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Helicity Induction and Memory of the Macromolecular Helicity in a Polyacetylene Bearing a Biphenyl Pendant

Katsuhiro Maeda,* Shinji Tamaki, Kazumi Tamura, and Eiji Yashima*[a]

Abstract: A novel, *cis-transoidal* poly(phenylacetylene) bearing a carboxybiphenyl group as the pendant (poly-**1**) was prepared by polymerization of (4′-ethoxycarbonyl-4-biphenylyl)acetylene with a rhodium catalyst followed by hydrolysis of the ester groups. Upon complexation with various chiral amines and amino alcohols in dimethyl sulfoxide (DMSO), the polymer exhibited characteristic induced circular dichroism (ICD) in the UV/Vis region due to the predominantly one-handed helix formation of the polymer backbone as well as an excess of a single-handed, axially twisted conformation of the pendant biphenyl group. Poly-**1** complexed with (*R*)-2-amino-1-propanol showed unique time-dependent inversion of the macromolecular helicity. Furthermore, the preferred-handed helical conformation of poly-**1** induced by a chiral amine was further "memorized" after the chiral amine was replaced with achiral 2-aminoethanol or *n*-butylamine in DMSO. In sharp contrast to the previously reported memory in poly((4-carboxyphenyl)acetylene), the present helicity memory of poly-**1** was accompanied by memory of the twisted biphenyl chirality in the pendants. Unprecedentedly, the helicity memory of poly-**1** with achiral 2-aminoethanol was found to occur simultaneously with inversion of the axial chirality of the biphenyl groups followed by memory of the inverted biphenyl chirality, thus showing a significant change in the CD spectral pattern.

Keywords: biaryls · chiral memory · chirality · helical structures · poly(phenylacetylene)

Introduction

Recently, much attention has been paid to the detection[1] and amplification[2] of chirality by helical polymers and supramolecular helical assemblies, because these systems can be applied to the development of novel chiroptical devices and chiral materials as enantioselective adsorbents and catalysts.[3] Previously, we reported that optically inactive, stereoregular poly((4-carboxyphenyl)acetylene) (PCPA; Scheme 1) can form either a right- or a left-handed helix upon complexation with optically active amines, thus showing a characteristic induced circular dichroism (ICD) in the UV/Vis region of the polymer backbone.[4] This methodology of preferred-handed helicity induction with specific chiral guests has been applied to other dynamically racemic helical polymers[5,6] after the introduction of specific functional groups as pendants.[7] Moreover, the right- or left-handed macromolecular helicity of PCPA induced by optically active amines can be "memorized" when the optically active amines are replaced by various achiral amines.[8] On the other hand, conformationally labile, atropoisomeric, and chromophoric biphenyls with interconverting *P* and *M* twists have often been used as a scaffold to determine the absolute

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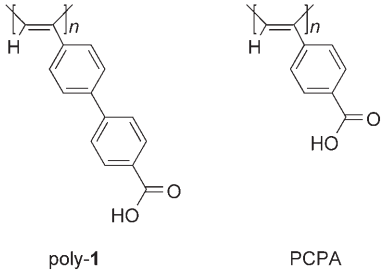


Scheme 1. Structures of poly-**1** and PCPA.

configuration of various chiral compounds[9] and to investigate the transfer of chiral information through chiral interactions.[10] Recently, the unique feature of axially chiral but dynamically racemic biphenyls was also employed for constructing chirality-sensing receptors[6o,11] as well as asymmetric catalysts.[12]

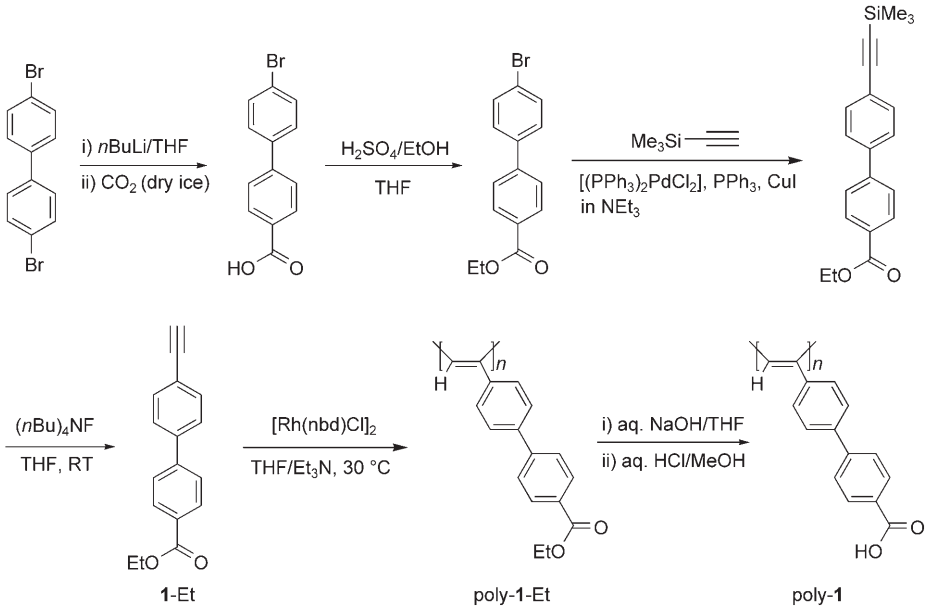
In the present study, we synthesized a novel, stereoregular poly(phenylacetylene) bearing a carboxybiphenyl group with dynamic axial chirality as the pendant, poly((4′-carboxy-4-biphenylyl)acetylene) (poly-**1**; Scheme 1), and investigated the effect of the dynamic axial chirality of the biphenyl pendants on helicity induction in the polymer backbone with chiral amines and the subsequent memory of the macromolecular helicity with achiral amines. We anticipated that the chiral information of the amines may first transfer to the axially chiral 4-carboxybiphenyl pendants through noncovalent interactions, and subsequently, the induced axial chirality with an excess twist sense could be amplified in the polymer backbone as an excess of a single-handed helix.[13] Furthermore, we also expected that the preferred-handed helicity and axially twisted conformation in the polymer backbone and the pendants, respectively, would be simultaneously memorized after removal of the chiral amines followed by replacement with achiral amines. Such a "dual-memory effect" has not yet been reported to date.[15]

Results and Discussion

Helicity Induction in Poly-1 with Chiral Amines and Amino Alcohols

Cis-transoidal stereoregular poly-**1** was prepared by polymerization of the corresponding monomer, (4′-ethoxycarbonyl-4-biphenylyl)acetylene (poly-**1**-Et), with a rhodium catalyst ($[Rh(nbd)Cl]_2$; nbd = norbornadiene) with a method similar to that previously reported,[4] followed by alkaline hydrolysis of the ester groups (Scheme 2). The stereoregularity of poly-**1** was investigated by ^1H NMR spectroscopy. The ^1H NMR spectrum of poly-**1** in $[D_6]$DMSO (DMSO = dimethyl sulfoxide) showed a sharp singlet centered at 5.85 ppm due to the main-chain protons, which indicates that this polymer has a highly *cis-transoidal*, stereoregular structure (see Supporting Information, Figure S1).[14b,16] The number-average molecular weight (M_n) and its distribution (M_w/M_n) of poly-**1** were estimated to be 1.4×10^4 and 5.3, respectively, by size-exclusion chromatography (SEC) of its methyl ester with polystyrene standards and chloroform as the eluent.

