

SHORT COMMUNICATIONS

Induced Helix of an Aliphatic Polyacetylene Detected by Circular Dichroism

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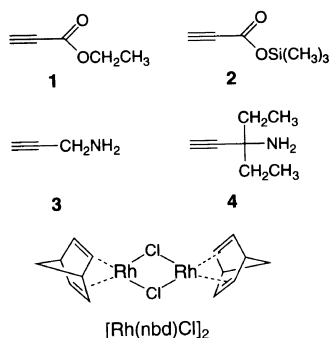
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Recently, we have found that optically inactive, stereoregular poly(phenylacetylene)s, such as poly((4-carboxyphenyl)acetylene),¹ poly((4-dihydroxyborophenyl)acetylene),² and poly((4-*N,N*-diisopropylaminomethyl)phenylacetylene)³ form a predominantly one-handed helix upon complexation with optically active compounds, such as amines, sugars, and acids, respectively, and the complexes exhibit a characteristic induced circular dichroism (ICD) in the UV-visible region. The Cotton effect signs of ICDs can be used as a novel probe for the assignments of the absolute configuration of the chiral compounds.

In the present study, we prepared aliphatic polyacetylenes bearing a carboxy or amino group by polymerization of propionic acids esters (**1**, **2**) and propargylamines (**3**, **4**) with [(norborene)-rhodium(I) chloride]₂ [Rh(nbd)Cl]₂ as a catalyst in order to investigate whether these aliphatic polyacetylenes would form an induced helix upon complexation with optically active compounds as seen in cases of the poly(phenylacetylene) derivatives bearing functional groups.^{1–3} We found that poly(1,1-diethylpropargylamine) can form an induced helix upon complexation with optically active acids. This may be the first example of the prevailing helix formation of an optically inactive, aliphatic polyacetylene ascribed to acid-base interaction.



EXPERIMENTAL

Materials

Ethyl propiolate (**1**) and propargylamine (**3**) were purchased from Tokyo Kasei and trimethylsilyl propiolate (**2**) and 1,1-diethylpropargylamine (**4**) were obtained from Aldrich. These monomers were dried over calcium hydride and distilled before use. [Rh(nbd)Cl]₂ was obtained from Aldrich and used as received. All solvents

were dried and distilled by the usual methods. Solvents used for measurements of CD and NMR spectra were purged with argon prior to use. (*R*)- and (*S*)-mandelic acids were purchased from Kishida and Wako, respectively. Other optically active compounds were available from Aldrich.

Polymerization

Polymerization was carried out in a dry glass ampoule under a dry nitrogen atmosphere using [Rh(nbd)Cl]₂ as a catalyst in a similar way as previously reported.^{1–3} Poly(trimethylsilyl propiolate) (poly-**2**) was converted to poly(propionic acid) by solvolysis of the ester groups using a small amount of HCl in methanol. Conversion of the poly(propionic acid) into the methyl ester was carried out using CH₂N₂ in ether solution according to the method reported previously.⁴

Hydrolysis of poly(ethyl propiolate) (poly-**1**) was carried out in tetrahydrofuran (THF)–aqueous NaOH (10 *N*) (4 : 1, v/v) in the same way for the hydrolysis of poly(4-((ethoxycarbonyl)phenyl)acetylene) into poly(4-carboxyphenyl)acetylenes.^{1b} However, the ¹H NMR spectrum of the recovered polymer showed that it contained more than 80% of the ethyl group. Completely hydrolyzed polymer was not obtained by further treatment of the polymer in an alkaline–THF or alkaline–ethanol (*ca.* 40 wt%) solution.

Because of poor solubility of poly(propargylamine) (poly-**3**) and poly(1,1-diethylpropargylamine) (poly-**4**) in common organic solvents including chloroform and THF, molecular weights of these polymers could not be estimated by gel permeation chromatography (GPC).

Measurements

¹H NMR spectra were measured on a Varian VXR-500 or Varian Gemini 400 NMR spectrometer operating at 500 or 400 MHz, respectively. Tetramethylsilane (TMS) was used as the internal standard. IR spectra were recorded using a JASCO Fourier Transform IR-7000 spectrophotometer with a JASCO PTL-396 data processor. Absorption spectra were taken on a JASCO Ubest-55 spectrophotometer. CD spectra were measured in a 0.10 cm quartz cell using a JASCO J-720 L spectropolarimeter at ambient temperature. GPC was performed using a JASCO 880-PU chromatography equipped with a UV-visible (254 nm; JASCO 875-UV) detector. GPC columns, Shodex KF-802.5 (30 × 0.72 (i.d.) cm) and AC-80 (50 × 0.72 (i.d.) cm) were connected

Table I. Polymerization of aliphatic acetylenes with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ at 30°C^a

Run	Monomer	Solvent	Time/h	Yield/% ^b
1	1	CH ₃ OH	1	40 ^{c,d}
2 ^e	2	Et ₂ O	68	12
3 ^e	2	THF	68	7 ^f
4	2	DMSO	24	18
5	2	DMF	24	12
6	2	CH ₃ CN	24	36 ^{g,h}
7	3	CH ₃ OH	18	19
8	3	NEt ₃	18	9
9	3	None	18	19
10	4	None	24	4
11	4	CH ₃ OH	18	2
12	4	NEt ₃	18	2

