

Helix-Sense-Selective Polymerization of Phenylacetylene Having Two Hydroxy Groups Using a Chiral Catalytic System

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Syntheses of many kinds of polymers having a chiral main chain have been reported.¹ However, there are only a few examples of chiral polymers whose chiral properties arise only from their chiral conformational structures, such as one-handed helicity, without the coexistence of any other chiral moieties such as chiral side groups, chiral end groups, or asymmetric carbons in their main chain.²

Nonsubstituted polyacetylenes have aroused interest because of their noteworthy physical properties such as conductivity and optical nonlinear susceptibility. Recently, polyacetylenes that have a chiral conformation have received much attention because the chiral structures might enhance these unique properties and create new properties. Such chiral substituted polyacetylenes have been synthesized by polymerization of monomers having bulky chiral substituents.³ However, after the chiral side groups were removed by hydrolysis, the resulting polymer did not maintain its chiral conformation in solution.⁴ Akagi et al. synthesized a chiral helical nonsubstituted *insoluble* polyacetylene by polymerization of acetylene in a chiral nematic reaction field.⁵ However, there are no reports of obtaining chiral helical substituted *soluble* polyacetylenes having no other chiral moieties by polymerizing an achiral substituted acetylene with a chiral catalyst.

We report herein that we have found a simple and novel synthetic method for obtaining a chiral polymer from an achiral substituted acetylene monomer by using a chiral catalytic system. The polymer contains only a one-handed helical backbone and no other chiral structures in the side or end groups. In addition, the helical conformation was stable in solution. This is the first example of helix-sense-selective polymerization of substituted acetylenes whose chiral helicity is stable in solution without the aid of other chiral substituents or other small molecules.⁶ We will discuss the reason for the stability and propose a molecular model.

We polymerized an achiral phenylacetylene (**1**) using a chiral catalytic system consisting of a rhodium dimeric complex, [Rh-(nbd)Cl]₂ (nbd = 2,5-norbornadiene), as a catalyst and a chiral amine, (*R*)-1-phenylethylamine ((*R*)-**5**), as a cocatalyst (Table 1, no. 1). The polymer showed Cotton effects at wavelengths around 430 and 310 nm where there are no UV absorptions of **1** and **5** (Figures 1a and 2a). The absorption band at 430 nm is assigned to the conjugated main chain, and the peaks at 310 nm may arise from a chiral position between adjacent pendant groups. The intensity of the band at 430 nm was similar, and the peaks at 310 nm were a little stronger as compared with other chiral helical polyphenylacetylenes having chiral side groups.⁷ The [α]_D value of poly**1** was –262° (c 0.30, CHCl₃). Therefore, we realized the first helix-sense-selective polymerization of a substituted acetylene using a chiral catalyst. When we used (*R*)-*N,N*-dimethyl-1-phenylethylamine ((*R*)-**6**) instead of (*R*)-**5**, a chiral polymer, whose [θ] was lower than that of (*R*)-**5**, was also obtained (Table 1, no. 3). The helical sense was controlled by changing the chirality of the cocatalyst (Table 1, nos. 3 and 4). On the other hand, no helix-sense-selective

Table 1. Helix-Sense-Selective Polymerization of **1** by a Chiral Catalyst at Room Temperature^a

no.	poly(monomer/comonomer) (composition)	cocat.	yield (%)	MW/10 ⁶ ^b	[θ] ₃₁₀ /10 ³ ^c (deg-cm/dmol)
1	poly 1	(<i>R</i>)- 5	36.5	5.17	31.1
2	poly 1	none	83.4	2.04	0
3 ^d	poly 1	(<i>R</i>)- 6	63.7	2.28	3.90
4 ^d	poly 1	(<i>S</i>)- 6	88.5	2.46	–3.07
5	poly 1/2 (92/8)	(<i>R</i>)- 5	13.1	8.69	11.1
6	poly 1/2 (70/30)	(<i>R</i>)- 5	14.2	7.31	1.36
7	poly 1/2 (53/47)	(<i>R</i>)- 5	10.8	8.69	0
8	poly 2	(<i>R</i>)- 5	33.2	2.97	0
9	poly 3	(<i>R</i>)- 5	33.7	6.02	0
10 ^d	poly 4	(<i>R</i>)- 5	95.8	^e	^e
11	polyTMSPA	(<i>R</i>)- 5	85.0	0.17	0

