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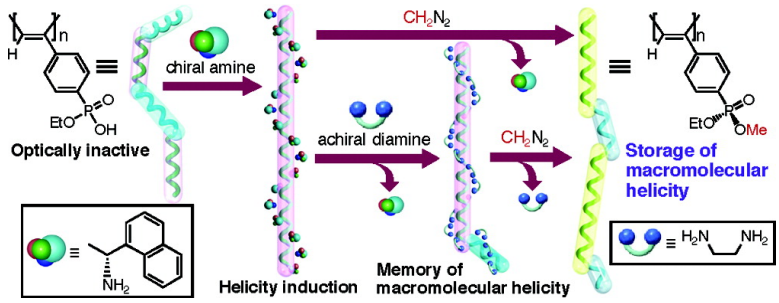

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Enantioselective Esterification of Prochiral Phosphonate Pendants of a Polyphenylacetylene Assisted by Macromolecular Helicity: Storage of a Dynamic Macromolecular Helicity Memory

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Abstract: A poly(phenylacetylene) bearing a phosphonic acid monoethyl ester as the pendant forms a one-handed helical structure induced by an optically active amine, and this helicity can be "memorized" after the amine is replaced by achiral diamines. The helicity memory lasts for an extremely long time but spontaneously disappears after the achiral diamines are removed by a stronger acid, indicating the dynamic nature of the helicity memory. Here we report that such a dynamic memory could be "stored" after the pendant was converted to its methyl ester with diazomethane, resulting in the generation of a phosphorus stereogenic center with optical activity. The esterification enantioselectively proceeded through chirality transfer from the induced helical conformation or the helicity memory of the polyacetylene backbone. Although the enantioselectivity was low, the pendant chirality was significantly amplified in the polymer backbone at low temperatures, resulting in higher optical activity as an excess single-handed helix than that expected from the enantiomeric excess of the pendants.

Introduction

The detection and sensing of chirality at molecular and supramolecular levels have attracted considerable interest in recent years,[1] and a number of receptor molecules,[2] supramolecules,[3] and π-conjugated macromolecules[4] have been developed for this purpose because they can be further applicable to chiroptical devices, enantioselective adsorbents, and catalysis.[5] In general, these receptors are achiral or dynamically racemic, but chromophoric, so that upon noncovalent binding to a nonracemic guest the chirality transforms to the receptors, resulting in the generation of one of the enantiomeric twisted or helical conformers, thus leading to a characteristic induced circular dichroism (ICD) in the absorption region of the receptors.[1] The induced chirality or helicity in the receptors is dynamic in nature but can be "memorized" in the specific receptors when the guest is replaced by an achiral guest.[6] This is a typical example of chiral amplification at the supramolecular level.[1e,6k,7] However, the use of achiral guests is essential to

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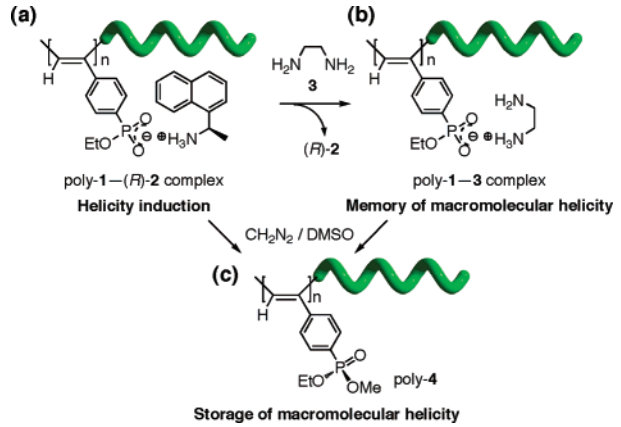

Figure 1. Schematic illustration of helicity induction in poly-**1** upon complexation with (*R*)-**2** (a), memory of the induced macromolecular helicity after replacement of (*R*)-**2** by achiral **3** (b), and storage of the induced helicity and helicity memory by enantioselective esterification with diazomethane (c). The absolute configuration of the pendant phosphorus atom is tentatively assigned to *R* (see text).

maintain the memory effect; in the absence of the achiral guest, the memory will be lost.[6,8] Here we show that such a dynamic memory in a helical poly(phenylacetylene) bearing a phosphonic acid monoethyl ester as the pendant (poly-**1**) can be "stored (saved)" by the further enantioselective esterification at the polymer's pendant assisted by helicity memory (Figure 1).

