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Stereospecific Polymerization of Propiolic Acid with Rhodium Complexes in the Presence of Bases and Helix Induction on the Polymer in Water

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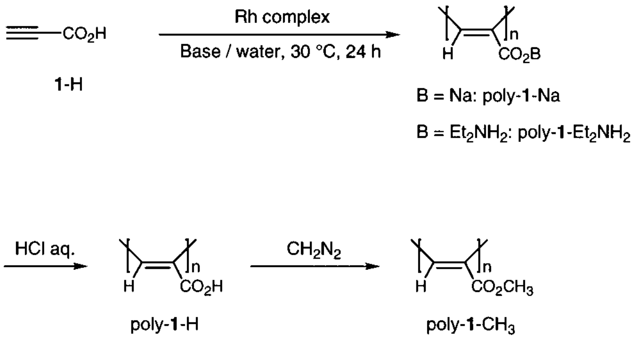
ABSTRACT: Propiolic acid was directly polymerized in water with water-soluble rhodium complexes in the presence of bases such as NaOH to yield the *cis*−*transoidal* poly(propiolic acid) sodium salt (poly-**1**−Na) in high yields. Moreover, poly-**1**−Na exhibited an induced circular dichroism (ICD) in the UV−visible region in water due to the formation of a predominantly one-handed helical structure responding to the chirality of the optically active amino alcohols. The stereoregularity of the polymer decreased when the poly-**1**−Na was converted into the acid form, poly(propiolic acid). However, poly(propiolic acid) also showed ICDs in the UV−visible region in water in the presence of optically active amino alcohols.

Introduction

The rhodium (Rh)-based complexes are excellent catalysts for the stereospecific polymerization of various monosubstituted acetylenes to give high-molecular-weight *cis*−*transoidal* polyacetylenes,[1,2] and some of them can polymerize phenylacetylenes in a living fashion in organic solvents.[3] We reported that an optically inactive *cis*−*transoidal* polyacetylene bearing a carboxy group, poly((4-carboxyphenyl)acetylene) (PCPA), can form a predominantly one-handed helical structure in the presence of optically active amines[4] and the macromolecular helicity can be memorized by replacing the chiral amines with various achiral amines.[5] PCPA was prepared by the polymerization of its ester derivatives with [Rh(nbd)Cl]$_2$ (nbd, norbornadiene) in organic solvents followed by hydrolysis of the ester groups.[4] Direct polymerization of the carboxy acetylenes with Rh complexes appeared to be impossible because acetic acid is used as an effective terminator to remove the active Rh moiety from the propagating species.[3,6] However, we have recently found that (4-carboxyphenyl)acetylene can be directly polymerized in water with water-soluble Rh complexes in the presence of bases such as alkaline hydroxide and amines to give high-molecular-weight *cis*−*transoidal* PCPA in high yields.[7] The use of bases might be necessary for the stereospecific polymerization of carboxyacetylenes in water, because the neutralization reaction of the carboxy group with bases results in the conversion of the carboxy group into the carboxylate ion which may not inactivate the Rh-based complexes. Moreover, we have also found that the sodium salt of PCPA exhibited a characteristic induced circular dichroism (ICD) in the UV−visible region due to the one-handed helix formation of the polymer in water by responding to the chirality of natural, free amino acids.[7]

In a previous study, we tried to prepare poly(propiolic acid) (poly-**1**−H) by the polymerization of the ethyl and trimethylsilyl propiolates with [Rh(nbd)Cl]$_2$ in organic solvents, followed by hydrolysis of the ester groups.[8] Although the high-molecular-weight *cis*−*transoidal* poly(ethyl propiolate) was obtained, alkaline hydrolysis of the polymer was unsuccessful. On the other hand, poly(trimethylsilyl propiolate) was quantitatively converted to poly-**1**−H, but the ^{1}H NMR spectrum of the polymer did not show any sharp signal due to the main chain's methine protons which are characteristic resonances of the *cis*−*transoidal* polyacetylenes, indicating that the polymer may have a stereoirregular structure. Furthermore, the polymer did not show any ICD in the presence of optically active amines in DMSO.[8]

Scheme 1



In the present study, we applied the methodology of the stereospecific polymerization of carboxyacetylenes with water-soluble Rh complexes in water in the presence of bases to propiolic acid (**1**−H)[9] and investigated if the obtained polymer could form a one-handed helical conformation in the presence of chiral amines in water.

