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Macromolecular Helicity Inversion of Poly(phenylacetylene) Derivatives Induced by Various External Stimuli

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Summary: Unique macromolecular helicity inversion of stereoregular, optically active poly(phenylacetylene) derivatives induced by external achiral and chiral stimuli is briefly reviewed. Stereoregular, *cis-transoidal* poly(phenylacetylene)s bearing an optically active substituent, such as (1*R*,2*S*)-norephedrine (poly-**1**) and *β*-cyclodextrin residues (poly-**2**), show an induced circular dichroism (ICD) in the UV-visible region of the polymer backbone in solution due to a predominantly one-handed helical conformation of the polymers. However, poly-**1** undergoes a helix—helix transition upon complexation with chiral acids having an *R* configuration, and the complexes exhibit a dramatic change in the ICD of poly-**1**. Poly-**2** also shows the inversion of macromolecular helicity responding to molecular and chiral recognition events that occurred at the remote cyclodextrin residues from the polymer backbone; the helicity inversion is accompanied by a visible color change. A similar helix—helix transition of poly((*R*)- or (*S*)-(4-((1-(1-naphthyl)ethyl)carbamoyl)phenyl)acetylene) is also briefly described.

Keywords: chiral, helix, helix—helix transition, induced circular dichroism, polyacetylenes

Introduction

In polymer and supramolecular chemistry, significant attention has been paid to developing synthetic polymers and polymeric assemblies that adopt a helical conformation even in solution not only to mimic nature but also to develop novel chiral materials for the use as liquid crystals, enantioselective catalysts, and chiral selectors.[1-4] To date, several synthetic helical polymers have been prepared, which can be classified into two types with respect to the nature of the helical conformation; one is a stable (or static) helical polymer even in solution and the other is a dynamic helical polymer. These synthetic helical polymers exhibiting an optical activity due