Our strategy for the storage of macromolecular helicity memory is based on a unique feature of dynamic helical poly(phenylacetylene)s with functional groups for the amplification of chirality with high cooperativity.[9] For instance, poly-**1**[10] formed a one-handed helix upon complexation with optically pure (*R*)-1-(1-naphthyl)ethylamine ((*R*)-**2**) and even with a nonracemic, 40% enantiomeric excess (ee) of **2** (*R* rich) in dimethyl sulfoxide (DMSO); both complexes exhibited a full ICD in the polymer backbone region independent of the ee of **2**.[6i] The molar ellipticity of the second Cotton effect ($\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1})) reached +16.9 ([**2**]/[poly-**1**] = 2). Moreover, the induced helix remained when the optically active amine was completely removed and replaced with achiral diamines such as ethylenediamine (**3**) in DMSO; the memory efficiency as estimated on the basis of the $\Delta\epsilon_{2nd}$ values before and after the replacement of (*R*)-**2** with the achiral **3** was 93%.[6i] The pendant phosphonate complexed with **3** appears to be achiral because of the resonance effect of the P−OH and P═O groups.[11] However, the further esterification with diazomethane results in the generation of the phosphorus stereogenic center; therefore, when the esterification could proceed enantioselectively, the polymer might preserve the helicity memory (Figure 1), because the pendant chirality can be significantly amplified in the polymer backbone as greater excess of a single-handed helix than that expected from the pendant chirality.[1e,7,9i,j]

Results and Discussion

Enantioselective Esterification of Helical Poly-1 Induced by Chiral Amines with Diazomethane. The methyl esterification of the pendants was then performed for the helical poly-**1** induced by (*R*)-**2** ([poly-**1**] = 1.0 mg/mL, [(*R*)-**2**]/[poly-**1**] = 10) in DMSO by the addition of an ether solution of diazomethane.[6i,12] The esterification immediately proceeded, yielding the corresponding methyl esters (poly-**4a**). The ^{1}H NMR and elemental analysis indicated that the pendant phosphonates were completely methylated and that poly-**4a** was free from the chiral ligand (*R*)-**2** (see Supporting Information). Figure 2A(a,c) shows the circular dichroism (CD) and absorption spectra of poly-**4a** in methanol at 25 °C. Poly-**4a** exhibited weak but apparent Cotton effects in the UV−visible region of the polymer backbone ($\Delta\epsilon_{2nd}$ = +2.2 (run 1 in Table 1)); the Cotton effect pattern was similar to those of the helical poly-**1** induced by (*R*)-**2** and poly-**1** with helicity memory assisted by achiral **3**.[6i] Poly-**4a** showed no further increase in the Cotton effects by the addition of excess (*R*)-**2**. Moreover, the fact that the

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(10) *Cis−transoid* poly-**1** was prepared by the polymerization of ethyl (4-ethynylphenyl)phosphonate (**1**) with $[Rh(cod)_2]BF_4$ (cod = cyclooctadiene) in water in the presence of sodium hydroxide at 30 °C for 24 h according to the previously reported method (see Supporting Information).[6i] The stereoregularity of poly-**1** was examined by ^{1}H NMR and laser Raman spectroscopies and found to be almost complete *cis−transoid*. The molecular weight (M_n) and the distribution (M_w/M_n) of poly-**1** were estimated to be 1.9×10^4 and 3.5, respectively, as its methyl ester by size exclusion chromatography (SEC) with poly(ethylene oxide) and poly(ethylene glycol) standards in DMF containing 10 mM lithium chloride.

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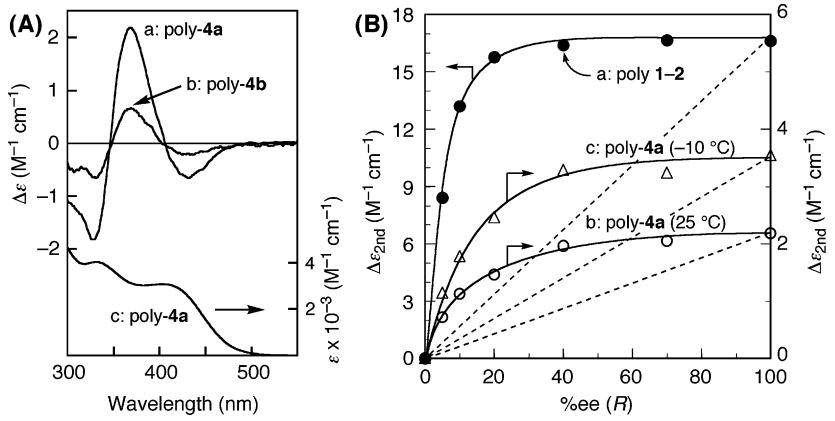
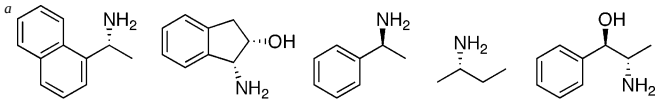


