Synthesis of Chiral Helical Poly(hydroxyl-containing phenylacetylene) Membranes by in-Situ Depinanylsilylation and Their Enantioselective Permeabilities

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ABSTRACT: Two new chiral helical poly(hydroxyl-containing phenylacetylene) membranes without the coexistence of any other chiral moieties were prepared in the following manner: (1) synthesis and homo- or copolymerization of two new chiral pinanylsiloxy-containing phenylacetylenes, (2) preparation of self-supporting membranes from the (co)poly(chiral pinanylsiloxy-containing phenylacetylene)s by a solvent-casting technique, and (3) depinanylsilylation of the preformed polymer membranes in situ. Complete depinanylsilylation was successfully achieved by treating with trifluoroacetic acid. The resulting membranes exhibited circular dichroism despite the absence of the chiral substituents, a fact indicating that the main chains of the polymers retained their chiral helicity. This is the first method to synthesizing such chiral poly(phenylacetylene) membranes. Since the membranes maintained their self-supporting properties, we were able to use them as enantioselective separation membranes in the permeation of an aqueous solution of a racemate. As a result, the importance of the contribution of the chiral main chain on enantioselective permeation was directly confirmed for the first time. In addition, since some of the depinanylsilylated membranes were insoluble in organic solvents, we could use them as an separation membrane for a toluene solution of a racemate.

Introduction

Since chiral compounds show varied bioactivities and each enantiomer often acts in completely different ways in the human body, to be safe and effective they should be used in optically pure forms in medicine and agriculture. Therefore, optical resolution of enantiomers is very important process. However, most practical methods for optical resolution are complex and are expensive because they can treat only small amounts of material in one operation. If we can achieve practical high permeability with high selectivity in enantioselective permeation through solid membranes, membrane separation will become the preferred method for optical resolution.[1] Although our group[2] and others[3] have reported several studies of solid membranes for optical resolution, they have not yet been used for industrial production to our knowledge. Part of the reason was because when the membrane showed high selectivity, the permeabilities were too low to be useful.

We have previously used poly(substituted acetylene)s having chiral pendant groups as optical resolution membrane materials because they have a good membrane-forming ability combined with chiral helicity in their main chain.[2] In addition, many membranes made from poly(substituted acetylene)s having both chiral pendant groups and a chiral helical main chain showed good enantioselective permeation. However, it was not clear which chiral moiety was more effective in conferring selective permeation, the pendant groups or the main chain. To resolve this problem, the chiral side groups were removed by polymer reaction, but the resulting polymer did not maintain its chiral conformation in solution. Therefore, we have developed two new ways of synthesizing chiral poly(substituted acetylene)s having only a chiral main chain as a chiral source without any chiral pendant groups.[4,5] We recently reported one of the methods in which a new chiral helical poly(diphenylacetylene) membrane was prepared by depinanylsilylation of a poly(chiral pinanylsilyldiphenylacetylene) membrane.[4] The success of this method results from the depinanylsilylation being carried out on an existing membrane and the insolubility of the resulting polymer. The depinanylsilylated membrane maintained the original chiral helicity, and formed, and retained molecular-scale voids. The chiral helicity caused enantioselective permeation while the pores enhanced the permeability.[4c] The maintenance of the chiral backbone and the pores may be due to the very rigid nature of the poly(diphenylacetylene) backbone.

In this present study, we used starting membranes made from poly(chiral pinanylsiloxy-containing phenylacetylene)s (poly(**1**), poly(**2**)) instead of poly(chiral pinanylsilyl-containing diphenylacetylene) (Scheme 1), and therefore, the resulting depinanylsilylated membranes contain hydroxyl groups (de-poly(**1**), de-poly(**2**)). Since the poly(phenylacetylene)s formed from a hy-