Experimental Section

Materials. Propiolic acid (**1**−H) was purchased from Aldrich and used after distillation under reduced pressure. [Rh(nbd)$_2$]ClO$_4$ was obtained from Aldrich and used as received. [Rh(cod)(tos)(H$_2$O)] (cod, cyclooctadiene; tos, *p*-toluenesulfonate)[10] and [Rh(cod)$_2$]BF$_4$ were prepared from [Rh(cod)Cl]$_2$ according to the reported methods.[11]

Polymerization. Polymerization was conducted according to Scheme 1 using water-soluble Rh complexes in a way similar to that previously reported.[7] A typical polymerization procedure is as follows.

Propiolic acid (2.0 mL, 32.5 mmol) was placed in a dry glass ampule attached to a three-way stopcock under dry nitrogen, and 13.9 mL of ion-exchanged, degassed water and 3.4 mL of 10 N NaOH aqueous solution (34.1 mmol) were added with a syringe. To the monomer solution (pH = 13.05) was added 13.2

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Table 1. Polymerization of 1-H with Water-Soluble Rh Complexes in Water in the Presence of Base at 30 °C for 24 h[a]

run	Rh complex	base	[base]/[**1**−H]	yield (%)[b]	$Mn \times 10^{-3c}$	$M_w/M_n{}^c$
1	$[Rh(cod)_2]BF_4$	none		trace		
2	$[Rh(cod)_2]BF_4$	NaOH	1.05	100	3.4	2.2
3[d]	$[Rh(cod)_2]BF_4$	NaOH	1.05	39	3.1	1.9
4	$[Rh(cod)_2]BF_4$	NaOH	1.5	24	2.8	2.0
5	$[Rh(nbd)_2]ClO_4$	NaOH	1.05	18	3.1	1.9
6	$[Rh(cod)(tos)(H_2O)]$	NaOH	1.05	100	3.3	2.3
7	$[Rh(cod)_2]BF_4$	diethylamine	2	47	0.5	2.1

[a] Polymerized under nitrogen; [**1**-H] = 1.0 M, [**1**-H]/[Rh] = 100. [b] Et_2O insoluble part (runs 1 and 7) and ethanol insoluble part (runs 2-6). [c] Determined by SEC (polystyrene standards) as its methyl ester. [d] Polymerized in air.

mL (0.325 mmol) of $[Rh(cod)_2]BF_4$ solution (0.025 M) in water at 30 °C. The molar ratio of the monomer to the Rh complex was 100. The color of the mixture changed instantly to dark red. After 24 h, the polymerization mixture was poured into a large amount of ethanol, collected by filtration, washed with ethanol, and then dried in vacuo at 50 °C for 3 h to give orange fibrous poly-**1**−Na in 100% yield.

Spectroscopic data of poly-**1**−Na. IR (Nujol): 1565, 1343 (ν_{COO^-}); ^1H NMR (D_2O, 21 °C): δ 6.57 (s, =CH, 1H). ^{13}C NMR (D_2O, 21 °C): δ 130.4, 138.1, 177.2. Anal. Calcd for $(C_3HNaO_2 \cdot 1.4H_2O)_n$: C, 30.73; H, 3.27. Found: C, 30.52; H, 3.11.