Figure 2. (A) CD and absorption spectra of poly-**4a** (a) and poly-**4b** (b) (1.0 mg/mL) in methanol at 25 °C obtained by esterification with diazomethane of a helical poly-**1** induced by (*R*)-**2** and a helical poly-**1** with helicity memory after isolation, respectively. The absorption spectrum of poly-**4a** is also shown in (c). (B) Nonlinear effects between ICD values for second Cotton effect and percent ee of **2** (*R* rich, 10 equiv) in complexation with poly-**1** (1 mg/mL) in DMSO at 25 °C (a, ●) and after esterification with diazomethane of helical poly-**1**'s induced by nonracemic **2**. The CD spectra of the resulting poly-**4a** were measured in methanol at 25 (b, ○) and −10 °C (c, △).

Table 1. Effect of Chiral Amines on Enantioselective Esterification of Induced Helical Poly-**1** with Diazomethane

		second Cotton effect ($\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1}))	
run	chiral amine[a]	poly-**1**[b]	poly-**4a**[c]
1[d]	(*R*)-**2**	16.9	2.2
2	(*R*)-**2**	16.7	1.9
3	(*S*)-**2**	−16.4	−2.0
4	(1*R*,2*S*)-**5**	18.9	2.8
5	(*S*)-**6**	−15.6	−2.1
6	(*S*)-**7**	−17.8	−2.2
7	(1*R*,2*S*)-**8**	18.4	1.8

[a]



(*R*)-**2** (1*R*,2*S*)-**5** (*S*)-**6** (*S*)-**7** (1*R*,2*S*)-**8**

[b] Induced CD intensity of poly-**1** (10 mg/mL) upon complexation with chiral amines in DMSO at ambient temperature (ca. 25 °C) before esterification; [amine]/[poly-**1**] = 5. [c] Reaction with diazomethane was performed in DMSO at ambient temperature. CD spectra were measured in methanol at 25 °C. [d] [Poly-**1**] = 1 mg/mL and [amine]/[poly-**1**] = 10.

optical activity of poly((4-phosphonophenyl)acetylene)[13] induced by (*R*)-**2** completely disappeared after the reaction with diazomethane in the presence of (*R*)-**2**, resulting in poly(dimethyl (4-ethynylphenyl)phosphonate) bearing the achiral phosphonate pendants, also supports the complete conversion of poly-**1** to poly-**4a**, and the optical activity of poly-**4a** was concluded to be derived from the pendant chirality generated during the reaction with diazomethane. These results clearly indicate that the induced macromolecular helicity of poly-**1** was successfully stored in the poly(phenylacetylene) even after complete removal of the chiral amine and that the helical chirality appears to play an important role in the enantioselective esterification, because the esterification of the corresponding monomer (**1**) under the same experimental conditions as poly-**1** resulted in the formation of completely racemic methyl esters (Supporting Information).[14] The importance of the induced helical chirality for the enantioselective esterification was also supported by the nonlinear effects between the ICD intensity of poly-**4a** and the ee of **2** for the helicity induction on poly-**1** and a chiral amplification effect on the enantioselective esterification of a helical poly-**1** induced by a small amount of (*R*)-**2** and excess achiral amine. These results will be described later in detail.

The enantioselective esterification results of helical poly-**1**'s induced by other chiral amines in DMSO are summarized in Table 1. When (1*R*,2*S*)-*cis*-1-amino-2-indanol ((1*R*,2*S*)-**5**) was used for the helicity induction on poly-**1**, the $\Delta\epsilon_{2nd}$ value of the resulting poly-**4a** in methanol slightly increased to +2.8 at 25 °C (run 4 in Table 1), but the enantioselectivity ($\Delta\epsilon_{2nd}$ value of poly-**4a**) appeared to be almost independent of the structures of the chiral amines used. The Cotton effect signs of poly-**1**, corresponding to the helix sense of poly-**1**, induced by the chiral amines depended on the configuration of the chiral amines used,[6i] which was maintained after the esterification reaction with diazomethane, resulting in a helical poly-**4a** with the same helix sense as that of the induced helical poly-**1**. Therefore, a helical poly-**1** induced by (*S*)-**2** was converted to poly-**4a** with macromolecular helicity opposite that induced by (*R*)-**2** (runs 2 and 3 in Table 1). The effects of temperature and solvents during the enantioselective esterification of poly-**1** with diazomethane were also investigated, but the enantioselectivity was not significantly improved (see Supporting Information).

