Detection of the Site of an Enantioselective Interaction between Chiral Polypinanylsilane and a Hydrophobic Enantiomer by Use of Circular Dichroism

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Since optically active poly(methylpinanylsilane) synthesized by Na-mediated polycondensation of the corresponding dichlorosilane showed an Cotton effect at the UV region of Siσ-Siσ^* transition of the main chain in the circular dichroism (CD) spectrum, the main chain was found to have a chirality. The Cotton bands in the presence of the (+)-isomer of a hydrophobic compound were different from those in the presence of the (-)-isomer. Therefore, this polymer was found to have an ability of the enantioselective recognition. On the other hand, a hydrophilic compound did not affect the CD band. These findings indicate that the recognition was caused mainly by hydrophobic diastereomeric interaction between the chiral compound and the chiral main chain in this polymer.

We reported that the membranes from several new polymers having bulky chiral pinanyl substitutents showed enantioselective recognition in permeation.[1a-f] However, the site of the interaction between these chiral polymers and enantiomers which caused their enantioselective recognitions was still not clear, because these polymer structures including the conformations were too complex to understand them.[1g] In order to clarify the site of the interaction, it is desirable that the structure of the polymer is as simple as possible. Since polysilanes have only one excitation chromophore in the σ-conjugated main chain,[2] their CD bands are simple and assignable.[3] Thus, it is easy to decide the site of the chirality of the polymer and to discuss the chiral interaction with a chiral compound using CD.[3] In this letter, we report the enantio-selective recognition of the (+)-poly(methylpinanylsilane) [(+)-poly(MPS)] and the site of its interaction with a chiral compound.

The monomer dichloromethylpinanylsilane (MPS) was prepared by hydrosilylation of dichloromethylsilane to (-)-β-pinene with a Pt catalyst [Figure 1 (a)].[1c,4] Condensation polymerization of MPS was carried out in toluene at the reflux temperature for 3 h under a dry nitrogen atmosphere using Na and 15-crown-5-ether [Figure 1 (a)].[2c,5] The resulting (+)-poly(MPS) was soluble in common organic solvents such as toluene, heptane, tetrahydrofuran, and chloroform, and has high-molecular-weight and unimodal molecular distribution [Figure 1 (b)].[2c,6] The crown ether is effective for the synthesis of an unimodal polysilane.

The chirality of the main chain of (+)-poly(MPS) was examined with CD in chloroform at -15 °C [Figure 1 (c)].[7] (+)-Poly(MPS) exhibited a positive and negative Cotton band at 280 nm and 303 nm, respectively. The bands were assigned to a ***P***-screw-sense and a ***M***-screw-sense[8] of the main chain, respectively, according to the Fujiki's report.[3]

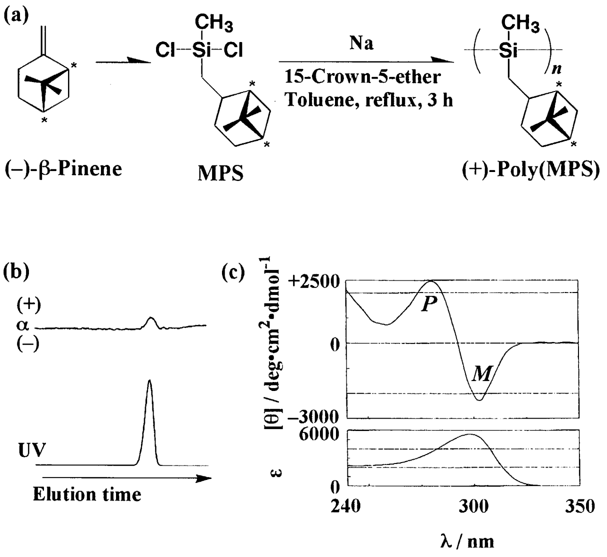

Figure 1. (a) Synthetic route to (+)-poly(MPS). (b) GPC trace of (+)-poly(MPS) detected with polarimeter (upper) and UV (bottom). (c) CD and UV spectra of (+)-poly(MPS) in chloroform at -15 °C.

Figures 2 (a) and (b) show the CD spectra of (+)-poly(MPS) in the presence of optically active (+)- or (-)-β-pinene and (+)- or (-)-menthol in chloroform at -15 °C, respectively.[9] In Figure 2 (a), the negative Cotton band assigned to ***M***-screw-sense in the presence of the (+)-isomer ($[\theta]_{303}$; -2400) of hydrophobic β-pinene was much stronger than that in the presence of the (-)-isomer ($[\theta]_{303}$; -2200), while the positive Cotton band assigned to ***P***-screw-sense in the presence of the (-)-isomer ($[\theta]_{280}$; +2500) was much stronger than that in the presence of the (+)-isomer ($[\theta]_{280}$; +2000). These facts indicate that the main chains of ***M***- and ***P***-screw-sense interacted differently with the (+)- and (-)-isomer. It was found the polymer had an ability of enantioselective recognition. In Figure 2 (b), the strengths of the bands assigned to ***M***-screw were different between in the presence of (+)-isomer and in the presence of (-)-isomer, while the strengths of the bands assigned to ***P***-screw were almost same.[10] Therefore, an ability of enantioselective recognition of this polymer was also confirmed. In addition, in this system (b), it was expected the polymer had an ability to separate the enantiomer.[11] On the other hand, no changes were observed in CD by adding an enantiomer of hydrophilic 1,3-butanediol. These findings indicate the enantioselective recognition of (+)-poly(MPS) was caused by the hydrophobic interaction between the main chain and the chiral isomer.

