Dual Memory of Enantiomeric Helices in a Polyacetylene Induced by a Single Enantiomer

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The helix is a central structural motif for biological macromolecules such as DNA and proteins that adopt a right-handed double helix and an α-helix, respectively, because of the homochirality of their components. However, the right-handed helices are not universal and can be transformed into an opposite left-handed helix regulated by external stimuli, as observed in natural and artificial DNAs and polypeptides.[1] Since the discovery of the biological helicity inversion, chemists have been interested in controlling and switching the helicity of artificial (macro)molecules not only to mimic biological helices but also for attractive applications in materials science, chiral sensing, and molecular devices.[2] Inversion of the helical chirality has been thermally and photo- or electrochemically achieved in some optically active synthetic polymers[3] and supramolecules.[4] The reversibly interconverting helices are not mirror images (enantiomers), but diastereomers because optically active components are covalently bonded to the molecules, so that one of the helices may be predominant under certain conditions. Here, we report an unexplored approach which produces both mirror-image enantiomeric helices from the interconverting diastereomeric helices of a polyacetylene, based on the noncovalent "*helicity induction and chiral memory*" concept[5] assisted by inversion of the macromolecular helicity with temperature (Figure 1).

We previously reported that a right- or left-handed helicity induced in optically inactive poly(phenylacetylene)s bearing a carboxy or a phosphonate as the pendant by an optically active amine can be "*memorized*" when the amine is replaced by achiral amines in dimethyl sulfoxide (DMSO).[6] Accordingly, the opposite enantiomeric helicity memory requires the opposite enantiomeric amine, followed by replacement with achiral amines. The chiral memory of the self-assembled supramolecular structures has also been achieved, but one of the enantiomers can be memorized from diastereomeric supramolecules.[7]

We synthesized a novel *cis-transoidal* poly(phenylacetylene) having a bulky phenyl phosphonate group at the pendant (poly-**1**; Figure 1),[8] which formed a one-handed helix upon complexation with chiral amines, such as (*R*)-1-(1-naphthyl)ethylamine ((*R*)-**2**) ([(*R*)-**2**]/[poly-**1**] = 2) in DMSO at 25 °C, thus showing an induced circular dichroism (ICD) in the polymer backbone region (Figure 2a). CD titration experiments indicated that 1 equiv of (*R*)-**2** is enough to induce an almost single-handed helix in poly-**1**, showing a full ICD. However, the ICD pattern dramatically changed with temperature and was inverted at 65 °C (Figure 2b and inset), accompanied by a change in the absorption spectra (Figure 2e,f). These spectral changes are completely reversible (Figure 2, inset), indicating inversion of the helicity of poly-**1** by temperature, despite

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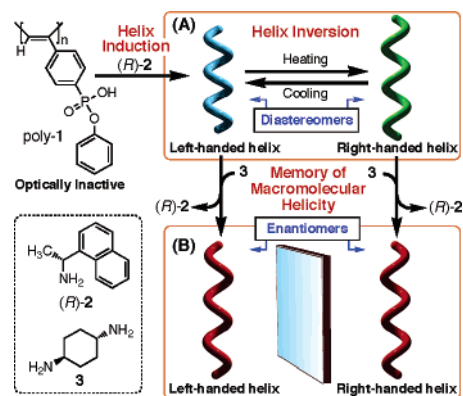
Figure 1. Schematic illustration of induced one-handed helicity in optically inactive poly-**1**, helix inversion with temperature, and subsequent memory of the diastereomeric macromolecular helicity at different temperatures. A left-handed helical conformation of poly-**1** induced by (*R*)-**2** at low temperature reversibly changes into the opposite right-handed helix at high temperature (A), and these diastereomeric helices of poly-**1** are memorized at different temperatures by replacement of the (*R*)-**2** with achiral **3**, resulting in the formation of enantiomeric mirror image helices of poly-**1** (B). The helix-senses of poly-**1** are tentatively assigned on the basis of the Cotton effect signs of the induced CDs of analogous helical polyacetylenes.[6a]

the noncovalent bonding interactions (Figure 1A). A similar temperature-dependent inversion of helicity has been observed in the covalent systems of helical polymers.[3]