Nonlinear Effects in the Helicity Induction on Poly-1 with Nonracemic 2 and Subsequent Storage of the Helical Chirality. We recently reported that the complex formation of

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poly-**1** with nonracemic **2** displayed a unique, positive nonlinear relationship (chiral amplification or "majority rule")[7,15] between the ee of **2** and the ICD intensities of poly-**1**, corresponding to the helical sense excesses in DMSO, and 40% ee of **2** was sufficient to induce a full ICD for poly-**1**[6i] (Figure 2B(a)). The excess enantiomers bound to the poly-**1** 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 **2**.[16] We then performed the same esterification reaction for the helical poly-**1**'s induced by nonracemic **2** (*R* rich) with different ee's (Figure 2B(b,c)). The resulting poly-**4a** also exhibited similar nonlinear effects. For instance, poly-**4a** obtained from a helical poly-**1** induced by 40% ee of **2** ((*R*)-**2**:(*S*)-**2** = 70:30) with diazomethane exhibited almost the same ICD intensity as that obtained from optically pure (*R*)-**2** even in the presence of the opposite enantiomer bound to the polymer's pendants, indicating that the enantioselectivity is mainly controlled by the helical chirality rather than the chirality of the bound **2**.[16,17]

Chiral Amplification in the Macromolecular Helicity of Poly-1 Assisted by Achiral Amine and Subsequent Storage of the Helical Chirality. Previously, we demonstrated that a slight excess of the one-handed helix sense of poly((4-carboxyphenyl)acetylene) (PCPA) induced by a small amount of chiral amines was significantly amplified by the coexistence of achiral bulky amines, thus showing an increase in the ICD magnitude of PCPA.[18] This can be considered a typical example of the chiral amplification in a polymer through a noncovalent interaction. The extent of macromolecular helicity amplification in PCPA tended to increase with an increase in the bulkiness of the achiral amines, and 1-naphthylmethylamine (NMA) showed the highest chiral amplification in PCPA among the achiral amines tested.[18] On the basis of these observations, we carried out the same chiral amplification experiments according to the previously reported method.[18] The esterification of the helical poly-**1** induced by a small amount of (*R*)-**2** and an excess achiral amine NMA with diazomethane was then performed.

In the presence of a small amount of (*R*)-**2** ([poly-**1**] = 1.0 mg/mL, [(*R*)-**2**]/[poly-**1**] = 0.3), poly-**1** showed a very weak ICD ($\Delta\epsilon_{2nd} = +1.1$). The $\Delta\epsilon_{2nd}$ value was only ca. 1/15 of the $\Delta\epsilon_{max}$ (+16.9) due to the lack of a single-handed helical conformation of poly-**1**; that is, a small amount of (*R*)-**2** bound to poly-**1** cannot induce the same helix on the major free monomeric phosphonic acid units. However, the ICD intensity of the poly-**1**−(*R*)-**2** complex ([(*R*)-**2**]/[poly-**1**] = 0.3) increased with the increasing concentration of achiral NMA and reached a maximum value at [NMA]/[poly-**1**] = 1.0 ($\Delta\epsilon_{2nd} = +15.7$) (Figure 3a). The ICD intensity was not time-dependent. These results indicate that the slight excess of single-handed helical chirality of poly-**1** induced by a small amount of (*R*)-**2** was significantly amplified by the coexistence of excess achiral amine to give poly-**1** with almost the complete one-handed helix;

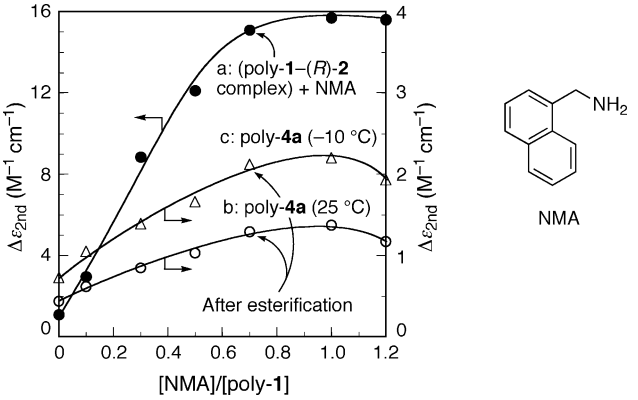

Figure 3. Results of chiral amplification in macromolecular helicity of poly-**1** (1.0 mg/mL) induced by (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 0.3) followed by achiral NMA in DMSO at 25 °C (a, ●) and storage of helical chirality by reaction with diazomethane (○ and △). CD spectra of poly-**4a** were measured in methanol at 25 (b, ○) and −10 °C (c, △).