In our previous report,[1e] we speculated that optically active poly(dimethylpinanylsilylpropyne) [(+)-poly(DPSP)] without polar groups recognized enantiomers by hydrophobic interaction. In order to clarify this interaction, we applied this method to (+)-poly(DPSP). As shown in Figure 2 (c), different

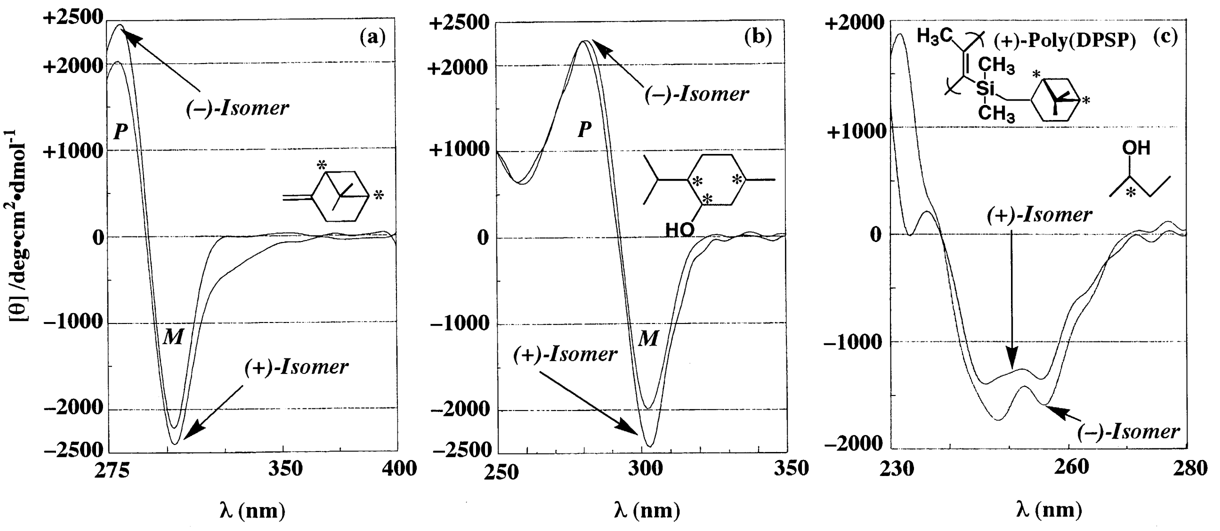

Figure 2. CD spectra of optically active polymers bearing pinanyl groups in the presence of various enantiomers in chloroform at -15 °C. (+)-Poly(MPS): (a) β-pinene and (b) menthol. (+)-Poly(DPSP): (c) 2-butanol.

interactions for (+)- and (-)-isomer were observed.[12] The estimation method proved the presence of the enantioselective recognition caused by hydrophobic interaction.[13]

In summary, we found an example of an qualitative' estimation method of an enantioselective recognition of a chiral polymer with hydrophobic enantiomers by using a CD spectrum of (+)-poly(MPS). This method was able to clarify the interaction site and proved the presence of hydrophobic interaction. We are now studying if other chiral polymers can be applied to this method and if quantitative analysis is possible.

References and Notes

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4 MPS: Yield 93.0%, bp 73.0 °C (0.45 mmHg), ^{1}H NMR (TMS, $CDCl_3$, 500MHz) δ; 0.784(s, 3H, $Cl_2SiC\underline{H}_3$), 0.844 and 1.20(2s, 6H, *gem*-$(C\underline{H}_3)_2$), 1.06-2.35(m, 11H, C$\underline{H}$ and C$\underline{H}_2$ in pinane), no self membrane forming ability.

5 (+)-Poly(MPS): Yield 36.0%, $\overline{M}w=1.02x10^4$, $\overline{M}w/\overline{M}n$ =1.75 (unimodal), $[\alpha]_D^{20}$=+18.0 (c 0.178, $CHCl_3$), ^{1}H NMR (TMS, $CDCl_3$, 500MHz) δ; 0.362(b, 3H, $SiC\underline{H}_3$) 0.840 and 1.19(2b, 6H, *gem*-$(C\underline{H}_3)_2$), 1.26-2.13(m, 11H, C$\underline{H}$ and C$\underline{H}_2$ in pinane), no self membrane forming ability.

6 The determination of $\overline{M}w$ and $\overline{M}w/\overline{M}n$ in GPC analysis was based on polystyrene standards. Eluent; THF, Detector; UV and polarimeter.

7 [(+)-Poly(MPS)]=4.0x10^{-4} mol/l, solvent; chloroform, cell length; 0.1 mm, temperature; -15 °C.

8 ***P*** and ***M*** mean right-handed and left-handed, respectively.[3]

9 [(+)-Poly(MPS)]=2.0x10^{-4}mol/l, [Enantiomer]/[(+)-poly (MPS)]=100, solvent; chloroform, cell length; 0.1mm, temperature; -15 °C. The UV and CD bands of these enantiomers did not overlap with that of the polymer.

10 The CD change may be caused by the change of the structure of the helix. The change of the structure of ***M***-screw may be easier than that of ***P***-screw because ***M***-screw had a looser helix than ***P***-screw.

11 However, we could not experiment on such a membrane separation, because this polymer had no self membrane forming ability. In addition, we detected no enantioselectivity of this polymer in adsorption because of a low quantity of adsorbed compound.

12 This method can not be applied to compounds which were separated by this membrane, such as tryptophan and mandelic acid, because the polymer and the compound had no common solvents.

13 Since the CD bands of (+)-poly(DPSP) were not assignable, the site of the interaction was not clear in contrast to (+)-poly(MPS).