A part of poly-**1**−Na was converted to poly-**1**−H through acidification with concentrated HCl and then to its methyl ester (poly-**1**−CH_3) by reaction with diazomethane in ether according to the previously reported method.[7] The molecular weight (M_n) of poly-**1**−CH_3 was estimated by size exclusion chromatography (SEC) with polystyrene standards using $CHCl_3$ as the eluent.

Spectroscopic data of poly-**1**−H. IR (Nujol): 1700 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6, 21 °C): δ 5.5−9.0 (broad, =CH, 1H).

CD Measurements. Throughout for all measurements, deionized and distilled water was used after degassing with nitrogen. The concentrations of poly-**1**−Na and poly-**1**−H were calculated based on monomer units. In the complexation of poly-**1**−Na or poly-**1**−H with optically active amines, 1 mg of poly-**1**−Na or poly-**1**−H was placed in a 1 mL flask equipped with a stopcock. An appropriate amount of (*S*)- or (*R*)-enantiomer was added to the flask, water was then added to the flask to keep the polymer concentration of 1.0 mg/mL, and the absorption and CD spectra were taken in a 0.02 cm quartz cell.

Instruments. NMR spectra were taken on a Varian Mercury 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C with dioxane as the internal standard. SEC measurements were performed with a Jasco PU-980 liquid chromatograph equipped with a UV (254 nm; Jasco UV-970) or a RI (Jasco RI-930) detector at 40 °C. A Tosoh TSK gel MultiporeH$_{XL}$-M (30 cm for $CHCl_3$) or a Tosoh TSKgel α-M (30 cm for aqueous eluents) SEC column was connected at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh) in $CHCl_3$ or standard pullulans in aqueous eluents. IR spectra were recorded using a Jasco Fourier Transform IR-620 spectrophotometer. Absorption and CD spectra were taken on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter, respectively. Laser Raman spectra were measured on a Jasco NRS-1000 spectrophotometer. The solution pH was measured with an HM-35V pH meter (TOA, Japan).

Results and Discussion

Polymerization of Propiolic Acid (1-H) in Water and Structures of the Polymers. The polymerization results of **1**−H with water-soluble Rh complexes are summarized in Table 1. In the absence of base, the polymerization hardly proceeded to give only a trace amount of the Et_2O insoluble polymer, and the Et_2O soluble part was unreacted monomer. This may be due to inactivation of the Rh complexes by the acidic proton of **1**−H in accordance with previous results.[3,6,7] When the polymerization of **1**−H with $[Rh(cod)_2]BF_4$ was carried out in the presence of 1.05 equivalents of NaOH, the polymerization rapidly and homogeneously took place, producing orange fibrous polymers in quantitative yield (run 2 in Table 1). The conversion of the carboxy groups into carboxylate ions by the neutralization reaction appeared to exclude the termination reaction by the acidic carboxy groups. On the other hand, in the presence of an excess amount of NaOH ([NaOH]/[**1**−H] = 1.5), the resulting polymer immediately precipitated after the addition of the Rh complex to give a slightly yellow, powdery polymer in lower yield (24%, run 4 in Table 1), probably because of the common ion effect by the excess sodium ion which results in decreasing the solubility of the formed sodium salt of the polymer (poly-**1**−Na) in water. Other water-soluble Rh complexes, $[Rh(nbd)_2]ClO_4$ and $[Rh(cod)(tos)(H_2O)]$, were also employed to examine the effect of the catalysts on the polymerizability of **1**−H in water. $[Rh(cod)(tos)(H_2O)]$ also afforded the orange, fibrous polymer in quantitative yield,[12] whereas $[Rh(nbd)_2]ClO_4$ exhibited poor polymerizability. These catalytic activities of the Rh complexes are different from those previously reported for the polymerization of the phenylacetylenes in organic solvents, where the Rh complexes bearing the nbd ligand showed higher polymerizability than those bearing the cod ligand.[1g,1h] The polymerization reaction also took place in air and water to yield poly-**1**−Na (run 3 in Table 1). In the presence of diethylamine instead of NaOH, the polymerization of **1**−H gave a slightly yellow, powdery polymer in moderate yield (run 7 in Table 1). Amines may not be effective bases for the polymerization of **1**−H because of their lower basicity than that of NaOH. The molecular weights of poly-**1**−CH_3 derived from poly-**1**−Na through acidification followed by methylation with diazomethane were relatively low (Table 1). This may be due to decomposition of the polymers during the reactions (see below). We then attempted to estimate the molecular weights of poly-**1**−Na by SEC using aqueous eluent systems. However, it was difficult for strong adsorption on an SEC column or aggregation of the polymer.[13] We believe that the original poly-**1**−Na might have a higher molecular weight than those of poly-**1**−CH_3.