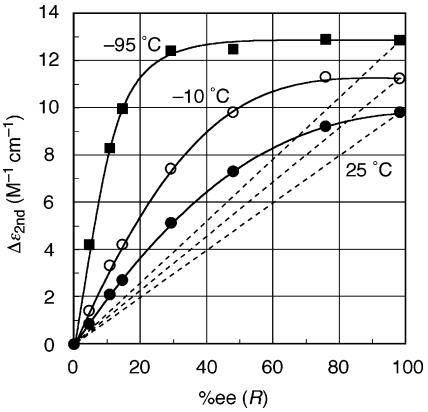

Figure 4. Plots of CD intensity at second Cotton effect of copolymers of nonracemic **4** (*R* rich) versus percent ee of feed monomers. The CD spectra were measured in methanol at 25 (●), −10 (○), and −95 °C (■).

the helix sense excess of the poly-**1** was 93% on the basis of the $\Delta\epsilon_{max}$ value.

The same enantioselective esterification was then performed for helical poly-**1**'s induced by a small amount of (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 0.3) with an increasing amount of NMA (Figure 3b,c). The $\Delta\epsilon_{2nd}$ value of poly-**4a** obtained from poly-**1** with 0.3 equiv (*R*)-**2** was small (0.44 at 25 °C), but it significantly increased with the increasing concentration of NMA; for instance, poly-**4a** obtained from a helical poly-**1** induced by 0.3 equiv (*R*)-**2** and 1.0 equiv NMA with diazomethane exhibited $\Delta\epsilon_{2nd} = +1.4$ at 25 °C even in the presence of the achiral NMA bound to the polymer's pendants (Figure 3b). Although this value is less than +2.2 for the poly-**4a** obtained from optically pure (*R*)-**2**, these results also support the belief that the enantioselectivity is mainly controlled by the helical chirality rather than the chirality of the bound **2**.

Enantioselective Esterification of Helical Poly-1 with Helicity Memory Assisted by Interaction with Achiral Amine. We next performed the same esterification reaction for the poly-**1** with macromolecular helicity memory. An optically active helical poly-**1** with helicity memory was prepared as follows. First, a one-handed helicity was induced in poly-**1** (1.0 mg/mL) with 2 equiv (*R*)-**2** in DMSO ($\Delta\epsilon_{2nd} = +16.4$).[19] To this was added excess achiral **3** ([**3**]/[poly-**1**] = 50) to replace the bound (*R*)-**2** with **3**; the $\Delta\epsilon_{2nd}$ value of the solution slightly decreased to +14.4 (88% memory efficiency). The solution was

(15) Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H.; Hoke, S.; Cook, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 4181−4182.
(16) There is another possibility to explain the positive nonlinear effect: the helical poly-**1** may act as a *chiral filter* to exclude one enantiomer for nonracemic amines; in other words, the helical poly-**1** enantioselectively adsorbs one of the enantiomers **2**. However, this possibility was excluded on the basis of the ee determination results of the bound **2** to poly-**1** (see Supporting Information).
(17) For chiral amplification in asymmetric synthesis with nonracemic polypeptides as catalysts, see: Kelly, D. R.; Meek, A.; Roberts, S. M. *Chem. Commun.* **2004**, 2021−2022.
(18) Morino, K.; Watase, N.; Maeda, K.; Yashima, E. *Chem.—Eur. J.* **2004**, *10*, 4703−4707.

Table 2. CD Results of Poly-**4a** and Poly-**4b** and Enantiomeric Excess of Their Pendants and Helix Sense Excess

		25 °C			−95 °C		
poly-**4**	amine	$\Delta\epsilon_{2nd}$[a] (M^{-1} cm^{-1})	ee of pendant[b] (%)	helix sense excess[c] (%)	$\Delta\epsilon_{2nd}$[a] (M^{-1} cm^{-1})	ee of pendant[b] (%)	helix sense excess[c] (%)
poly-**4a**	(*R*)-**2**	+2.2	11	17	+6.1	7.5	47
poly-**4a**	(1*R*,2*S*)-**5**	+2.8	15	22	+8.0	10	62
poly-**4b**	**3**	+0.65	3.5	5	+1.9	2.1	15

[a] CD intensity of poly-**4** measured in methanol. [b] Estimated based on the observed $\Delta\epsilon_{2nd}$ value using the plots in Figure 4 at 25 or −95 °C. [c] Estimated based on $\Delta\epsilon_{2nd}$ = +12.9 as the base value for the one-handed helical poly-**4** (see the plot in Figure 4 at −95 °C).