The CD spectra of *cis-transoidal* poly-**1** in the presence of various chiral amines and amino alcohols (Scheme 3) were



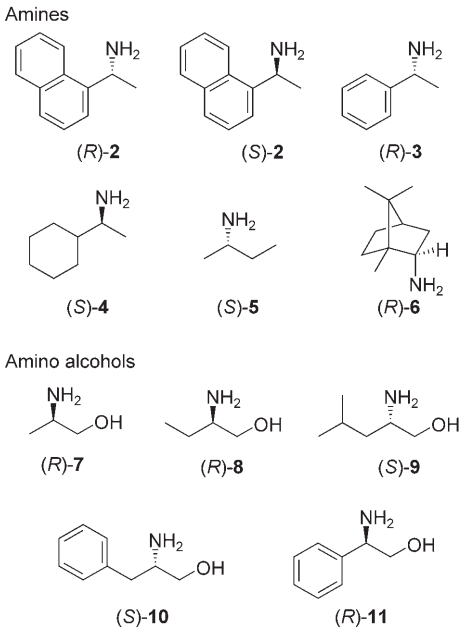
Scheme 2. Synthesis of poly-**1**.

Abstract in Japanese:

側鎖にカルボキシビフェニル基を有する新規ポリフェニルアセチレン誘導体が、光学活性アミン存在下、そのキラリティーに応答して一方向巻きに片寄ったらせん構造を形成するとともに、側鎖のビフェニル基にもどちらか一方の軸性キラルなコンホメーションが誘起され、ポリマー主鎖および側鎖のビフェニル基の吸収領域に誘起円二色性を示すことを見い出した。さらに、光学活性アミンにより誘起された主鎖のらせん構造とビフェニルの軸性キラルなコンホメーションは、光学活性アミンをアキラルなアミンに置き換えた後も記憶として保持可能であった。記憶の際に、2-アミノエタノールを用いて置換を行うと、ビフェニルの軸性キラリティーの反転を伴って主鎖のらせん構造が記憶として保持される可能性が高いことが示唆された。また、光学活性な2-アミノ-1-プロパノールを用いてらせん誘起を行うと、主鎖のらせん構造が時間の経過とともに反転を起こすことを見い出した。

recorded to investigate whether the polymer could respond to the chirality of the chiral amines and amino alcohols, thus showing characteristic ICD signals.

Typical CD and absorption spectra of poly-**1** in the presence of (*R*)-**2** and (*S*)-**2** (50 equiv to monomer units of poly-**1**) in DMSO are shown in Figure 1. Poly-**1** complexed with (*R*)-**2** and (*S*)-**2** exhibited intense, split-type ICD signals in the UV/Vis region of the polymer backbone, and these signals are mirror images of each other. The CD titration experiments with (*S*)-**2** showed that the CD intensity increased with an increase in the concentration of (*S*)-**2** and reached an almost constant value in the presence of about 10 equivalents of (*S*)-**2** (see Supporting Information, Figure S2).[17] These results indicate that poly-**1** formed a preferred-



Scheme 3. Structures of chiral amines (**2**–**6**) and amino alcohols (**7**–**11**).

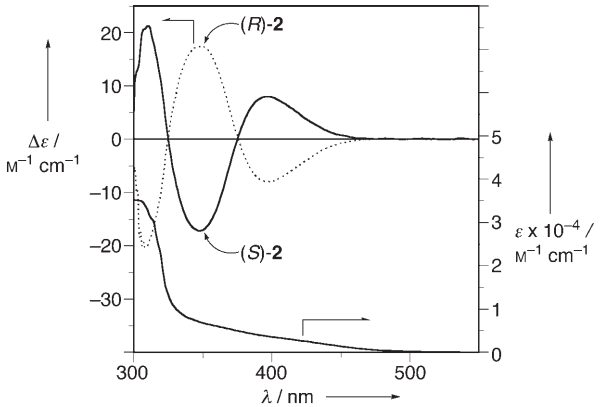


Figure 1. CD spectra of poly-**1** with (*S*)- and (*R*)-**2** in DMSO at room temperature. The absorption spectrum of poly-**1** with (*S*)-**2** is also shown. The concentration of poly-**1** was 1.0 mg (4.5 μmol monomer units) mL^{-1}. [**2**]/[poly-**1**] = 50.

handed helical conformation upon noncovalent complexation with the chiral amine in DMSO, as was observed in other dynamic helical poly(phenylacetylene)s.[5]

Poly-**1** also responded to other chiral amines and amino alcohols (Scheme 3), and the complexes exhibited similar ICD signals in their patterns except for (*R*)-**7**. The ICD results for the complexation of poly-**1** with various chiral amines (**2**–**6**) and amino alcohols (**7**–**11**) are summarized in Table 1.[17] Structurally similar chiral amines of the same configuration (**2**–**5**) afforded the same signs of the Cotton effect, whereas there is no clear relation between the signs of the induced Cotton effect for poly-**1** and the absolute configurations of the amino alcohols (**7**–**11**), although all amines (**2**–**6**) and amino alcohols (**7**–**11**) of the same configuration used in this study gave the same signs of the Cotton effect for PCPA.[4,8]

Interestingly, the CD spectral pattern of poly-**1** complexed with (*R*)-**7** slowly and dramatically changed with time, accompanied by a slight change in the absorption spectra (Figure 2A). These spectral changes may suggest inversion of the macromolecular helicity of poly-**1** with time. A similar helicity inversion assisted by external stimuli, such as a change in temperature and solvent, through noncovalent interactions has been observed in dynamic helical polymers but is still quite rare.[15f,g,18] In particular, such a slow inversion of the macromolecular helicity has not yet been reported. Other chiral amines and amino alcohols did not show such a time-dependent inversion of the signs of the Cotton effect in the UV/Vis regions of the polymer backbone as well as the pendant groups.