^a [Monomer] = 2.0 M (run 1, 3–12), 0.35 M (run 2), [Monomer]/[Rh] = 100 (run 3–6, 8, 12), 70 (run 2), 50 (run 1, 7, 9, 10, 11). ^b Et₂O insoluble fraction. ^c $M_n = 4.7 \times 10^4$. ^d Methanol insoluble fraction. ^e Triethylamine was used as a cocatalyst: [NEt₃] = 0.1 M. ^f Acetone insoluble fraction. ^g Hexane insoluble fraction. ^h $M_n = 1.7 \times 10^3$ (methyl ester).

in series and THF was used as the eluent at a flow rate of 1.0 ml min⁻¹. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh).

RESULTS AND DISCUSSION

Table I shows the results of polymerization of aliphatic acetylenes (1~4) with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ which is well known to be effective for the stereospecific polymerization of mono-substituted phenylacetylenes⁵ and propiolates^{6,7} to afford high molecular weight, *cis*-transoidal polyacetylene derivatives. Polymerizability of monomers with the rhodium catalyst was low except for 1 compared with that of phenylacetylenes and the resulting powdery polymers were precipitated during the polymerization reaction, while monomer 1 showed the highest polymerizability and afforded a relatively high molecular weight ($M_n = 47000$), yellow polymer. Poly-1 was soluble in common organic solvents including chloroform, THF, and dimethylsulfoxide (DMSO), whereas poly-3 was not soluble in common organic solvents even in the presence of acids. A similar observation was reported by Gal, *et al.*⁸ They found that poly-3 and poly-4 prepared with W- and Mo-based catalysts⁹ were insoluble in organic solvents, although the poly-4 prepared in this study was soluble in THF in the presence of mandelic acid and in methanol. Direct introduction of the electron-donating amino group appeared to reduce the polymerizability and the solubility of polymers.^{3b,10}

The stereoregularity of polyacetylenes was examined by ¹H NMR spectroscopy. As for the structure of polyacetylenes, there exist at least four possible conformers; *cis*-transoid, *cis*-cisoid, *trans*-transoid, and *trans*-cisoid.¹¹ Poly-1 showed the resonance centered at 6.89 ppm with a well-resolved sharp line width which can be assigned to the *cis*-transoidal main chain's protons.^{5,6} Attempts to convert poly-1 to poly(propionic acid) by alkaline hydrolysis were unsuccessful. Moreover, the sharp resonances of poly-1 completely disappeared during the hydrolysis process and changed to broad resonances at 5.0–8.0 ppm. This suggests that the *cis*-transoidal conformation of poly-1 may be changed

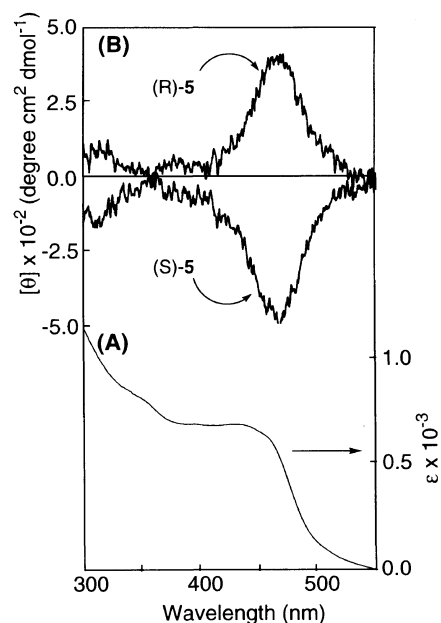
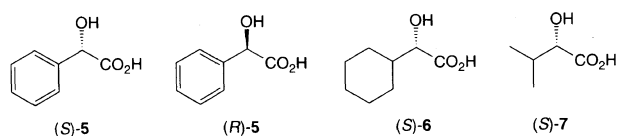


Figure 1. Absorption (A) and CD spectra (B) of poly-4 with (*S*)-5 and (*R*)-5; molar ratio of 5 to monomeric units of poly-4 is 100. The absorption and CD spectra were measured in THF solutions in a 0.1 cm quartz cell at ambient temperature (*ca.* 20–22°C) with a poly-4 concentration of 1.0 mg ml⁻¹.

to another one during the reaction. Trimethylsilyl propiolate (2) was then polymerized to obtain poly(propionic acid), since trimethylsilyl groups can be easily deprotected with an acid. Although poly-2 was quantitatively converted into poly(propionic acid), the molecular weight of poly-2 obtained was low (1700, run 6 in Table I). Moreover, the ¹H NMR spectrum of the poly(propionic acid) exhibited very broad resonances at around 4.5–8.6 ppm, probably due to the stereoirregular structure of the polymer. On the other hand, the ¹H NMR spectrum of poly-4 was not broad but complicated; there are several rather sharp resonances at around 5.6–6.5 ppm. We could not fully assign these peaks, and the *cis* content could not be estimated. However, we assume that poly-4 may have a *cis*-transoidal unit in part, which may contribute to the appearance of ICD. Regular *cis*-transoidal main chain structure seems to be essential for the formation of a helical conformation to exhibit an ICD, since stereoirregular poly((4-carboxyphenyl)acetylene) prepared with Mo- or W-based catalysts with high molecular weight showed very weak or almost no ICD in the presence of optically active amines.^{1b}