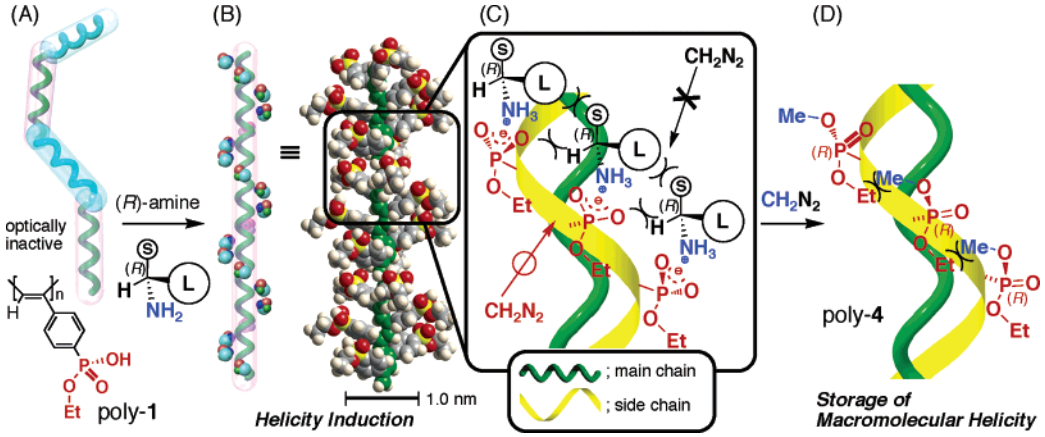

Figure 5. Schematic illustrations of the mechanism of enantioselective esterification of pendant phosphonates of a helical poly-**1** induced by (*R*)-amines with diazomethane. (A) Poly-**1** has interconvertible, right-handed (green) and left-handed (blue) dynamic helical conformations. (B) Right-handed helix of poly-**1** is induced with (*R*)-amines (left). Calculated right-handed helical structure of poly-**1** (20-mer) is shown using a space-filling model in the side view (right): scale bar, 1.0 nm. The main chain carbon atoms of poly-**1** and oxygen and phosphorus atoms are shown in green, red, and yellow, respectively. (*R*)-Amines are omitted for clarity. (C) A possible interaction model of right-handed helical poly-**1** with (*R*)-amines, where "S" and "L" represent small and large substituents, respectively. The main chain has a right-handed helix (green) with a left-handed helical array of the pendants (yellow). (D) Reaction of the poly-**1**−(*R*)-amine complexes with diazomethane enantioselectively proceeds, resulting in storage of the helical sense through the generation of (*R*)-rich pendant phosphonates.

then poured into a large amount of THF to isolate the poly-**1**−**3** complex. The molar ratio of **3** to poly-**1** in the complex was estimated by ^{1}H NMR measurements and found to be unity (see Supporting Information), indicating that (*R*)-**2** was completely replaced by the achiral **3**.[20] The precipitated poly-**1**−**3** complex was not soluble in DMSO once isolated; it was then suspended in 1 mL of DMSO and the poly-**1** completely converted to poly-**4b** by reaction with diazomethane in diethyl ether (72.7% yield) (see Supporting Information).[21]

Interestingly, poly-**4b** showed an ICD in methanol (Figure 2A(b)). Although the ICD intensity ($\Delta\epsilon_{2nd}$ = +0.65 at 25 °C) was weaker than that of poly-**4a**, the present results indicate that the enantioselective esterification really occurred at the remote pendants assisted by the macromolecular helicity memory.[22,23] The reason for this low enantioselectivity is not clear at present, but the structure of the achiral amine interacting with the pendant phosphonate group of the helical poly-**1** may play a role in the enantioselective reaction with diazomethane.