We considered that the observed CD signals of poly-**1** induced by chiral amines and amino alcohols may consist of contributions arising from the main-chain helicity and the

Table 1. Signs of the Cotton effect and differential molar absorptivities ($\Delta\varepsilon$) for the complexes of poly-**1** with chiral amines (**2**–**6**) and amino alcohols (**7**–**11**) in DMSO.[a]

Entry	Amine	1st Cotton		2nd Cotton		3rd Cotton		Calcd CD[b]	
		Sign	$\Delta\varepsilon$ [$M^{-1}cm^{-1}$] (λ [nm])	Sign	$\Delta\varepsilon$ [$M^{-1}cm^{-1}$] (λ [nm])	Sign	$\Delta\varepsilon$ [$M^{-1}cm^{-1}$] (λ [nm])	*X*	*Y*
1	(*R*)-**2**	n.o.[c]		−	7.90 (398)	+	17.45 (348)	3.69	2.55
2	(*S*)-**2**	n.o.[c]		+	7.97 (398)	−	17.23 (348)	−3.68	−2.57
3	(*R*)-**3**	n.o.[c]		−	8.46 (398)	+	17.47 (350)	3.31	2.72
4	(*S*)-**4**	n.o.[c]		+	2.04 (392)	−	3.69 (349)	−0.67	−0.63
5	(*S*)-**5**	n.o.[c]		+	1.32 (402)	−	1.64 (357)	0.10	−0.41
6	(*R*)-**6**	n.o.[c]		+	0.97 (391)	−	2.02 (350)	−0.54	−0.25
7	(*R*)-**7**	−	2.54 (460)	+	6.89 (401)	−	8.04 (361)	2.03	−2.24
8	(*R*)-**8**	n.o.[c]		+	5.02 (398)	−	8.41 (349)	1.35	1.61
9	(*S*)-**9**	−	0.99 (461)	+	8.02 (397)	−	14.19 (349)	−2.46	−2.60
10	(*S*)-**10**	n.o.[c]		+	8.68 (393)	−	15.99 (344)	−3.42	−2.63
11	(*R*)-**11**	n.o.[c]		+	3.58 (393)	−	7.43 (345)	−1.68	−1.07

[a] CD spectra were recorded at room temperature (20–22 °C) with a poly-**1** concentration of 1.0 mg (4.5 μmol) mL^{-1} after the samples had been allowed to stand at room temperature for 5 days (entries 1–6, 8, 10, and 11) and 14 days (entries 7 and 9). The molar ratio of chiral amine to monomeric units of poly-**1** is 50. [b] Calculated CD obtained from CD_{bip} and CD_{helix} (Figure 2B and C, respectively) by using the following equation: Calculated CD = $X(CD_{bip}) + Y(CD_{helix})$, in which *X* and *Y* represent each contribution (see text). [c] Not observed.

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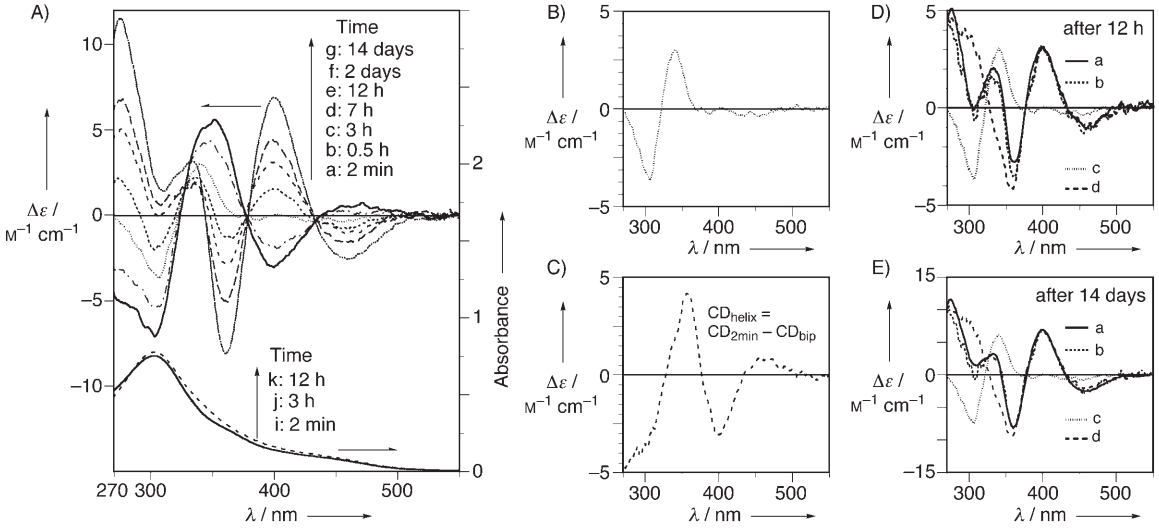

Figure 2. A) Time-dependent CD spectral changes of poly-**1** (1.0 mg mL^{-1}) with (*R*)-**7** ([(*R*)-**7**/[poly-**1**] = 50) after standing of the sample at room temperature (20–22 °C) in DMSO. Absorption spectra of poly-**1** with (*R*)-**7** after standing of the sample for 2 min, 3 h, and 12 h in DMSO are also shown. B) Observed CD spectrum (CD_{bip}) of the complex after 3 h (from trace c in Figure 2A). C) Differential CD spectrum (CD_{helix}), in which the contribution arising from CD_{bip} (Figure 2B) due to the axial chirality of the biphenyl units was subtracted from the observed CD (trace a in Figure 2A). D) Observed and calculated CD spectra of the poly-**1**–(*R*)-**7** complex after 12 h: a) observed CD spectrum of the complex (from trace e in Figure 2A); b) calculated CD spectrum of the complex; c) 1.13·CD_{bip}; d) −1.01·CD_{helix}. E) Observed and calculated CD spectra of the poly-**1**–(*R*)-**7** complex after 14 days: a) observed CD spectrum of the complex (from trace g in Figure 2A); b) calculated CD spectrum of the complex; c) 2.03·CD_{bip}; d) −2.24·CD_{helix}.

axial chirality of the pendant biphenyl units with excess single-handedness. By careful analysis of the CD spectral changes of the poly-**1**–(*R*)-**7** complex with time (Figure 2A), we noticed that CD due to the polymer backbone region above 380 nm almost completely disappeared after 3 h (trace c in Figure 2A and B), and an exciton-coupled, split-type ICD signal remained in the shorter-wavelength region (Figure 2B). We assigned this CD signal (CD_{bip}) as being probably generated in the pendant carboxybiphenyl units with an excess of a single-handed axially twisted conformation.[11a,d,f,19] If this assignment is correct, the differential CD spectrum obtained by subtracting the contribution arising from the induced axial chirality in the biphenyl units (CD_{bip} in Figure 2B) from the observed CD signal after 2 min (trace a in Figure 2A) will result in a CD pattern derived from the helical conformation of the polymer backbone induced after 2 min (CD_{helix}; Figure 2C). We found that the observed CD spectra in Figure 2A could be calculated by using the two components derived from CD_{bip} and CD_{helix} (Figure 2B and C, respectively) on the basis of Equation (1):

$$\text{Calculated CD} = X(\text{CD}_{\text{bip}}) + Y(\text{CD}_{\text{helix}}) \quad (1)$$

in which X and Y represent each contribution. For example, the observed CD spectrum of the complex after 12 h (trace a in Figure 2D) can be calculated from the sum of 1.13·CD_{bip} (trace c in Figure 2D) and −1.01·CD_{helix} (trace d in Figure 2D), whereby −1.01·CD_{helix} indicates an opposite helix sense; the calculated CD spectrum (trace b in Figure 2D) is in fair agreement with the observed one (trace a in Figure 2D), which indicates that the helical conformation of poly-**1** induced by (*R*)-**7** really inverted to the opposite sense after 12 h while maintaining the axial chirality of the biphenyl units as induced at the initial stage. In the same way, the CD spectrum after 14 days can be calculated from the sum of 2.03·CD_{bip} and −2.24·CD_{helix} (Figure 2E), which showed good agreement with the observed CD spectrum, thus suggesting that the CD intensities due to the biphenyl units as well as those from the main-chain helicity increase with time after inversion of the helix.[20]