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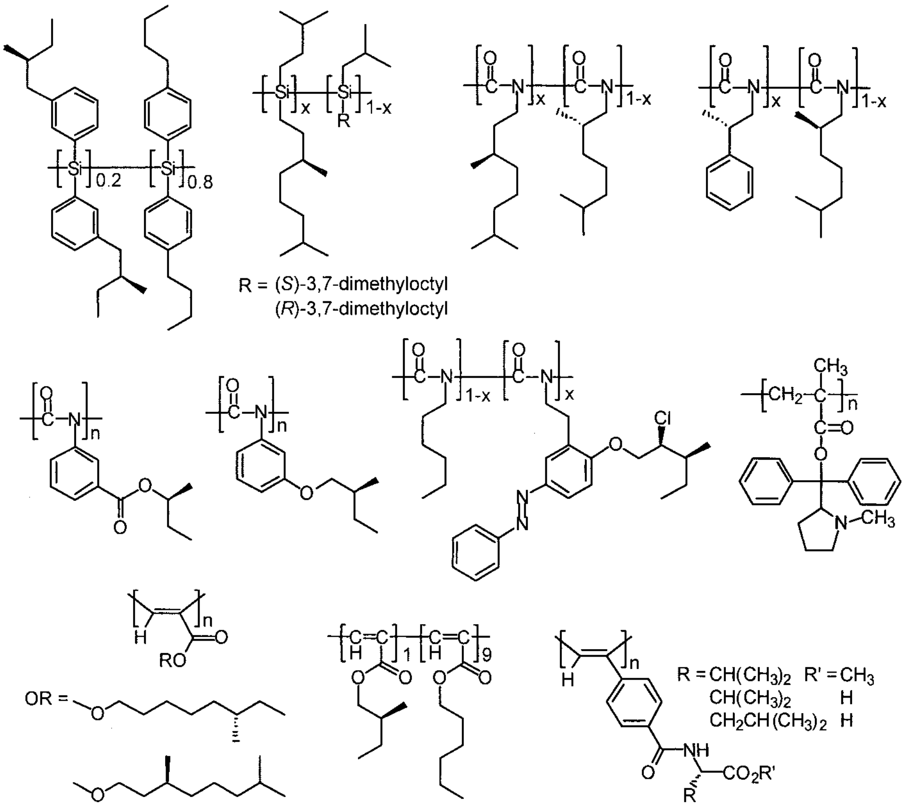
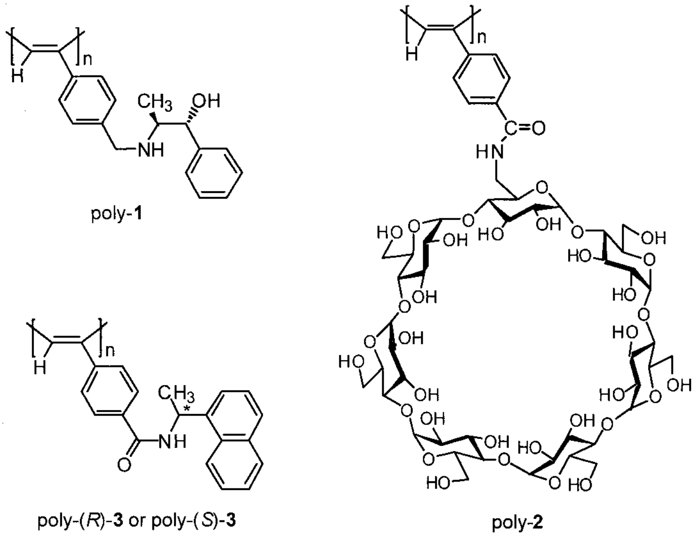
to the one-handed helicity can be prepared either by polymerization of optically active monomers[2-4] or by asymmetric polymerization of achiral or prochiral monomers with chiral catalysts or initiators.[1] Therefore, the helix-sense can be controlled thermodynamically by chiral substituents covalently bonded to the polymer main chain or kinetically during the polymerization. Besides these helical polymers, we recently succeeded in developing a conceptually new helical polymer, which is an induced helical polymer. A predominantly one-handed helicity can be induced on optically inactive polymers including polyacetylenes bearing various functional groups upon complexation with optically active small molecules capable of interacting with the functional groups.[5-7] Details of these helical polymers have been thoroughly reviewed elsewhere.[1-4,8]

Chart 1. Structures of synthetic helical polymers that exhibit a helix—helix transition.



Another interesting feature of helical polymers is their helix-helix transition. As shown in Chart 1, several synthetic polymers[9] as well as biopolymers[10] that undergo a helix-helix transition by various external achiral stimuli such as temperature, solvent, light, and the addition of acids, have been reported. In this paper, we describe unique helix—helix transitions of *cis-transoidal* poly(phenylacetylene)s bearing an optically active substituent (poly-**1**—**3**) (Chart 2) responding to external achiral and chiral stimuli. To the best of our knowledge, synthetic helical polymers exhibiting a helix-helix transition by external chiral stimuli have not yet been reported except for our examples.[11-13]

Chart 2. Structures of poly-**1**—poly-**3**.



poly-**1**

poly-(*R*)-**3** or poly-(*S*)-**3**

poly-**2**

Helix—Helix Transition of Poly(phenylacetylene)s by External Stimuli

A *cis-transoidal* poly(phenylacetylene) having an optically active amino alcohol residue derived from norephedrine as the side group (poly-**1**) is optically active and exhibits a characteristic ICD in the UV-visible region in dimethyl sulfoxide (DMSO) due to a predominantly one-handed helical conformation of the polymer (Figure 1). However, the poly-**1** undergoes a transition from one-helix to another induced by diastereomeric complexation with optically active acids such as mandelic acid (**4**).[11] As shown in Figure 1, the addition of (*R*)-**4** to the poly-**1** solution in DMSO induces drastic changes in the ICD of poly-**1** to give an almost mirror image at [(*R*)-**4**]/[poly-**1**] = 50. On the other hand, in the presence of excess (*S*)-**4**, the ICD of poly-**1** hardly changed. These results indicate that the poly-**1** undergoes a helix—helix transition upon complexation with (*R*)-**4** and that the optically active **4** can be used to regulate the helix-sense of poly-**1**.