The stereoregularity of the obtained poly-**1**−Na was investigated by NMR spectroscopy. The ^1H NMR spectrum of the poly-**1**−Na prepared with $[Rh(cod)_2]BF_4$ (run 2 in Table 1) showed a sharp singlet centered at 6.57 ppm in D_2O, which can be assigned to the main chain's protons, indicating that the polymer possesses a highly *cis*−*transoidal*, stereoregular structure (Figure 1A).[1,2] The ^{13}C NMR spectrum of the poly-**1**−Na in D_2O also supports the high stereoregularity of the polymer and shows sharp peaks similar to those reported for the *cis*−*transoidal* poly(alkyl propiolate)s by Tabata et al. (Figure 1B).[2a]

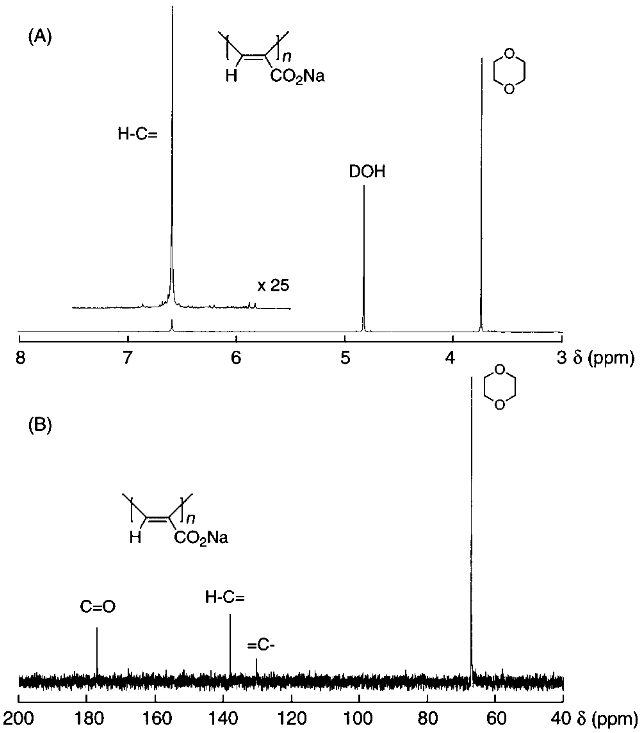


Figure 1. ^1H (A) and ^{13}C (B) NMR spectra of poly-**1**−Na (run 2 in Table 1) in D_2O with dioxane as the internal standard at 21−23 °C.