As described above, poly-**1** complexed with (*R*)-**7** showed a time-dependent inversion of the main-chain helix sense. Figure 3A schematically illustrates a possible conformational change in poly-**1** upon complexation with (*R*)-**7**. The binding of (*R*)-**7** through acid–base interactions probably induces an excess of a single-handed, axially twisted conformation in the biphenyl units, which may determine the initial helical sense of poly-**1**.[21] However, the successive cooperative hydrogen-bond formation of the hydroxy group of (*R*)-**7** with a carboxy residue of poly-**1**,[4,8] which favors a helix sense opposite to that of poly-**1**, may result in inversion of the helicity of poly-**1** that slowly takes place with time.[22]

As for the complexes of poly-**1** with other chiral amines and amino alcohols, the contributions from the axial chirality and helical conformation induced in the biphenyl groups and the polymer backbone, respectively, could also be calculated according to Equation (1). The results are listed in Table 1 as X and Y values, and the calculated CD spectra are in fair agreement with those observed (see Supporting Information, Figures S4 and S5). These results clearly indicate that complexation with chiral amines and amino alcohols induced a preferred-handed helix and twist in the polymer backbone and the biphenyl pendants, respectively,

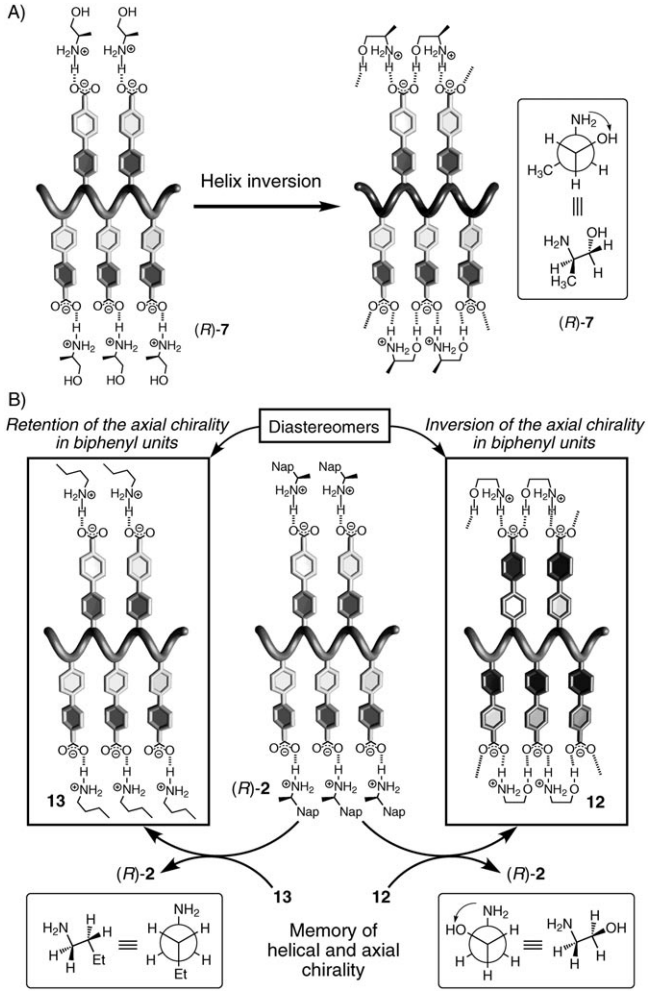

Figure 3. Schematic illustrations of the mechanism of A) helix inversion of poly-**1** upon complexation with (*R*)-**7** and B) memory of the macromolecular helicity and axial chirality of the biphenyl units of poly-**1** induced by (*R*)-**2** assisted by interactions with achiral **12** and **13**. The helicity memory of poly-**1** with **12** was accompanied by inversion of the axial chirality of the biphenyl units followed by memory of the inverted biphenyl chirality.

which occurred simultaneously, although each contribution is different depending on the structures of the chiral amines and amino alcohols used.

As previously reported for PCPA, stereoregularity appears to be important for the induction of a preferred-handed helical structure of PCPA with chiral amines.[4] We then prepared a stereoirregular poly-**1** with a WCl_6/nBu_4Sn catalyst, which is known to give *trans*-rich poly(phenylacetylene)s,[4b,23] and its CD spectra were recorded under identical conditions. The stereoirregular poly-**1** showed no ICD signals in the 300–500-nm range in the presence of (*R*)-**2** and (*S*)-**7**. Therefore, the regular *cis-transoidal* main-chain structure was found to be essential for macromolecular and axially twisted helicity induction in the polymer backbone and in the biphenyl units, respectively.

Memory of the Macromolecular Helicity and Axial Chirality

The macromolecular helicity of PCPA induced by (*R*)-**2** can be "memorized" after complete replacement of (*R*)-**2** by various achiral amines in DMSO.[8] We then investigated if similar macromolecular helicity memory could be possible for an analogous stereoregular poly-**1** that bears carboxybiphenyl groups as the pendants instead of 4-carboxyphenyl groups. 2-Aminoethanol (**12**; Figures 3B and 4) and *n*-butylamine (**13**; Figures 3B and 5) were selected as the achiral amino alcohol and amine for the memory experiments, because they are good chaperone molecules that assist in the memory of the macromolecular helicity of PCPA induced by (*R*)-**2**.[8] The memory experiments were performed in the same way as previously reported.[8] The complex of poly-**1** with 10 equivalents of (*R*)-**2** was first prepared in DMSO; the complex showed an ICD trace with maximal CD signal intensities (trace a in Figure 4A). An excess amount of achiral **12** (**12**/(*R*)-**2**/poly-**1** = 50:10:1) was then added to the solution of poly-**1**–(*R*)-**2** complex. As reported previously for PCPA, **12** is a strong base similar to (*R*)-**7** ($K = 2003\,M^{-1}$), so the complex of (*R*)-**2** ($K = 48\,M^{-1}$) with poly-**1** would be completely replaced by the excess of **12**.[8b] Nevertheless, the ICD signal was still observed, and quite surprisingly, the spectral pattern was significantly changed immediately after the addition of **12** (trace b in Figure 4A). This indicates that a dynamic conformational change in either the main chain and/or the biphenyl units may occur during the exchange reaction of bound (*R*)-**2** with achiral **12**, although the preferred-handed helical conformation of poly-**1** induced by (*R*)-**2** might be memorized after (*R*)-**2** was replaced by achiral **12**. A possible explanation for this unusual spectral change after memory will be described later.