^a In toluene for 3 h, [monomer] = 0.1 mol/L, [[Rh(nbd)Cl]₂] = 0.2 mmol/L, [cocat.] = 0.05 mol/L. ^b By GPC (polystyrene, THF). ^c In chloroform. ^d In toluene for 1 h, [monomer] = 0.1 mol/L, [[Rh(nbd)Cl]₂] = 1 mmol/L, [cocat.] = 0.02 mol/L. ^e Insoluble.

polymerizations occurred in the case of monomer **2** and *p*-trimethylsilylphenylacetylene (TMSPA) that have no hydroxy groups (Table 1, nos. 8 and 11).

Monomer **4** gave only an insoluble polymer. Intermolecular hydrogen bonds may make poly**4** insoluble. The length of the dodecyl groups in poly**1** may be enough to avoid such intermolecular hydrogen bonds, whereas hexyl groups may be too short.

The polyphenylacetylene without chiral substituents derived from the chiral homopolymer showed no CD as described above.⁴ On the other hand, the chiral structure of poly**1** in this study was stable in chloroform at room temperature for 5 months. Moreover, even when the solution was heated to 50 °C, almost no change was detected in CD (see Supporting Information). Because **2** and TMSPA did not give a chiral polymer, the hydroxy groups in **1** were thought to play a very important role in this stable chiral structure. This stability may be caused by intramolecular hydrogen bonds between hydroxy groups in different monomer units. To confirm this, we measured the CD and IR in various two-component solvents which have different polarities. As the content of polar DMSO increased, the CD signal became smaller (Figure 1b–d) and then disappeared (Figure 1e).⁸ Simultaneously, the OH absorption at 3300 cm^{–1} shifted to higher wavelength, indicating that the hydrogen bonds became weaker (see Supporting Information). Therefore, the intramolecular hydrogen bonds were found to be effective in making the chiral structure stable.⁹ When excess amounts of (*R*)-**5** were added to an achiral poly**1** (Table 1, no. 2) solution, no induced CD was observed in contrast to the case in poly(monocarboxyphenylacetylene).¹⁰ Therefore, poly**1** has a stable conformation.

In addition, we copolymerized **1** with **2** (Table 1, nos. 5–7). The CD and UV spectra of the resulting copolymers are shown in

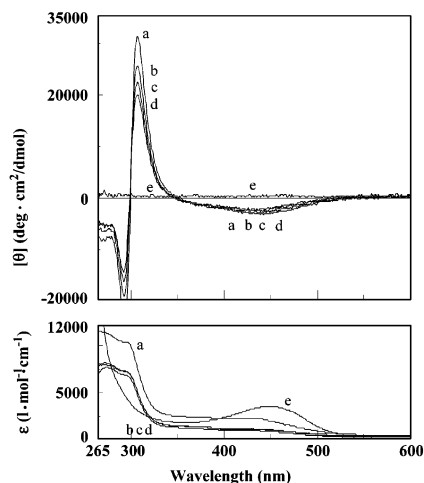


Figure 1. CD and UV spectra of poly1 in various solvents at 20 °C. (a) In CCl_4 , (b) in CCl_4/DMSO (50/1), (c) in CCl_4/DMSO (30/1), (d) in CCl_4/DMSO (20/1), (e) in CCl_4/DMSO (10/1).

