A Stereoregular Polyphenylacetylene Derivative Bearing an Amino Group as a Probe for Chirality Assignments of Acids by Circular Dichroism

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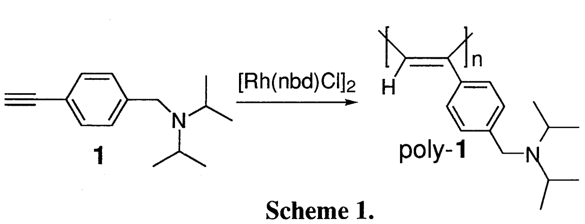
Cis-transoidal poly(4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene) prepared by polymerization with $[Rh(nbd)Cl]_2$ was found to exhibit an induced circular dichroism in the UV-visible region upon complexation with optically active acids probably due to a prevailing one-handed helix formation of the polymer, the sign of which reflects the absolute configuration of the acids.

Chiral recognition by chiral host molecules using circular dichroism (CD) spectroscopy is one of the current topics in host-guest chemistry.[1] Recently, we have found that achiral, stereoregular poly((4-carboxyphenyl)acetylene) can change its structure into a prevailing one-handed helix upon complexation with chiral amines, and its helical sense can be used as a probe for the chirality assignment of amines using the circular dichroism of the complexes.[2] We expect that related stereoregular polyphenylacetylenes bearing an amino group will also respond to chiral acids showing a characteristic induced CD (ICD) depending on the stereostructure of acids. Here, we report the complexation of poly(4-(*N*,*N* -diisopropylaminomethyl)phenylacetylene) (poly-**1**) with optically active carboxylic acids and their ICDs.



Scheme 1.

The coupling of (trimethylsilyl)acetylene to commercially available 4-bromo-N,N-diisopropylbenzylamine (Aldrich) with a palladium catalyst, followed by desilylation of the trimethylsilyl protecting group, was employed for preparing monomer **1**.[3] Polymerization was carried out in THF at 30 °C for 22 h under a dry nitrogen atmosphere using $[Rh(nbd)Cl]_2$ (nbd: norbornadiene) ([**1**] / [Rh]=100) as a catalyst (Scheme 1).[4] The rhodium catalyst has been known to be effective for the polymerization of mono-substituted phenylacetylenes to afford high molecular weight, stereoregular, cis-transoidal polyphenylacetylenes.[5] Yellow colored poly-**1** obtained quantitatively[6] was not soluble in common organic solvents including THF, chloroform, and acetonitrile. However, it can be dissolved in the solvents in the presence of carboxylic acids such as trifluoroacetic acid and mandelic acid.

The stereoregularity of poly-**1** was then examined by ^1H NMR in CD_3CN containing a minimum amount of trifluoroacetic acid to dissolve poly-**1**. The ^1H NMR spectrum showed a sharp singlet centered at 5.74 ppm due to the main chain protons, indicating that the polymer possesses a highly cis-transoidal, stereoregular structure.[5] The spectrum was identical even after several days at room temperature, suggesting that the poly-**1** is stable in solution.

Preliminary CD experiments were carried out using several optically active α-hydroxy carboxylic acids (**2** - **5**) and carboxylic acids (**6** - **8**). Figure 1 shows typical CD and absorption spectra of poly-**1** in the presence of (*S*)-mandelic acid ((*S*)-**2**) or (*R*)-**2** in THF. The poly-**1**–**2** complexes showed intense, split-type ICDs in the UV-visible region which are mirror images. The intensity of the ICD increased with an increase in the concentration of the optically active acid. This clearly indicates that the complexation involves an acid-base equilibrium, and the poly-**1** having the random twist of the adjacent double bonds around a single bond may be transformed into the helical conformation with a predominant screw-sense by interacting with the chiral acid.

These ICDs were similar in pattern to those of the acid-base complexes of the cis-transoidal poly((4-carboxyphenyl)acetylene) with optically active amines[2] and polyphenylacetylenes bearing a chiral substituent at the *para*-position.[4,7]

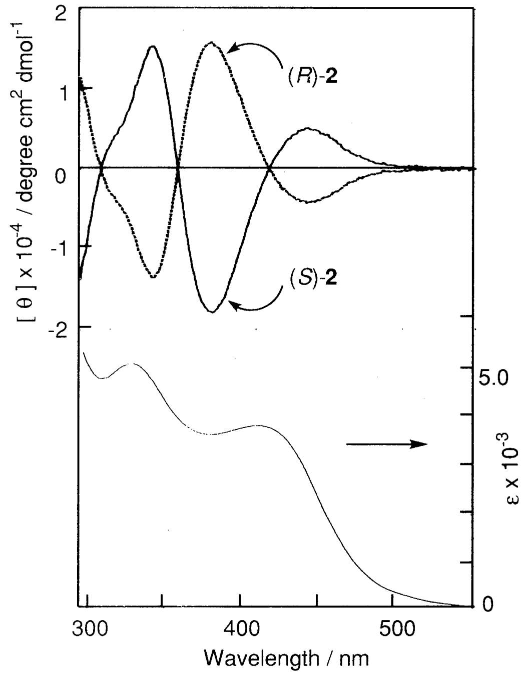
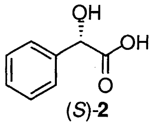
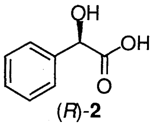