To gain further definite evidence for the macromolecular helicity memory, poly-**1** was isolated from the poly-**1**–(*R*)-**2** complex by SEC by using a solution in DMSO containing 0.8 M **12** as the mobile phase (see Supporting Information, Figure S6). Poly-**1** eluted first followed by (*R*)-**2**, and they were completely separated. Each fraction was collected and subjected to CD and absorption measurements. On the basis of the UV/Vis spectrum of the (*R*)-**2** fraction, more than 99% of the (*R*)-**2** was recovered. The poly-**1** fraction containing a large excess of achiral **12** (0.8 M) showed an intense ICD signal in the long-wavelength region due to the polymer backbone after SEC fractionation (trace c in Figure 4A), which suggests that the macromolecular helicity of poly-**1** induced by (*R*)-**2** was memorized by achiral **12**, although the CD spectral pattern changed considerably after the replacement process. The macromolecular helicity memory of poly-**1** assisted by interactions with achiral **12** lasted for a long time, over 15 days, as observed in PCPA (see Supporting Information, Figure S7A).[8]

We found that the CD spectrum of poly-**1** induced by (*R*)-**2** and that of poly-**1** isolated by SEC could also be calculated by using Equation (1) (Figure 4B and C, respectively). The calculated CD signals for poly-**1** complexed with (*R*)-**2** and isolated poly-**1** gave best-fit spectra for the observed

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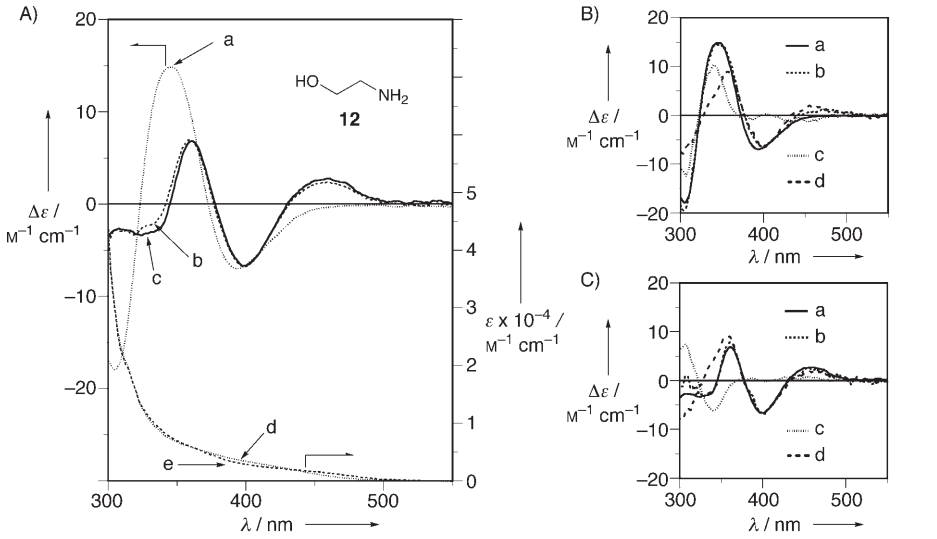

Figure 4. A) CD spectra of poly-**1** (1.0 mg mL^{-1}) with (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 10) (a), a mixture of the poly-**1**–(*R*)-**2** complex with **12** ([**12**]/[poly-**1**] = 50) (b), and isolated poly-**1** (c) by SEC fractionation with a solution of **12** (0.8 M) in DMSO as the mobile phase, in DMSO at ambient temperature (20–22 °C). Absorption spectra of poly-**1** with (*R*)-**2** (d) and a mixture of the poly-**1**–(*R*)-**2** complex with **12** (e) are also shown. B) Observed and calculated CD spectra of the poly-**1**–(*R*)-**2** complex: a) observed CD spectrum of the complex (from trace a in Figure 4A); b) calculated CD spectrum of the complex; c) 3.39·CD_{bip}; d) 2.14·CD_{helix}. C) Observed and calculated CD spectra of isolated poly-**1** by SEC: a) observed CD spectrum of the complex (from trace c in Figure 4A); b) calculated CD spectrum of the complex; c) −2.02·CD_{bip}; d) 2.17·CD_{helix}.

CD signals when the *X* and *Y* values in [Eq. (1)] were 3.39 and 2.14 (Figure 4B) and −2.02 and 2.17 (Figure 4C), respectively. These results indicate that the axial chirality at the biphenyl pendant was inverted during the exchange reaction between the bound (*R*)-**2** and **12**, while the induced macromolecular helicity of the polymer backbone was retained. On the basis of the calculated *Y* values before and after SEC fractionation (2.14 and 2.17, respectively), which correspond to the ICD intensities due to the poly-**1** backbone, the memory efficiency can be estimated to be about 100%.

As shown in Figure 3B, hydrogen-bond formation of the hydroxy group of **12** to a carboxy residue of poly-**1** may contribute to inversion of the axial chirality of the biphenyl units during the exchange reaction between the bound (*R*)-**2** and **12**; amino alcohol **12** may enter the chiral binding sites (carboxy groups of poly-**1**) with a chiral *gauche*,*staggered* conformation so as to retain the helical conformation with the same helix sense induced by (*R*)-**2**. Because the analogous chiral amino alcohol (*R*)-**7** induced the opposite helix sense in the poly-**1** backbone to that by (*R*)-**2** (Table 1), the bound **12** might have a chiral conformation similar to that of (*S*)-**7** (Figure 3B). This chiral conformation of **12** probably induces the opposite chirality at the biphenyl units to that induced by (*R*)-**2**. Therefore, the axial chirality of the biphenyl units may be inverted after replacement of the bound (*R*)-**2** with **12**.[24] This speculation was supported by the fact that the CD spectra of the poly-**1**–(*R*)-**7** complex after 14 days and poly-**1** memorized by **12** are almost-perfect mirror images of each other (see Supporting Information, Figure S8).

Next, we used a simple amine, *n*-butylamine (**13**), instead of **12** to investigate the effect of the hydroxy group on inversion of the axial chirality of the biphenyl units during the memory process. We anticipated that the induced preferred-handed helicity and axially twisted conformation in the polymer backbone and the biphenyl units, respectively, might be retained after replacement of (*R*)-**2** with **13** without inversion of the axial chirality because of the lack of a hydroxy group in **13**. The addition of an excess amount of **13** to the poly-**1**–(*R*)-**2** complex resulted in precipitation of the polymer. Therefore, the poly-**1**–(*R*)-**2** complex in DMSO was directly injected into the SEC system with a solution of DMSO containing **13** (0.8 M) as the mobile phase to remove (*R*)-**2** and replace it with achiral **13** during SEC fractionation. The isolated poly-**1** fraction containing a large excess of achiral **13** also exhibited an ICD signal in the long-wavelength region (Figure 5A). In sharp contrast to the memory of poly-**1** with achiral **12**, the CD spectral pattern did not change after SEC fractionation, although the ICD intensity decreased considerably. The CD signals before and after SEC fractionation calculated by using [Eq. (1)] gave best-fit spectra for the observed CD signals when the *X* and *Y* values were 3.39 and 2.14 (Figure 5B) and 1.14 and 1.25 (Figure 5C), respectively. These results suggest that both the induced macromolecular helicity of the polymer backbone and the axial chirality at the biphenyl units remained upon assistance by achiral **13** with a memory efficiency of 58 and 34% for the main chain and biphenyl units, respectively.[25]