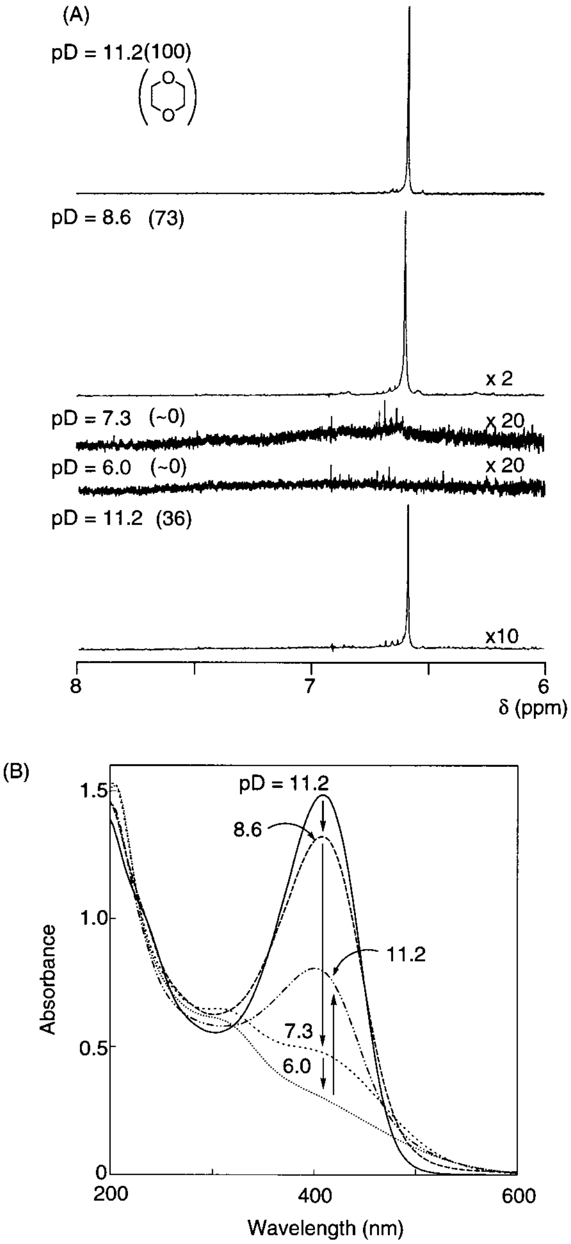


Figure 2. ^1H NMR (A) and absorption (B) spectral changes of poly-**1**−Na in D_2O at various pD at room temperature (ca. 21−22 °C). The peak intensity at 6.57 ppm relative to that of the internal standard (1,4-dioxane) was shown in the parentheses in part A.

The stereoregular poly-**1**−Na was converted into the acid form (poly-**1**−H) through acidification with concentrated HCl. The conversion into the carboxy group was confirmed by IR spectroscopy. However, the ^1H NMR spectrum of the poly-**1**−H exhibited very broad resonances in DMSO-d_6 due to the methine protons of the main chain at around 5.5−9.0 ppm. This suggests that the stereoregularity of the polymer may be changed during the acidification. To confirm this, the ^1H NMR (Figure 2A) and absorption (Figure 2B) spectral changes were followed during the acidification of poly-**1**−Na with 1 N DCl in D_2O. The intensity of the sharp singlet peak at 6.57 ppm due to the main chain's *cis*-vinyl protons decreased as the pD[14] of the solution became lower, and the signal completely disappeared at pD = 7.3 with extremely broad resonances at around 6−8 ppm. However, the sharp peak was again observed when the pD was readjusted to 11.2 by adding an aqueous NaOD solution, although the peak intensity decreased to about one-third (36%) that of the original peak intensity. These results indicate that the cis component of the polymer decreased probably due to the isomerization of the cis to trans form during the conversion of poly-**1**−Na into poly-**1**−H, although the poly-**1**−H partially maintains the *cis−transoidal* structure. The absorption spectral changes also support the cis to trans isomerization of the polymer during the course of the acidification of poly-**1**−Na, showing a decrease in the absorption at around 400 nm accompanied by the appearance of an absorption at a longer wavelength (>500 nm).[2a,15,16] Similar changes in the ^1H NMR and absorption spectra were also observed with time without changing the solution pH (pH = 11.2) when the poly-**1**−Na solution in D_2O was allowed to stand at room temperature (ca. 21 °C) (see Figure S-1 in the Supporting Information). The *cis−transoidal* structure of poly-**1**−Na in solution may not be stable and gradually changes to another one with time even at room temperature, although the poly(alkyl propiolates) are quite stable at high temperatures.[2b]