Enantiomeric Excess Determination of the Pendants of Poly-4a and Poly-4b and Their Helix Sense Excesses. To estimate the ee of the pendants of poly-**4a** and poly-**4b** together with the relationship between the pendant's ee of the polymers and their ICD intensities corresponding to the helix sense excess of the polymer backbone, the copolymerization of the corresponding nonracemic monomer **4** (*R* rich) was carried out using a rhodium catalyst (Supporting Information).[24] The CD spectra of the poly-**4**'s with different ee's measured in methanol showed a positive nonlinear relationship relative to the ee of the feed monomers (Figure 4). The departure from linearity was significant at lower temperatures, in particular at −95 °C,[25] and the CD intensity of the completely one-handed helical poly-**4** showing the maximum CD value at −95 °C was estimated to be +12.9 (Figure 4).[26] This phenomenon (majority rule)[7,15] originates from a unique feature of dynamic helical polyacetylenes with high cooperativity, so that the chirality of the pendants

(19) The enantioselectivity ($\Delta\epsilon_{2nd}$ value of poly-**4a**) was almost constant (ca. 2) when the [(*R*)-**2**]/[poly-**1**] ratio was greater than 2, because poly-**1** had a single-handed helix, thus showing a full ICD at that ratio. However, the enantioselectivity decreased with decreasing ICD intensity of poly-**1** because of the lack of a single-handed helix of poly-**1**. For example, the $\Delta\epsilon_{2nd}$ value of poly-**4a** obtained from poly-**1** with 0.3 equiv (*R*)-**2** was 0.44 (see Figure 3b at [NMA]/[poly-**1**] = 0).

(20) The recovery of (*R*)-**2** (100%) was estimated based on the UV spectrum of the recovered (*R*)-**2** in DMSO, which had been obtained by evaporating the solvents in the supernatant, followed by dilution with DMSO.

(21) The memorized poly-**1** was also isolated from the poly-**1**−(*R*)-**2** complex by SEC using a DMSO solution of **3** (0.8 M) as the eluent according to the previously reported method,[6g−i,18] and the memorized poly-**1** was treated with diazomethane. However, the reaction was not complete and yielded complex mixtures. Therefore, the isolated poly-**1**−**3** complex was used for the esterification reaction with diazomethane.

(22) We repeated the same esterification reaction for a helical poly-**1** with helicity memory assisted by achiral **3** and confirmed the reproducibility. When the esterification was performed for the poly-**1**−**3** complex in the presence of (*R*)-**2** in DMSO, an optically active poly-**4b** showing a $\Delta\epsilon_{2nd}$ value of 0.63 was quantitatively obtained.

(23) For asymmetric synthesis with helical polymers as chiral ligands, see: Reggelin, M.; Doerr, S.; Klussmann, M.; Schultz, M.; Holbach, M. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5461−5466.

(24) The optically pure (−)-**4** (99.7% ee) was obtained by resolution of racemic **4** by HPLC on a preparative Chiralcel OD column. The absolute configuration of (−)-**4** was tentatively assigned to be *R* based on the optical rotation sign of an analogous compound, (*R*)-(−)-ethyl methyl phenylphosphonate. See: DeBruin, K. D.; Tang, C. W.; Johnson, D. M.; Wilde, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5871−5879.

(25) The concentrations of polymers at −95 °C were corrected using the reported density value of methanol at −95 °C. See: Brunel, R. F.; Bibber, K. V. In *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology;* Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. 3, p 27.

is amplified as described above, resulting in a higher optical activity than that expected from the ee of the monomer units.

On the basis of the observed relationship between the $\Delta\epsilon_{2nd}$ value and the percent ee of the pendants at 25 and −95 °C in Figure 4, the percent enantiomeric excesses of the pendants of poly-**4a** and poly-**4b** were roughly estimated to be 11 and 3.5% (*R* rich) at 25 °C, respectively (Table 2). The enantioselectivity at the pendants of poly-**4** was low, but their helical sense excesses were amplified in the polymer backbone as evidenced by the nonlinear effect (Figure 4), particularly at low temperatures; the $\Delta\epsilon_{2nd}$ values of poly-**4a** and poly-**4b** in methanol significantly increased from +2.2 and +0.65 at 25 °C to +6.1 and +1.9 at −95 °C, respectively.[27] On the basis of the maximum ICD value of poly-**4** in Figure 4 ($\Delta\epsilon_{2nd}$ =12.9 at −95 °C), the helical sense excesses of poly-**4a** and poly-**4b** at −95 °C could be calculated to be 47 and 15%, respectively. When (1*R*,2*S*)-**5** was used for the helicity induction on poly-**1** instead of (*R*)-**2**, followed by esterification with diazomethane in DMSO, the $\Delta\epsilon_{2nd}$ value of the resulting poly-**4a** in methanol slightly increased to +2.8 and +8.0 at 25 and −95 °C, respectively, which corresponds to 15% ee of the pendants at 25 °C, and the helical sense excess reached 62% at −95 °C (Table 2).