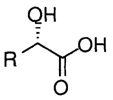
Figure 1. CD spectra of poly-**1** with (*S*)- and (*R*)-**2** and absorption spectrum with (*R*)-**2** in THF; ([**2**] / [poly-**1**]=100). The CD spectra were measured in dry THF solutions in a 0.1 cm quartz cell at *ca*. 20-22 °C with a poly-**1** concentration of 0.75 mg / ml on a Jasco J-720 L spectropolarimeter. A solution of poly-**1**-(*R*)-**2** gave the same CD spectrum after the sample had been allowed to stand for 3 days at room temperature.



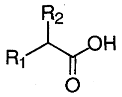
(*S*)-**2**



(*R*)-**2**



R = CH_2Ph (*S*)-**3**
$CH(CH_3)_2$ (*S*)-**4**
CH_3 (*S*)-**5**



R_1 = Ph, R_2 = Et (*S*)-**6**
R_1 = Ph, R_2 = CH_3 (*S*)-**7**
R_1 = Et, R_2 = CH_3 (*S*)-**8**

Poly-**1** also complexed with other α-hydroxy acids (**3** - **5**) in THF to show ICDs, and the split type and magnitude of the Cotton effects appear to reflect the absolute configuration and bulkiness of the chiral acids. α-Hydroxy acids **2** - **5** of the same configuration gave the same Cotton effect signs and the magnitude of the ICDs seems to depend on the bulkiness of the α-hydroxy acids; *i.e.*, the observed ICD increased in the order of **2** > **3** > **4**, **5**.[9] However, poly-**1** showed almost no ICDs in THF even in the presence of a large excess of carboxylic acids **6** - **8** (150 fold). The chelation effect of the hydroxy group of the α-hydroxy acids must play a role in the intense ICD. However, in acetonitrile the complexes with the carboxylic acids (**6** - **8**) showed intense ICDs, although their Cotton effect signs were opposite to those of the complexes with α-hydroxy acids of the same configuration.[10] The reason for the opposite ICD signs is not apparent at present.

In summary, poly-**1** provides a new probe for chirality assignments of carboxylic acids using CD. It will be expected that related polyacetylene derivatives bearing other amino or pyridyl groups will also respond to chiral acids.

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References and Notes

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3 **1**: 32% yield; bp 54 - 56 °C / 0.13 mmHg; IR (KBr): 3298 ($\nu_{\equiv C\text{-}H}$), 2110 ($\nu_{C\equiv C}$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.01 (d, CH_3, 12H), 3.01 (m, CH, 2H), 3.03 (s, ≡CH, 1H), 3.63 (s, CH_2, 2H), 7.35 (d, aromatic, 2H), 7.43 (d, aromatic, 2H). Anal. Found: C, 83.67; H, 9.80; N, 6.70%. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50%.

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6 Poly-**1**: 93% yield; ^1H NMR (CD_3CN with *ca.* 20 μl of CF_3CO_2H, 60 °C, 500 MHz): δ 1.24 (d, CH_3, 12H), 3.57 (m, CH, 2H), 4.09 (s, CH_2, 2H), 5.74 (s, =CH, 1H), 6.70 (s, aromatic, 2H), 7.43 (s, aromatic, 2H). Anal. Found: C, 83.61; H, 10.03; N, 6.42%. Calcd for $(C_{15}H_{21}N)_n$: C, 83.67; H, 9.83; N, 6.50%.

7 There are at least three Cotton effects with the exciton-type splittings[8] in the ICDs. However, the assignments of the Cotton effects have not yet been made.

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9 Molar ellipticities ($[\theta] \times 10^{-3}$ (degree cm^2 $dmol^{-1}$) and λ (nm)) of the second Cotton for the complexes with (*S*)-**3**, (*S*)-**4**, and (*S*)-**5** in THF in a 0.5 mm cell were -4.6 (371), -2.1 (368), and -2.6 (372), respectively; [poly-**1**]= 1.0 mg / ml, [acid] / [poly-**1**]=100 for (*S*)-**3** and 150 for (*S*)-**4** and (*S*)-**5**.

10 Molar ellipticities ($[\theta] \times 10^{-3}$ (degree cm^2 $dmol^{-1}$) and λ (nm)) of the second Cotton for the complexes with (*S*)-**6**, (*S*)-**7**, and (*S*)-**8** in acetonitrile in a 0.5 mm cell were 13.3 (370), 12.0 (370), and 0.7 (372), respectively; [poly-**1**]= 1.0 mg / ml, [acid] / [poly-**1**]=50. For solvent effects in acid-base equilibria, see: C. Reichardt, in *"Solvents and Solvent Effects in Organic Chemistry,"* VCH, Weinheim (1990), Chaps. 3 and 4, p. 51; K. Izutsu, in *"Acid-Base Dissociation Constants in Dipolar Aprotic Solvents,"* Blackwell, Oxford (1990).