To get further detailed information on the stereoregularity of the obtained polymers, the laser Raman spectra of poly-**1**−Na and poly-**1**−H derived from the original poly-**1**−Na by acidification were measured in H_2O and NaOH aqueous solution (pH = ca. 13), respectively (Figure 3). The stereoregular poly-**1**−Na (a, run 2 in Table 1) showed intense peaks at 1560, 1327, and 901 cm^{-1}, which can be assigned to the C═C, C−C, and C−H bond vibrations, respectively, in the cis polyacetylenes according to the literature.[2a,15a,17,18] On the other hand, the poly-**1**−Na derived from poly-**1**−H obtained through acidification of the original poly-**1**−Na showed a new intense peak at 1163 cm^{-1} in alkaline solution (line d in Figure 3) assigned to the C−C bond vibration in the trans form,[2a,15a,17,18] whereas such a peak was not

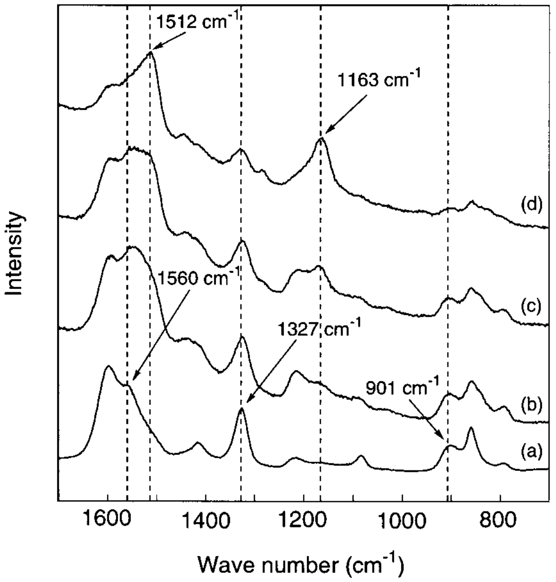


Figure 3. Laser Raman spectra of poly-**1**−Na (run 2 in Table 1) immediately after dissolving in H_2O (line a) and after 2 (line b) and 10 days (line c). Raman spectrum of poly-**1**−Na in H_2O derived from poly-**1**−H is also shown (line d).

observed for the original poly-**1**−Na (line a in Figure 3). The peak intensity of the original poly-**1**−Na at 1163 cm^{-1} increased with time after the polymer dissolved in water was allowed to stand at room temperature for 2 (line b in Figure 3) and 10 days (line c in Figure 3). Moreover, the shift in the cis peak at 1560 cm^{-1} (line a) to the lower wavelength (1512 cm^{-1}) observed for poly-**1**−H (line d) and poly-**1**−Na after 2 (line b) and 10 days (line c) can be explained by the increase in the trans structure because quite similar changes were reported for the cis to trans isomerization of highly *cis*−*transoidal* polyacetylenes induced by compression,[2a,15a] and the peak at 1512 cm^{-1} can be assigned to the C=C bond vibration in the trans form.[2a,15a,17,18] These results support the above speculation that the cis to trans isomerization might occur when the poly-**1**−Na was transformed into poly-**1**−H by acidification or in solution over time. The peaks at 1327 and 901 cm^{-1} were observed for all samples more or less, and therefore, the poly-**1**−H derived from poly-**1**−Na by acidification may maintain the partially *cis*−*transoidal* structure. These Raman spectral results are quite consistent with the previously described ^{1}H NMR results (Figure 2).