In chloroform, an equimolar amount of chiral carboxylic acids having an *R* configuration was sufficient for an almost complete inversion of the ICD of poly-**1** because ion association between poly-**1** and carboxylic acids in less polar chloroform might be stronger than that in polar DMSO. This helix inversion behavior can be applicable to predict the absolute configuration of chiral acids because only acids with an *R* configuration bring about a helix—helix transition of poly-**1**.

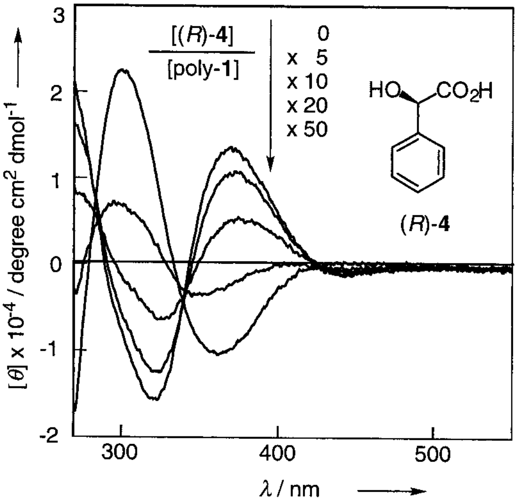


Fig. 1. CD spectral change of poly-**1** (1 mg/mL) with (*R*)-**4** in DMSO at room temperature.[11]

An optically active *cis-transoidal* poly(phenylacetylene) bearing a *β*-cyclodextrin (*β*-CyD) residue as the side group (poly-**2**) also exhibits an interesting macromolecular helicity inversion accompanied by a visible color change responding to various external stimuli.[12] Poly-**2** shows an ICD in the UV-visible region in DMSO and alkaline water, due to the prevailing one-handed helical conformation because the polymer has an optically active *β*-CyD unit. However, at high temperatures, the ICD pattern dramatically changed in DMSO, and the sign inverted accompanied by a color change from red to yellow. This indicates that the polymer underwent a helix—helix transition due to changing the temperature. Poly-**2** also exhibited a similar color change in the presence of an increasing amount of water and alcohols accompanied by inversion of the Cotton effect at 25°C. Moreover, the transition temperature can be controlled by tuning the solvent compositions.

It is well-known that *β*-CyD possesses a chiral hydrophobic cavity to form inclusion complexes with a variety of organic molecules that fit the cavity size. Poly-**2** was found to show a similar helicity inversion of the main chain with a color change through inclusion complexation with guest molecules such as 1-adamantanol and (-)-borneol into the cyclodextrin cavity.

The macromolecular helicity of poly-**2** can also be switched by complexation with chiral molecules. For instance, poly-**2** exhibited a color change (from yellow-orange to red) with a negative first Cotton effect sign in the presence of excess (*S*)-1-phenylethylamine ((*S*)-**5**) in DMSO-alkaline water (3/7, v/v), while the solution color remained yellow with a positive first Cotton effect sign in the presence of excess (*R*)-**5** (Figure 2). The chirality of **5** might induce the macromolecular helicity inversion of poly-**2**, which can be observed by the naked eye. The present system may be based on a change in the tunable helical pitch arising from the helicity inversion and can be used for the construction of conceptually new chiral materials as chiral sensors and chiral selectors.