Conclusions

In summary, a stereoregular poly(phenylacetylene) derivative bearing carboxybiphenyl units with dynamic axial chirality as the pendants was found to form a predominantly one-handed helical conformation upon complexation with various chiral amines and amino alcohols through noncovalent acid–base interactions in DMSO. The complexes exhibited characteristic ICD signals in the UV/Vis region due not only to the preferred-handed helix formation of the main chain but also to an excess of a single-handed, axially twisted conformation of the biphenyl units. The induced macromolecular helicity in the polymer backbone and the twisted biphenyl chirality in the pendants were further memorized

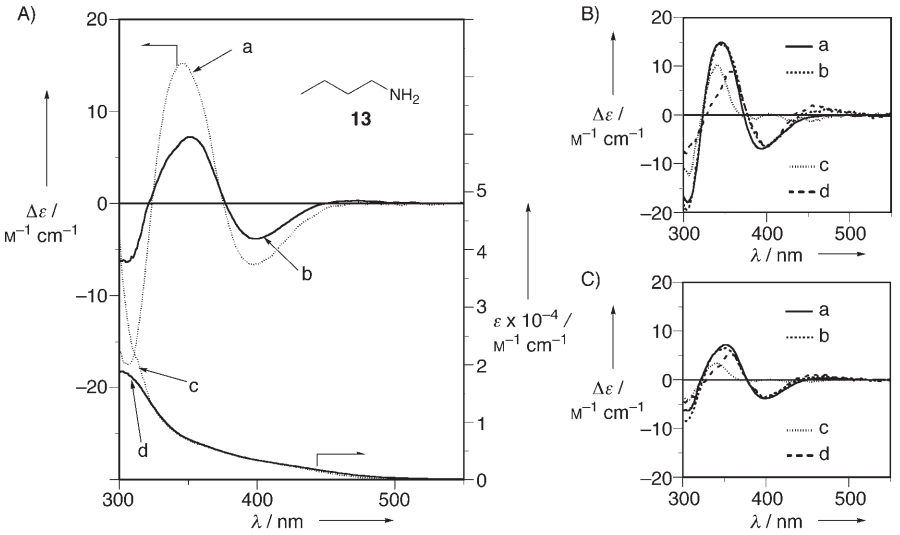

Figure 5. A) CD spectra of poly-**1** (1 mg mL^{-1}) with (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 10) (a) and isolated poly-**1** (b) by SEC fractionation with a solution of **13** (0.8 M) in DMSO as the mobile phase, in DMSO at ambient temperature (20–22 °C). Absorption spectra of poly-**1** with (*R*)-**2** (c) and isolated poly-**1** (d) by SEC fractionation are also shown. B) Observed and calculated CD spectra of the poly-**1**–(*R*)-**2** complex: a) observed CD spectrum of the complex (from trace a in Figure 5A); b) calculated CD spectrum of the complex; c) 3.39·CD_{bip}; d) 2.14·CD_{helix}. C) Observed and calculated CD spectra of isolated poly-**1** by SEC: a) observed CD spectrum of the complex (from trace b in Figure 5A); b) calculated CD spectrum of the complex; c) 1.14·CD_{bip}; d) 1.25·CD_{helix}.

by replacement of the chiral amines with achiral amines. Moreover, the memory was accompanied by inversion of the axial chirality of the biphenyl units when achiral 2-ethanolamine (**12**) was used as the chaperone molecule. Consequently, the diastereomeric helices of poly-**1** with opposite axial chirality at the biphenyl units could be successfully memorized by different amines. We believe that such helical polymers with macromolecular helicity memory together with memory of the twisted biphenyl chirality can be used in asymmetric catalysis for enantioselective reactions after modification of the biphenyl units with designer functional groups such as phosphoric acid residues.[26] Work along these lines is now in progress in our laboratory.

Experimental Section

Materials

DMSO was dried over calcium hydride and distilled under reduced pressure. Ethanol was dried over magnesium turnings and iodine and distilled onto 4-Å molecular sieves (Nacalai Tesque, Japan). THF was dried over sodium benzophenone ketyl and distilled onto $LiAlH_4$ under nitrogen. Triethylamine (NEt_3) was dried over KOH pellets and distilled onto KOH under nitrogen. These solvents were stored under nitrogen. THF and NEt_3 were redistilled under high vacuum just before polymerization. 4,4′-Dibromobiphenyl was purchased from Tokyo Kasei (TCI, Tokyo, Japan). Bis(triphenylphosphanyl)palladium dichloride and tetra-*n*-butylammonium fluoride (1 M in THF) were obtained from Wako (Osaka, Japan). (*R*)-(+)- and (*S*)-(−)-1-(1-naphthyl)ethylamine ((*R*)-**2** and (*S*)-**2**) and (*R*)-(+)-1-phenylethylamine ((*R*)-**3**) were kindly supplied by Yamakawa Chemical (Tokyo, Japan), distilled under reduced pressure, and stored under nitrogen. Other optically active amines (**4**–**11**) were available from Aldrich, TCI, or Wako. 2-Aminoethanol (**12**; Kishida, Osaka, Japan) was dried over calcium oxide under nitrogen and distilled under reduced pressure. *n*-Butylamine (**13**; Kishida) was dried over calcium hydride and distilled under nitrogen. These amines were stored under nitrogen. (Trimethylsilyl)acetylene was kindly supplied by Shinetsu Chemical (Tokyo, Japan). Triphenylphosphine and copper(I) iodide (CuI) were obtained from Kishida. *n*-Butyllithium (1.6 M in hexane) was purchased from Kanto Kagaku (Tokyo, Japan). [Rh(nbd)Cl]$_2$ was obtained from Aldrich. Trimethylsilyldiazomethane (10% hexane solution) was from Nacalai Tesque. WCl_6 was purchased from Mitsuwa Chemical (Osaka, Japan) and used as received.

Instruments

Melting points were measured on a Yanako melting-point apparatus and are uncorrected. NMR spectra were taken on a Varian Mercury 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) or a Varian VXR-500S (500 MHz for ^{1}H) spectrometer in $CDCl_3$ or [D_6]DMSO with tetramethylsilane (TMS; for $CDCl_3$, ^{1}H and ^{13}C) or a residual solvent peak (for [D_6]DMSO, ^{1}H and ^{13}C) as the internal standard. SEC measurements were performed with a JASCO PU-980 liquid chromatograph equipped with a UV/Vis (JASCO UV-970) detector at 40 °C. The temperature was controlled with a JASCO CO-965 column oven. A Tosoh TSKgel MultiporeH_{XL}-M SEC column (30 cm) was connected, and chloroform was used as the eluent at a flow rate of 1.0 mL min^{-1}. The molecular-weight calibration curve was obtained with polystyrene standards (Tosoh). IR spectra were recorded with a JASCO Fourier transform IR-7000 spectrophotometer. Laser Raman spectra were recorded on a JASCO NRS-1000 spectrophotometer. Absorption and CD spectra were recorded in a 0.1-, 1.0-, or 4.0-mm quartz cell on a JASCO V-570 or Ubest-55 spectrophotometer and a JASCO J-725 spectropolarimeter, respectively. The concentration of poly-**1** was calculated on the basis of the monomer units and was corrected by using the ε (molar absorptivity) value of the polymer ($\varepsilon_{400} = 3636\ M^{-1}cm^{-1}$ in DMSO).