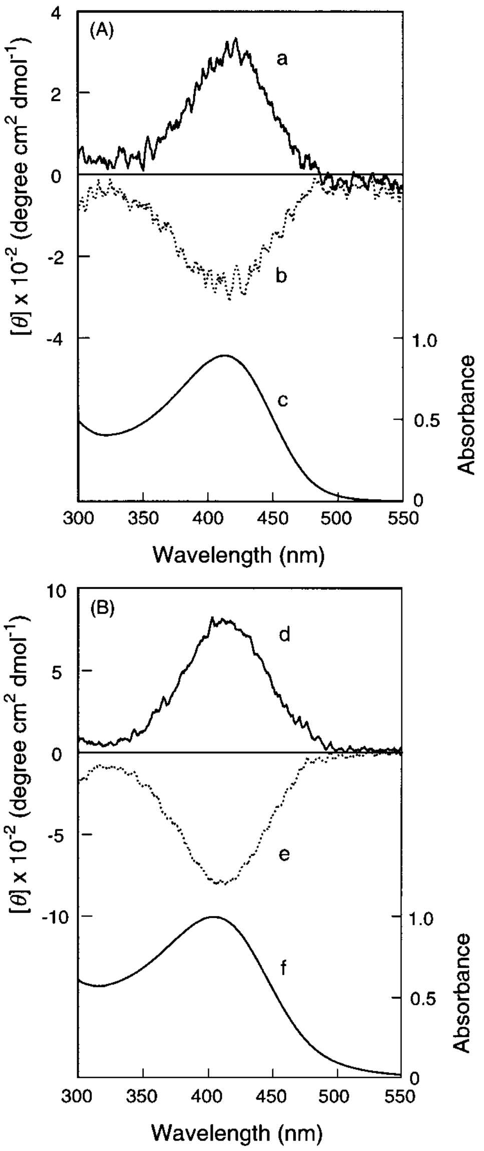
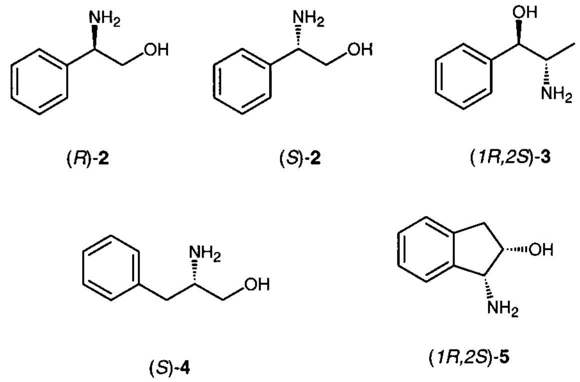


Figure 4. CD spectra of poly-**1**−Na (A) and poly-**1**−H (B) (1.0 mg/mL) with (*R*)-**2** (lines a, d) and (*S*)-**2** (lines b, e) in H_2O (pH = 11.2 (lines a, b), and 11.1 (lines d, e)) at 25 °C. Absorption spectra with (*S*)-**2** at 25 °C are also shown by lines c and f. The molar ratio of **2** to monomer units of poly-**1**−Na and poly-**1**−H is 50.