The mechanism of the enantioselective esterification of the pendant phosphonates with diazomethane through chirality transfer from the induced helical conformation or the helicity memory of the poly-**1** backbone is not clearly elucidated at the present, but a possible model can be proposed on the basis of the previously proposed induced helical structure of poly-**1** with chiral amines together with the present results (Figure 5). The main chain of poly-**1** complexed with (*R*)-amines showing a positive second Cotton effect may have a right-handed helix, leading to a left-handed helical array of the pendants from the side view (Figure 5A,B).[6i,9f] The pendant phosphonates complexed with amines seem to be achiral independent of the chirality of the amines because the P−OH and P═O groups must attain equivalence in intermediate ion pairs when complexed with amines (Figure 5C).[11] Therefore, the ion pairs of a model compound **1** with (*R*)-**2** gave the racemic methyl ester of **1** by the reaction with diazomethane as described above. However, the pendant phosphonates arrange in a left-handed screw sense along the helically twisted right-handed polymer backbone induced by (*R*)-**2** (Figure 5C) and the induced helical conformation can be memorized by achiral **3**; therefore, diazomethane could preferentially react with one of the equivalent phosphonate groups. The formation of diastereomeric ion pairs could not be exclusively ruled out. The ethyl ester moiety of the pendants as well as the chiral and achiral amines complexed with the phosphonate groups contributes to the enantioselective esterification process, which may control the reaction direction of diazomethane as schematically illustrated in Figure 5C, resulting in the generation of (*R*)-rich phosphorus stereogenic centers to maintain the same helical sense of poly-**4** as that of the induced helical poly-**1** (Figure 5D). A similar model can be possible for the enantioselective esterification of the pendant phosphonates of poly-**1** with helicity memory, because the same right-handed helical conformation can be retained after replacement of the (*R*)-**2** with achiral diamine **3**.

The enantioselectivity for the esterification of the polymer's pendants is low, and subsequent chiral amplification in the polymer backbone as an excess of a single-handed helix is presently possible at low temperatures. However, we believe that the rational design and synthesis of a helical polyacetylene bearing more bulky phosphonate pendants with helicity memory assisted by interaction with more bulky achiral amines will result in a higher enantioselectivity at the pendants. In principle, if the enantioselectivity were extremely low, a perfect one-handed helicity could be stored in a specific polyacetylene when its positive nonlinear effect is sufficiently high even at ambient temperature, as observed in a poly(phenylacetylene) with a bulky crown ether pendant.[28]

Conclusions

In summary, the macromolecular helicity induced and memorized in a polyacetylene backbone was for the first time successfully stored as a result of the chirality transfer from the main chain helicity into the pendant chirality through enantioselective esterification. This concept will be applicable to other induced helical polymers bearing prochiral pendants, and the resulting polymers will be used as novel chiral materials for sensing chirality, enantiomer separations, and catalysis.[1,5]

Experimental Section

Full experimental details are available in the Supporting Information.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The absorption spectra of poly-**4** and poly-**1** complexed with (*R*)-**2** are different from one another; the absorption spectrum of poly-**4** exhibited a large red shift, the absorbance over 400 nm increased, and a peak at around 330 nm diminished (see Figure S-4 in the Supporting Information). These differences in their absorption spectra indicate that poly-**1** complexed with (*R*)-**2** may have a more tightly twisted helical conformation than that of poly-**4**, probably because of the bulkiness of (*R*)-**2** complexed with the pendants of poly-**1**. Therefore, the maximum CD intensities of the poly-**1**−(*R*)-**2** complex and poly-**4** with a complete single-handed helix may be different from each other due to their different helical conformations.

(27) The $\Delta\epsilon_{2nd}$ values of poly-**4a** and poly-**4b** in methanol at −95 °C were lower than those expected from the ee of the pendants at 25 °C. This may be due to a difference in the molecular weights of poly-**4a** and poly-**4b** and the poly-**4** prepared from nonracemic **4**, because the helix sense excess could be significantly amplified in high molecular weight polymers at low temperatures.[7,9i]

(28) (a) Nonokawa, R.; Yashima, E. *J. Am. Chem. Soc*. **2003**, *125*, 1278−1283. (b) Nonokawa, R.; Oobo, M.; Yashima, E. *Macromolecules* **2003**, *36*, 6599−6606.