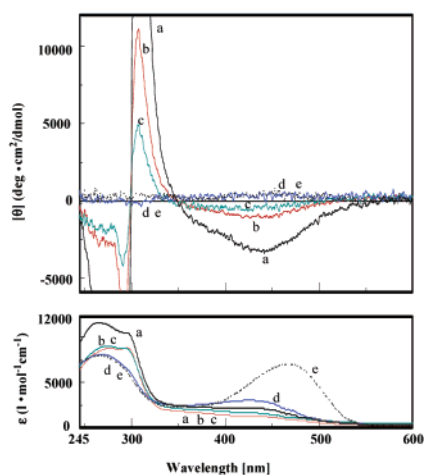


Figure 2. CD and UV spectra of copoly(1/2) in chloroform at 20 °C. (a) poly1 (no. 1 in Table 1), (b) copoly(1/2) (92/8) (no. 5 in Table 1), (c) copoly(1/2) (70/30) (no. 6 in Table 1), (d) copoly(1/2) (53/47) (no. 7 in Table 1), (e) copoly2 (no. 8 in Table 1).

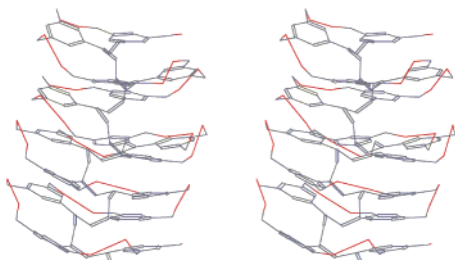


Figure 3. Stereoviews of chiral helical poly1 ($\text{C}_{12}\text{H}_{25}\text{O}$ groups are omitted). (Both covalent and hydrogen bonds are shown in solid lines.)

Figure 2. Even when small amounts of **2** were incorporated into the copolymer, the intensity of the CD signal decreased significantly (Figure 2b). When the amount of **2** exceeded ca. 50%, the CD signal disappeared (Figure 2d). Also, polymers of **3** with only one hydroxyl group showed no CD.

Judging from these experimental results, we propose that the helical conformation is maintained by hydrogen bonds between two hydroxyl groups in adjacent phenyl groups. We postulate the possible conformation in Figure 3. To make the molecular model, the length of hydrogen bonds between hydroxyl groups in adjacent monomer units was fixed at 2.7 Å. After making several models using an MM2 program for minimization, we selected the most

probable one. The most probable model has a main chain that is highly strained cis–transoid. This highly strained structure is in agreement with the observation that poly1 absorbed at shorter UV wavelengths in a hydrophobic solvent than in a polar solvent (Figure 1a,e) and the fact that poly1 absorbed at shorter wavelengths than poly2 (Figure 2a,e). In addition, a WAXD measurement supported the observed difference in the UV spectra because the radius of the columnar¹¹ of poly1 was shorter than that of poly2 (see Supporting Information).

In conclusion, we have found two new findings: one is the helix-sense-selective polymerization of an achiral acetylene by a chiral catalyst, and the other is that the chiral helical conformation of the obtained polymer is stabilized by intramolecular hydrogen bonds in solution without the use of extra reagents. On the other hand, the chiral helicities of the polyisocyanide of Nolte,^{1a,2c} prepared by optical resolution, and the poly(triethyl methacrylate) of Okamoto,^{2a,b} synthesized by asymmetric polymerization, were stabilized by bulky substituents. Additionally, Yashima's polymer,⁶ having an induced CD, needed the coexistence of an excess of achiral amino alcohols to maintain the chiral helicity, and Masuda's polyacetylene,⁹ whose helicity was stabilized by intramolecular hydrogen bonds, was obtained from a chiral monomer and contained many chiral substituents. Our new asymmetric polymerization reported here is expected to be applicable to other monomers which can make hydrogen bonds. Investigations of the degree of the one-handedness¹² and the polymerization mechanism¹³ are now in progress.

Supporting Information Available: Experimental procedures for synthesis, CD, IR, WAXD charts, and models (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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