Chart 1



Helix Induction on the Polymer. Figure 4A shows the CD and absorption spectra of poly-**1**−Na in the presence of the (*S*)- and (*R*)-phenylglycinols (**2**) (Chart 1) ([**2**]/[poly-**1**−Na] = 50) in water. The complexes showed ICDs of the mirror images in the absorption region due to the main chain even in water. Poly-**1**−H derived from poly-**1**−Na also showed similar ICDs (Figure 4B) under the same conditions. These ICDs were quite similar in pattern to those observed for the poly-(1,1-diethylpropargylamine) complexed with optically active α-hydroxy acids in THF.[8] A similar helical induction has been reported for other optically inactive polyphenylacetylenes bearing functional groups with chiral compounds.[19] The magnitude of the ICDs decreased by adding a salt such as NaCl due to increases in ionic strength. This indicates that the nature of the interaction of poly-**1**−Na and poly-**1**−H with **2** may be ionic rather than hydrophobic and these polymers form a predominantly one-handed helical conformation by ionically interacting with the optically active **2** even in water. Other optically active amino alcohols such as (*1R,2S*)−(−)-norephedrine (**3**), (*S*)-phenylalaninol (**4**), and (*1R,2S*)-*cis*-1-amino-2-indanol (**5**) were examined for the induction of helicity on the polymers. Poly-**1**−Na and poly-**1**−H also exhibited ICDs in the UV−visible region in water in the presence of **3** and **3**−**5**, respectively, but clear ICDs were not observed for poly-**1**−Na in the presence of **4** and **5**; the molar ellipticities ($[\theta] \times 10^{-2}$ (deg cm^2 $dmol^{-1}$) (λ (nm), pH, [amino alcohol]/[poly-**1**−Na or poly-**1**−H])) of the first Cotton for the complexes of poly-**1**−Na−(*1R,2S*)-**3**, poly-**1**−H−(*1R,2S*)-**3**, poly-**1**−H−(*S*)-**4**, and poly-**1**−H−(*1R,2S*)-**5** were −4.1 (365, 10.8, 30), −5.2 (370, 10.7, 30), −2.2 (358, 10.9, 30), and −2.0 (420, 10.5, 10), respectively. We also used several natural, free amino acids, such as L-tryptophan and L-methionine which were effective helical inducers for the sodium salt of PCPA,[7] but the apparent ICDs could not be observed in water.

In summary, we found that an aliphatic acetylene bearing a carboxy group, propiolic acid, was directly polymerized in water in the presence of bases to yield the *cis*−*transoidal* polymer, and the polymer exhibited an ICD in the presence of optically active amino alcohols even in water. The present results demonstrate that the simple methodology of the stereospecific polymerization and helix induction on the polymer in water, which we have recently developed for aromatic acetylenes bearing a carboxy group, was applicable to aliphatic acetylenes bearing a carboxy group. This may be the first example of the stereospecific polymerization of aliphatic carboxy acetylenes and the helix induction on the polymer in water.

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Supporting Information Available: Figures of absorption spectral changes with time and plots of changes in relative absorption intensities and ^1H NMR peak intensities of poly-**1**−Na in D_2O with time at ambient temperature (ca. 21 °C). These materials are available free of charge via the Internet at http://pubs.acs.org.

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(12) Tang et al. reported that the polymerization of aliphatic acetylenes, such as $HC{\equiv}C(CH_2)_5CH_3$, $HC{\equiv}C(CH_2)_2OH$, $HC{\equiv}C(CH_2)_3CO_2H$, and $HO_2CC{\equiv}CCO_2H$, with the water-soluble Rh complex ([Rh(cod)(tos)(H_2O)]) in water did not yield polymeric products and the lack of the Rh-aromatic interaction between the Rh complex and the aliphatic monomers might be responsible for the failure of the polymerization. However, the present results indicate that such a Rh−aromatic interaction may not be necessary for the polymerization of aliphatic acetylenes with the Rh-based complexes, although a Rh−carbonyl interaction could not be ruled out. Tang, B. Z.; Poon, W. H.; Leung, S. M.; Leung, W. H.; Peng, H. *Macromolecules* **1997**, *30*, 2209−2212.

(13) Several aqueous eluents (0.2 M NaCl aq, 0.2 M $NaNO_3$ aq, and 0.2 M $NaNO_3$ aq/CH_3CN (8/2, v/v)) were examined in the SEC measurements, but the polymer strongly adsorbed on the gel and eluted after the time corresponding to $M_n = 0$. When 5 wt % aqueous glycine was used as the eluent, the adsorption to the gel was suppressed. However, the molecular weight of poly-**1**−Na (run 2 in Table 1) calibrated with standard pullulans was calculated to be more than 1.0×10^7, indicating that in this eluent, the polymer may aggregate, and the molecular weight of poly-**1**−Na could not be estimated.

(14) pD values were estimated from the reading of pH meter according to the equation $pD = pH_{\text{meter reading}} + 0.40$ reported by Glasoe et al., see: Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188−190.

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