The right- and left-handed helices of poly-**1** induced at 25 and 65 °C are not enantiomers, but diastereomers because of the presence of the chiral amine complexed with poly-**1**; therefore, their CD and absorption spectra differ from one another. When (*S*)-**2** is used instead, poly-**1** with the opposite helicity is induced, which undergoes a reversible inversion of the helicity by temperature (Figure S1 and Table S2 in the Supporting Information).[9] We assume that this specific inversion of the helicity may be governed by a difference in the chiral twisting power between the chiral amine and the pendant phosphonate chirality, which forces the poly-**1** into either a right- or left-handed helix depending on the temperature. Other chiral (*R*)-amines, such as (*R*)-1-phenylethylamine ((*R*)-**4**), did not show such a temperature-induced inversion of the helicity in poly-**1**, and the complexes exhibited the same positive second Cotton effect (Δε$_{second}$) over the temperature range (25−100 °C); the sign was the same as that of the poly-**1**−(*R*)-**2** complex at high temperature (Table S1).[9]

The vibrational CD (VCD) and IR spectra provide strong evidence of the pendant phosphonate chirality (Figure 3). The poly-**1**−(*R*)-**2** complex exhibits a positive couplet VCD in DMSO-d_6 at ca. 25 °C in the P=O stretching band region (1180−1260 cm^{-1}) (Figure 3a, left), whose intensity significantly diminished at 70 °C,
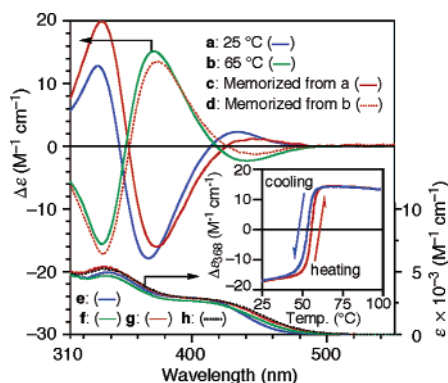
Figure 2. Macromolecular helicity inversion of poly-**1**−(*R*)-**2** complex with temperature in DMSO, and the memory of the diastereomeric helices at different temperatures. Shown are the CD spectra of poly-**1** (1 mg/mL) with (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 2) at 25 (a, blue line) and 65 °C (b, green line), and the isolated poly-**1** from (a) (c, red solid line) and (b) (d, red dotted line) by SEC fractionation using a DMSO solution of **3** (0.08 M) as the mobile phase. Five equivalents of **3** was added to the poly-**1**−(*R*)-**2** solution at 65 °C before the SEC fractionation for (d). Absorption spectra of poly-**1** with (*R*)-**2** in DMSO at 25 and 65 °C and the memorized poly-**1** from (a) and (b), in DMSO at 25 °C, are also shown in (e) (blue line), (f) (green line), (g) (red line), and (h) (black dotted line), respectively. Inset shows the temperature-dependent CD intensity (368 nm) changes of the poly-**1**−(*R*)-**2** complex; heating and cooling rates = 1 °C/min.
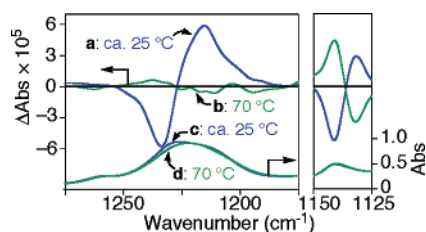
Figure 3. VCD (a and b) and FT-IR spectra (c and d) of poly-**1**−(*R*)-**2** complex ([poly-**1**] = 60 mg/mL, [(*R*)-**2**]/[poly-**1**] = 5) in DMSO-*d*₆ at ca. 25 (a and c, blue lines) and 70 °C (b and d, green lines). All spectra were measured in a 0.05 mm BaF₂ cell and collected for 2 h at a resolution of 4 cm⁻¹. Note that the poly-**1**−(*R*)-**2** complex shows intense ICDs with the opposite Cotton effect signs from one another in the main-chain chromophore region (300−500 nm) at 25 and 70 °C.