Synthesis and Polymerization

1-Et: (4′-Ethoxycarbonyl-4-biphenylyl)acetylene: Prepared according to Scheme 2. *n*BuLi (1.6 M in *n*-hexane, 27 mL, 42 mmol) was added dropwise to a solution of 4,4′-dibromobiphenyl (18.7 g, 60.0 mmol) in THF (280 mL) at −78 °C. After the mixture was stirred at −78 °C for 5 min, an excess of CO_2 (dry ice) was added to the solution. After being stirred at −78 °C for 20 min, the reaction mixture was allowed to warm to room temperature and was further stirred at room temperature for 1 h. After acidification with 1 N HCl, the precipitated solid was extracted with THF (500 mL). The organic layer was washed with brine and then dried over $MgSO_4$. After filtration, the filtrate was evaporated under reduced pressure. The resulting crude 4-bromo-4′-carboxybiphenyl, which contained a small amount of 4,4′-dicarboxybiphenyl (12.5 mol%), was suspended in THF (100 mL) and ethanol (200 mL). Concentrated H_2SO_4 (20 drops) was added to this suspension, and the mixture was heated under reflux for 5 days. After evaporation of the solvent, the residue was diluted with ethyl acetate. The organic layer was washed with saturated aqueous Na_2CO_3 and water and dried over Na_2SO_4. After filtration, the solvent was removed by evaporation to yield crude 4-bromo-4′-ethoxycarbonylbiphenyl. This was used for the next reaction without further purification. Bis(triphenylphosphanyl)palladium dichloride (1.2 g, 1.7 mmol), triphenylphosphine (0.25 g, 1.0 mmol), and copper(I) iodide (0.25 g, 1.3 mmol) were added to a solution of 4-bromo-4′-ethoxycarbonylbiphenyl (6.1 g,

20 mmol) in Et_3N (125 mL), and the reaction mixture was stirred under nitrogen at room temperature for 1 h. (Trimethylsilyl)acetylene (15 mL, 105 mmol) was then added, and the reaction mixture was stirred under reflux at 90 °C. After 48 h, the reaction mixture was filtered to remove the catalyst, and the filtrate was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (50 mL), and the solution was washed with water. After the solvent was removed under reduced pressure, the resulting (4′-ethoxycarbonyl-4-biphenylyl)trimethylsilylacetylene was dissolved in THF (50 mL), and a solution of tetrabutylammonium fluoride in THF (99 mL, 99 mmol) was added to this solution. The resulting solution was stirred under nitrogen at room temperature for 25 min before evaporation of the solvent. The crude product was diluted with diethyl ether, the solution was washed with 1% aqueous HCl and water, and then the ether layer was dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to chromatography on silica gel with hexane/ethyl acetate (20:1 *v*/*v*). After evaporation of the solvent, the residue was further purified by recrystallization from hexane to give **1**-Et as a light-yellow powder (1.7 g, 31%). M.p.: 96.5–97.5 °C; IR (nujol): $\tilde{\nu}$ = 3240 (≡C−H), 1700 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$, room temperature): δ = 1.42 (t, J = 7.0 Hz, 3H; CH_3), 3.16 (s, 1H; ≡CH), 4.40 (q, J = 7.0 Hz, 2H; CH_2), 7.59 (s, 4H; aromatic), 7.61 (d, J = 7.0 Hz, 2H; aromatic), 8.12 ppm (d, J = 7.0 Hz, 2H; aromatic); ^{13}C NMR (75 MHz, $CDCl_3$, room temperature): δ = 14.5, 61.2, 79.4, 83.4, 122.0, 126.5, 127.8, 129.8, 130.3, 132.8, 140.5, 144.6, 166.5 ppm; elemental analysis: calcd (%) for $C_{17}H_{14}O_2$ (250.3): C 81.58, H 5.64; found: C 81.48, H 5.50.

Poly-**1**-Et: The polymerization was carried out according to Scheme 2 in a dry glass ampoule under dry nitrogen atmosphere with $[Rh(nbd)Cl]_2$ as a catalyst. A typical polymerization procedure is described below.[4,5f] Monomer **1**-Et (1.13 g, 4.53 mmol) was placed in a dry ampoule, 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 ampoule, and dry THF (3.0 mL) and Et_3N (9.0 mL) was added with a syringe. A solution of $[Rh(nbd)Cl]_2$ (0.05 M) in THF was added to this mixture at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.35 and 0.0035 M, respectively. The solution immediately gelated within 1 min. After 3 min, the resulting polymer was precipitated in a large amount of methanol. The precipitated polymer was collected by centrifugation, washed with methanol, and dried in vacuo at 50 °C for 2 h (1.10 g, 97%). Poly-**1**-Et was partly soluble in DMSO but insoluble in chloroform, dioxane, *N*,*N*-dimethylformamide (DMF), acetonitrile, and toluene. IR (nujol): $\tilde{\nu}$ = 1717 cm^{-1} (C=O); elemental analysis: calcd (%) for $(C_{17}H_{14}O_2)_n$: C 81.58, H 5.64; found: C 81.57, H 5.67.

Poly-**1**: Poly-**1**-Et was converted into poly-**1** by hydrolysis of the ester groups in THF/aqueous NaOH (10 N) (13:1 *v*/*v*) at room temperature for 24 h. The hydrolyzed polymer was collected by centrifugation and washed with methanol. The same hydrolysis procedure was repeated two times. The hydrolyzed polymer was suspended in methanol/aqueous HCl (10%) (7.5:1 *v*/*v*), and the suspension was stirred at room temperature for 2 h. The acidified polymer was collected by centrifugation, washed with water, and dried in vacuo at 50 °C for 2 h. The ^1H NMR spectrum of the obtained poly-**1** showed that it contained about 3% of the ethyl ester group. Poly-**1** is soluble in DMSO. IR (nujol): $\tilde{\nu}$ = 1692 cm^{-1} (C=O); ^1H NMR (500 MHz, $[D_6]$DMSO, 80 °C): δ = 5.85 (s, 1H; =CH), 6.84 (singletlike, 2H; aromatic), 7.32 (singletlike, 2H; aromatic), 7.86 (singletlike, 2H; aromatic), 7.91 ppm (singletlike, 2H; aromatic); elemental analysis: calcd (%) for $(0.97C_{15}H_{10}O_2{\cdot}0.03C_{17}H_{14}O_2)_n$: C 81.08, H 4.57; found: C 81.08, H 4.60. The ^1H NMR spectrum of poly-**1** in $[D_6]$DMSO showed a singlet centered at 5.85 ppm due to the main-chain protons, which indicates that the polymer has a highly *cis-transoidal*, stereoregular structure (see Supporting Information, Figure S1).[16] The Raman spectrum of poly-**1** exhibited intense peaks at 1548, 1344, and 970 cm^{-1}, which are characteristic peaks due to the *cis* polyacetylenes and can be assigned to the C=C, C−C, and C−H vibrations, respectively. On the other hand, peaks of the *trans* polyacetylenes were hardly observed (see Supporting Information, Figure S9).[27] This result also supports the hypothesis that poly-**1** has a highly *cis-transoidal* structure.

