}H) in $CDCl_3$ or DMSO-d_6 using TMS (for $CDCl_3$, ^{1}H and ^{13}C) or a solvent residual peak (for DMSO-d_6, ^{1}H and ^{13}C) as the internal standards. H_3PO_4 (for $CDCl_3$ and DMSO-d_6) was used as the external standard for ^{31}P NMR measurements. SEC measurements of poly(diethyl (4-ethynylphenyl)phosphonate) and poly(ethyl methyl (4-ethynylphenyl)phosphonate) were performed with a Jasco PU-980 liquid chromatograph equipped with an RI detector (Jasco RI-930) using Tosoh TSKgel α-3000 (30 cm) and α-5000 (30 cm) SEC columns in series. DMF containing 10 mM LiCl was used as the eluent at a flow rate of 0.5 mL/min. The molecular weight calibration curves were obtained with poly(ethylene oxide) and poly(ethylene glycol) standards (Tosoh). IR spectra were recorded with a Jasco Fourier Transform IR-620 spectrophotometer. The absorption and CD spectra were measured in a 0.1-, 0.5-, 1.0-, or 10-mm quartz cell on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter, respectively. The concentrations of polymers were calculated on the basis of the monomer units and were corrected using the ϵ (molar absorptivity) values of the polymers: $\epsilon_{400} = 2253$ (poly-**1** in DMSO) and 2623 (poly-**2** in DMSO).

CD Measurements. A typical experimental procedure is described below. Stock solutions of poly-**1** (2 mg/mL) and (*R*)-**3** (22.0 mM) in DMSO were prepared. A 180 μL aliquot of the stock solution of poly-**1** was transferred to a vessel equipped with a screwcap using a micropipet (Mettler-Toledo GmbH, Switzerland). To the vessel was added 180 μL of the stock solution of (*R*)-**3** ([(*R*)-**3**]/[poly-**1**] = 2), and the CD and absorption spectra were measured.

The nonlinear effects between intensities of ICD and percent ee of **3** and **4** in the complexation with poly-**1** and poly-**2** were investigated in DMSO. A typical experimental procedure is described below. Stock solutions of poly-**1** (2 mg/mL, 10 mL), (*S*)-**3** (200 μL/2 mL), and (*R*)-**3** (200 μL/2 mL) were prepared. Aliquots of the stock solutions of (*S*)- and (*R*)-**3** were placed into six 1 or 2 mL flasks so that the percent ee of the mixtures (*R* rich) became 5, 10, 20, 30, 50, and 70, respectively. The solutions were then diluted with DMSO until the total volume of the solutions was less than half of the column of the flasks. To the flasks was added a 0.5 or 1 mL aliquot of the stock solution of poly-**1**, and the resulting solutions were immediately mixed using a vibrator (Iuchi, Japan) and finally diluted with DMSO. The poly-**1** concentration was held constant at 1 mg/mL in all runs ([**3**]/[poly-**1**] = 50 mol/mol). The same procedure was performed in the experiments with poly-**1** and **4** ([**4**]/[poly-**1**] = 50 mol/mol) and poly-**2** and **3** and **4** ([**3** or **4**]/[poly-**2**] = 10 mol/mol).

Memory of Macromolecular Helicity: SEC Fractionation of Induced Helical Poly-1 and Poly-2. A typical experimental procedure is described below. Stock solutions of poly-**1** (2 mg/mL) and (*R*)-**3** (0.11 mM) in DMSO were prepared. A 150 μL aliquot of the sock solution of poly-**1** was transferred to a vessel equipped with a screwcap, and to this was added 30 μL of the stock solution of (*R*)-**3**. The solution was then diluted with DMSO so as to keep the total volume of the solution to be 300 μL. The initial CD and absorption spectra were taken using a 0.01-cm quartz cell. SEC fractionation was performed using a Jasco PU-980 liquid chromatograph equipped with a UV (300 nm; Jasco UV-970) detector. A Shodex KF-806L SEC column (30 cm) was connected, and 0.8 M of **14** in DMSO was used as the mobile phase at a flow rate of 1.0 mL/min. One hundred microliters of the solution of the poly-**1**−(*R*)-**3** complex was injected to the SEC system, and the poly-**1** and (*R*)-**3** fractions were separately collected. The recovery of (*R*)-**3** was estimated on the basis of the UV spectrum of the (*R*)-**3** fraction using the ϵ value of (*R*)-**3** ($\epsilon_{284} = 6150$ or $\epsilon_{300} = 2520$ M^{-1} cm^{-1}). The CD and absorption spectra of the fractionated poly-**1** were measured in a 10-mm quartz cell. The same procedure was done for the SEC fractionation of helical poly-**1** and poly-**2** induced by (*R*)-**3** using DMSO containing other achiral amines as the mobile phase.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and the 21st Century COE Program "Nature-Guided Materials Processing" of the Ministry of Education, Culture, Sports, Science, and Technology. H.O. expresses thanks for a JSPS Research Fellowship (No. 05704) for Young Scientists.

Supporting Information Available: ^{1}H NMR and laser Raman spectra of poly-**1** and poly-**2** and stability of the memorized poly-**1** and poly-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) We recently reported that a macromolecular helicity induced in an achiral polyisocyanide, the sodium salt of poly(4-carboxyphenyl isocyanide), with chiral amines in water can be memorized. However, in sharp contrast to the helicity memory effects of the present polyacetylenes and the previously reported PCPA,[8] the helicity of the polyisocyanide remains after complete removal of the chiral amines without use of achiral amines. This may be due to configurational isomerization around the C═N double bonds of the polyisocyanide during the helix formation. Ishikawa, M.; Maeda, K.; Mitsutsuji, Y.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 732−733.

MA049066V