accompanied by a slight change in the IR spectra (Figure 3b,d). These results indicate that the pendant phosphonate of poly-**1** is quite optically active rich in either the (*R*)- or (*S*)-enantiomer with (*R*)-**2**, which may determine the helix-sense of the poly-**1** at low temperature. Upon heating, however, the pendant phosphonate may racemize or exist as the achiral form due to the resonance effect of the P−OH and P=O groups. Therefore, the chirality of the amine (*R*)-**2** will, in turn, determine the helix-sense of the poly-**1**, resulting in inversion of the helicity and the Cotton effect signs at high temperature. The corresponding monomer **1** complexed with (*R*)-**2** showed no VCD in the region, indicating no asymmetric induction in the monomer level.[10] Moreover, the fact that a positive couplet VCD in the main-chain related vibration region (1125−1150 cm⁻¹) of poly-**1** at 25 °C completely changed to the opposite sign, a negative couplet at 70 °C (Figure 3, right), also supports the inversion of the helicity of poly-**1** due to temperature.

The resulting diastereomeric right- and left-handed helices of poly-**1** obtained at 25 and 65 °C were successfully memorized when the chiral amine was replaced by an achiral diamine such as **3** at those temperatures (Figure 1B).[6,9] The perfect mirror image Cotton effects and identical absorption spectra of the isolated poly-**1**s by size exclusion chromatography (SEC) indicate that the separated species indeed correspond to enantiomeric forms[13] (Figure 2c,d). The memorized poly-**1** may have a different helical conformation

from those before the memory because the absorption and CD spectra differ from one another; the memory efficiency estimated on the ICD values of the poly-**1**−(*R*)-**2** or −(*S*)-**2** complex at 25 and 65 °C as the base values was ca. 90% (Table S2).[9] The memory lasted for the extremely long time of over 1 month at ambient temperature with a decrease in the CD intensity of ca. *6%*.

Because of the unique feature of the dynamic helical poly-**1**, even with a low enantiomeric excess (ee), **2** can induce a predominantly one-handed helix in poly-**1**.[2d,6b] For example, a 35% ee of **2** induced an intense ICD in poly-**1** similar to that of the 100% ee at 25 °C and the event at 65 °C after inversion of the helicity (Figure S2).[9] The replacement of the nonracemic amine with achiral **3** produced the enantiomeric helices of poly-**1** with a high optical activity (Table S2). Consequently, both enantiomeric helices can be produced from the dynamically diastereomeric helical polyacetylenes induced by a single enantiomer with a low optical activity. The present results not only demonstrate this new phenomenon but also will provide new approaches for the rational design of novel switchable helical architectures and the construction of new chiral materials in areas such as liquid crystals, chiral selectors, and chiral sensors.[2b,c,5]

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(8) The *cis-transoidal* poly-**1** was prepared by the polymerization of the corresponding monomer (**1**) with [Rh(nbd)Cl]₂ (nbd = norbornadiene) (100% yield); the number-average molecular weight and its distribution were 2.3 × 10⁵ and 1.7, respectively.[9]
(9) For more details, see Supporting Information.
(10) The X-ray crystallographic analyses of the monomer **1** and a complex of phenyl phenylphosphonate, a model compound of poly-**1** with (*R*)-**2**, showed that **1** chirally exists as a racemic mixture in the crystal, but the model phosphonate becomes achiral when complexed with (*R*)-**2** through proton transfer.[9] Similar achiral phosphonates in the crystal have been reported,[11] but the chirality of the phosphonates in solution has not yet been considered.[12] Consequently, asymmetric induction in the phosphonate by chiral amines may be specific for dynamic helical polyacetylenes, such as poly-**1**, and may not occur in small molecular systems.
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