Poly-**1** methyl ester: Conversion of poly-**1** into the methyl ester was carried out with trimethylsilyldiazomethane according to the method reported previously.[28] The obtained methyl ester was soluble in chloroform containing a small amount of trifluoroacetic acid (2 vol%). The number-average molecular weight (M_n) and its distribution (M_w/M_n) of poly-**1** were estimated in the form of its methyl ester to be 1.4×10^4 and 5.3, respectively, by SEC with polystyrene standards and chloroform as the eluent.

Poly-**1′**-Et: Poly[(4′-ethoxycarbonyl-4-biphenylyl)acetylene] (poly-**1′**-Et) with a different stereostructure was prepared by a different route.[4b] Compound **1**-Et (0.2 g in toluene, 0.5 M) was polymerized with WCl_6/$n$$Bu_4Sn$ (1:1 mol/mol, [**1**]/[WCl_6] = 100) in dry toluene at 60 °C. The resulting polymer was precipitated in a large amount of methanol, collected by centrifugation, and dried in vacuo at 50 °C for 2 h. The obtained polymer was found to contain a small amount of oligomers by ^1H NMR spectroscopy. To remove the oligomers, the crude polymer was dissolved in THF (5 mL), and the solution was poured into toluene/hexane (1:3 *v*/*v*). The resulting dark-brown precipitate of poly-**1′**-Et was collected by centrifugation and dried in vacuo at 50 °C for 2 h (0.15 g, 74%). The M_n and M_w/M_n values of poly-**1′**-Et were 4.0×10^4 and 2.4, respectively, as determined by SEC with polystyrene standards and THF as the eluent. IR (nujol): $\tilde{\nu}$ = 1720 cm^{-1} (C=O); ^1H NMR (500 MHz, $[D_6]$DMSO, 60 °C): δ = 5.2–8.2 ppm (br, 8H; =CH and aromatic); elemental analysis: calcd (%) for $(C_{17}H_{14}O_2)_n$: C 81.58, H 5.64; found: C 81.78, H 5.49.

Poly-**1′**: Poly-**1′**-Et was converted into poly[(4′-carboxy-4-biphenylyl)acetylene] (poly-**1′**) by hydrolysis of the ester groups in a similar way to that described above. The ^1H NMR spectrum of the obtained poly-**1′** showed that it contained about 4% of the ethyl group. The ^1H NMR spectrum of poly-**1′** showed very broad resonances at 5.2–8.8 ppm, which indicates that the polymer prepared by the WCl_6/$n$$Bu_4Sn$ catalyst may not be stereoregular in the main-chain configuration and conformation.[4b,23] The Raman spectrum of poly-**1′** exhibited intense peaks at 1520 and 1232 cm^{-1}, which are characteristic peaks due to the *trans* polyacetylenes and can be assigned to the C=C and C−C vibrations, respectively (see Supporting Information, Figure S9). This indicates that poly-**1′** has a *trans*-rich structure.[27] IR (nujol): $\tilde{\nu}$ = 1693 cm^{-1} (C=O); ^1H NMR (500 MHz, $[D_6]$DMSO, 60 °C): δ = 5.2–8.8 ppm (br, 8H; =CH and aromatic).

CD Measurements

Anhydrous DMSO was used throughout for all measurements. A typical experimental procedure is described below. The concentration of poly-**1** was calculated based on the monomer units and was 1 mg mL^{-1} (4.5 mM monomer units) unless otherwise stated. A stock solution of poly-**1** (1 mg mL^{-1}) in DMSO was prepared in a 10-mL flask equipped with a stopcock. A 1-mL aliquot of the solution of poly-**1** was transferred to a vessel equipped with a screwcap by using a Hamilton microsyringe. An appropriate amount of *R* or *S* amine was added to the vessel. The solution was immediately mixed with a vibrator (Iuchi, Japan), and absorption and CD spectra were recorded. For CD titration experiments, stock solutions of poly-**1** (20 mg/10 mL) and (*S*)-**2** (100 μL/1 mL) in DMSO were prepared. A 500-μL aliquot of the solution of poly-**1** was transferred to five 1-mL flasks equipped with stopcocks by using a Hamilton microsyringe. An appropriate amount of the stock solution of (*S*)-**2** was added to the flasks. The solutions were immediately mixed with a vibrator and finally diluted with DMSO to keep the poly-**1** concentration at 1 mg mL^{-1}. Then, absorption and CD spectra were taken for each flask to give the titration curve (see Supporting Information, Figure S2).

Memory of Macromolecular Helicity and Pendant Axial Chirality

SEC fractionation of induced helical poly-**1**: Experiments on the memory of the macromolecular helicity and the pendant axial chirality were carried out according to the reported methods.[8] A stock solution of (*R*)-**2** (100 μL mL^{-1}) in DMSO was prepared. A solution of poly-**1** in DMSO (5 mg/≈4 mL) was prepared in a 5-mL flask equipped with a stopcock. The stock solution of (*R*)-**2** (366 μL) was added to this solution by using a Hamilton microsyringe, and the resulting solution was diluted with DMSO to keep the poly-**1** concentration at 1 mg mL^{-1} (4.5 mM) ([(*R*)-**2**]/

[poly-**1**] = 10 mol/mol). The initial CD and absorption spectra were recorded in a 0.1-mm quartz cell. The solution of the poly-**1**–(*R*)-**2** complex (500 μL) was transferred to a vessel with a screw cap by using a transfer pipette. Compound **12** (6.9 μL; [**12**]/[poly-**1**] = 50) was directly added to this solution by using a Hamilton microsyringe, and then the CD and absorption spectra were recorded in a 0.1-mm quartz cell. SEC fractionation was performed by 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 **12** in DMSO was used as the mobile phase at a flow rate of 1.0 mL min^{-1}. The solution (100 μL) of poly-**1** with (*R*)-**2** and **12** was injected into the SEC system, and the poly-**1** and (*R*)-**2** fractions were collected separately. The recovery of (*R*)-**2** was estimated to be more than 99% on the basis of the UV/Vis spectrum of the (*R*)-**2** fraction (ε value of (*R*)-**2**: $\varepsilon_{284} = 6150$, $\varepsilon_{300} = 2520\ \text{M}^{-1}\text{cm}^{-1}$). The CD and absorption spectra of the fractionated poly-**1** were recorded in a 4.0-mm quartz cell.

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[21] The helix senses of poly-**1** in Figure 3 were assigned on the basis of the signs of the Cotton effect of the ICD signals of analogous helical polyacetylenes and their helical senses determined by atomic force microscopy (AFM).[16g,h] The twist senses of the axial chirality of the biphenyl groups were tentatively assigned on the basis of the signs of the Cotton effect of the ICD signals of an analogous biphenyl compound.[19]

[22] Structurally similar chiral amino alcohols, such as (*R*)-**8** and (*S*)-**9**, did not show such a time-dependent inversion of the helix sense, and the complexes exhibited the same CD pattern even after heating at 80 °C. The reason is not clear at present, but a delicate balance in the bulkiness of the substituents of the amino alcohols may be important for the time-dependent inversion of the helix, as observed for the poly-**1**–(*R*)-**7** system.

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