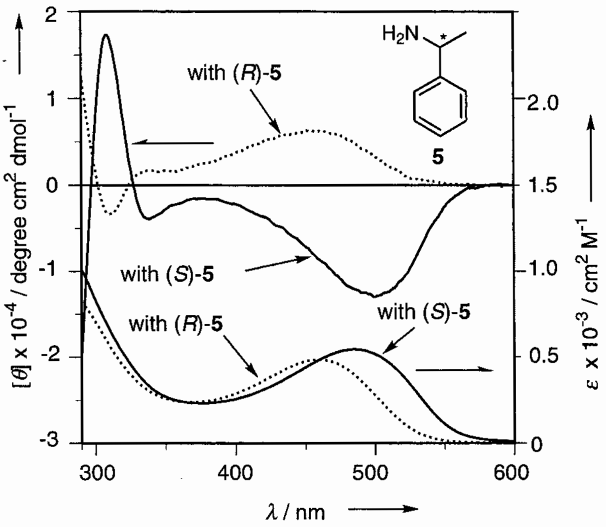


Fig. 2. CD and absorption spectra of poly-**2** (1 mg/mL) in an alkaline water (pH 11.7)-DMSO (7/3, v/v) in the presence of (*R*)-**5** (dotted line) and (*S*)-**5** (solid line) at 25 °C.[12]

A similar stimuli-responsive, macromolecular helicity inversion was also observed for poly((*R*)- or (*S*)-(4-((1-(1-naphthyl)ethyl)carbamoyl)phenyl)acetylene) (poly-(*R*)-**3** and poly-(*S*)-**3**) by changing the external conditions, such as temperature, solvent, or by interacting with optically active small molecules such as (*R*)- and (*S*)-1-(1-naphthyl)ethylamine (**6**).[13] A typical helix inversion of poly-(*R*)-**3** responding to chiral interaction with amines is described below. Figure 3 shows the CD spectra of poly-(*R*)-**3** in the absence and presence of (*R*)- and (*S*)-**6** ([**6**]/[poly-**3**] = 400) in DMF. The ICD of poly-(*R*)-**3** changed with an excess of (*R*)-**6** and gave an almost mirror image. The ICD of poly-(*R*)-**3** also changed in the presence of the same amount of (*S*)-**6**, but the Cotton effect sign was the same as that of poly-(*R*)-**3**. A similar inversion of the Cotton effect sign was also observed for poly-(*S*)-**3** in the presence of (*R*)- and (*S*)-**6**. Thus, optically active **6** can be used to regulate the helix-sense of poly-**3**.

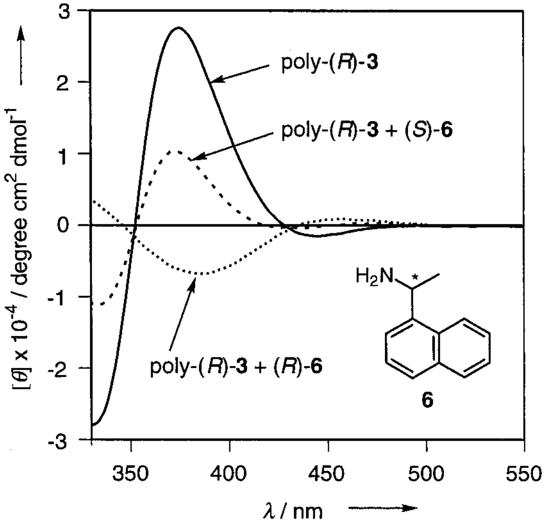


Fig. 3. CD spectra of poly-(*R*)-**3** (1 mg/mL) in DMF in the absence (solid line) and presece of (*R*)-**6** (dotted line) and (*S*)-**6** (broken line) ([**6**]/[poly-(*R*)-**3**] = 400) at room temperature.[13]

Conclusion

We have demonstrated in this article that the macromolecular helicity of some helical polyacetylenes can be switched by external chiral stimuli as well as achiral ones. Although helical polymers exhibiting a helix—helix transition by chiral stimuli are still rare, we expect that related helical polyacetylenes bearing other chiral functional substituents would also respond to various chiral small molecules, thus exhibiting a unique helix—helix transition.

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