CD spectra of these polymers in the presence of optically active amines or carboxylic acids were measured in order to investigate the possibility whether they will respond to chiral compounds, showing a characteristic ICD. Figure 1 shows CD and absorption spectra of poly-4 (run 10 in Table I) in the presence of (*R*)-mandelic acid ((*R*)-5) or (*S*)-5 in THF. Poly-4 showed broad electronic absorptions up to *ca.* 550 nm with a peak at around 450 nm and exhibited ICDs which are mirror images. The poly-4 having the irregular twist of the adjacent double bonds around a single bond may be transformed into the helical conformation with a predominant screw-sense through acid-base interaction.¹ These ICDs were different in pattern from those of the acid-base complexes of the *cis*-transoidal poly((4-

carboxyphenyl)acetylene) with optically active amines¹ and poly(phenylacetylene)s bearing a chiral substituent at the *para*-position.¹¹ Aliphatic polyacetylenes may have a different helical conformation from those of the aromatic poly(phenylacetylene)s.



Poly-4 also complexed with other α -hydroxy acids such as (*S*)-hexahydromandelic acid (**6**) and (*S*)-2-hydroxy-3-methylbutyric acid (**7**) in THF to show ICDs; molar ellipticities ($[\theta] \times 10^{-2}$ (degree $\text{cm}^2 \text{d mol}^{-1}$) and λ (nm)) of the first Cotton for the complexes with (*S*)-**6** and (*S*)-**7** were -2.2 (473) and -1.3 (467), respectively. The sign of the Cotton effects appears to reflect the absolute configuration of the chiral acids. α -Hydroxy acids **5**–**7** of the same configuration gave the same Cotton effect signs. The induced helical structure of poly-4 in the presence of mandelic acids was not stable enough in solution and the ICD disappeared after 1 day.

Poly(propionic acid) derived from poly-2 (run 6 in Table I) did not show any ICD in the 300–500 nm range in the presence of an excess of (*R*)-2-amino-1-propanol in DMSO. This may be due to its low molecular weight and the stereoirregular structure of the polymer.

In summary, we have, for the first time, found that an aliphatic polyacetylene, poly(1,1-diethylpropargylamine), exhibited an ICD in the presence of optically active acids, probably due to the induced helix formation of the polymer. The present results in addition to the previous ones^{1–3} indicate that the various derivatives of aliphatic and aromatic polyacetylenes bearing a functional group will form an induced helix when they are complexed with optically active compounds.

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REFERENCES AND NOTES

- (a) E. Yashima, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **117**, 11596 (1995). (b) E. Yashima, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **119**, 6345 (1997).
- E. Yashima, T. Nimura, T. Matsushima, and Y. Okamoto, *J. Am. Chem. Soc.*, **118**, 9800 (1996).
- (a) E. Yashima, Y. Maeda, and Y. Okamoto, *Chem. Lett.*, 955 (1996). (b) E. Yashima, Y. Maeda, and Y. Okamoto, *Chirality*, **9**, 593 (1997).
- T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc.*, **114**, 1318 (1992).
- (a) A. Furlani, C. Napoletano, M. Russo, A. Camus, and N. Marsich, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 75 (1989). (b) M. Tabata, W. Yang, and K. Yokota, *Polym. J.*, **12**, 1105 (1990). (c) M. Tabata, W. Yang, and K. Yokota, *J. Polym. Sci., Part A, Polym. Chem.*, **32**, 1113 (1994).
- M. Tabata, Y. Inaba, K. Yokota, and Y. Nozaki, *J. Macromol. Sci., Pure Appl. Chem.*, **A31**, 465 (1994).
- Masuda *et al.* reported that Mo-based catalysts were also effective for the polymerization of propionic acid and its derivatives: T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, **23**, 744 (1982).
- Y.-S. Gal, B. Jung, W.-C. Lee, and S.-K. Choi, *J. Polym. Sci., Part A, Polym. Chem.*, **30**, 2657 (1992).
- T. Masuda and H. Tachimori, *J. Macromol. Sci., Pure Appl. Chem.*, **A31**, 1675 (1994).
- M. Lindgren, H.-S. Lee, W. Yang, M. Tabata, and K. Yokota, *Polymer*, **32**, 1531 (1991).
- (a) A. Furlani, C. Napoletano, M. V. Russo, and W. J. Feast, *Polym. Bull.*, **16**, 311 (1986). (b) A. Furlani, S. Licoccia, and M. V. Russo, *J. Polym. Sci., Part A, Polym. Chem.*, **24**, 991 (1986). (c) E. Yashima, S. Huang, T. Matsushima, and Y. Okamoto, *Macromolecules*, **28**, 4184 (1995).