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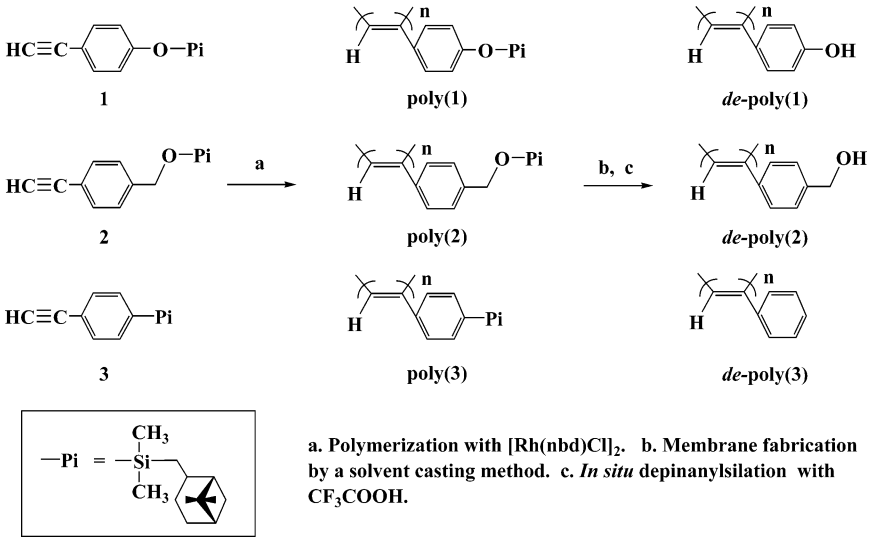
Scheme 1. Polymerization and in-Situ Depinanylsilylation of Pinanylsiloxy- or Pinanylsilyl-Containing Phenylacetylenes



droxyl-containing monomer tend to be insoluble, this method is very useful for making poly(hydroxyl-containing phenylacetylene) membranes.

In this paper, we discuss the following five points concerning the membrane preparation via in-situ depinanylsilylation of poly(chiral pinanylsiloxy-containing phenylacetylene) membranes (poly(**1**), poly(**2**)) and their performance in enantioselective permeation: (1) maintaining the chiral backbone and the molecular scale voids after in-situ depinanylsilylation in the case of a poly(phenylacetylene) which has a more flexible backbone than does poly(diphenylacetylene); (2) confirming that the depinanylsilylated membranes possess enantioselectivity in permeation by virtue of the main-chain chirality retained; (3) enhancing the permeation rate of the membranes by depinanylsilation, i.e., making molecular-scale voids; (4) understanding the effect of hydroxyl groups on the enantioselective permeability through the depinanylsilylated membranes; (5) achieving enantioselective permeation of an organic solution of a racemate using the depinanylsilylated membranes having insolubility in organic solvents.

Experimental Section

Materials. All the solvents used for monomer synthesis were distilled as usual. The polymerization initiator, [Rh(nbd)Cl]$_2$(nbd = 2,5-norbornadiene), was purchased from Aldrich Chemical Co., Inc., and was used as received. Chlorodimethyl(10-pinanyl)silane[2c] and (−)-4-[dimethyl(10-pinanyl)silyl]phenylacetylene (**3**),[2f,g] which has no ether linkage, were prepared according to the reported manner.[3]

Synthesis of Monomers (Scheme 2). All the following reaction procedures were conducted under dry nitrogen.

Synthesis of 1-Bromo-4-{dimethyl(10-pinanyl)siloxy}benzene (4). Chlorodimethyl(10-pinanyl)silane (8.0 mL, 31.8 mmol) was added dropwise to a solution of 4-bromophenol (5.0 g, 28.9 mmol) in dry THF (80 mL) and triethylamine (12 mL) at 0 °C. The solution was stirred for 3 h at room temperature. The formed salt was removed by filtration, and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by a silica gel column chromatography to give **4** as a slightly yellow liquid. Yield: 94%. R_f = 0.61 (ethyl acetate:hexane = 1:9). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.31 (d, 2H, aromatic protons), 6.70 (d, 2H, aromatic protons), 2.16−0.67 (m, 11H, in pinanyl group), 1.18, 0.81 (2s, 6H, *gem*-$(CH_3)_2$), 0.24 (s, 6H, Si−$(CH_3)_2$).

Synthesis of 4-{Dimethyl(10-pinanyl)siloxy}-1-(trimethylsilylethynyl)benzene (5). Trimethylsilylacetylene (6 mL, 43.4 mmol) was added dropwise to a solution of **4** (9.95 g, 27.1 mmol), bis(triphenylphosphine)palladium(II) chloride (190 mg, 0.271 mmol), copper(I) iodide (103 mg, 0.542 mmol), and triphenylphosphine (142 mg, 0.542 mmol) in dry triethylamine (150 mL) at room temperature. The solution was stirred for 12 h at the reflux temperature. The formed salt was removed by filtration, and the solvent of the filtrate was evaporated to yield a crude oily product. The crude product was purified with silica gel column chromatography to give **5** as a slightly yellow liquid. Yield: 91%. R_f = 0.64 (ethyl acetate: hexane = 1:9). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.30 (d, 2H, aromatic protons), 6.71 (d, 2H, aromatic protons), 2.19−0.67 (m, 11H, in pinanyl group), 1.18, 0.81 (2s, 6H, *gem*-$(CH_3)_2$), 0.20 (s, 6H, Si−$(CH_3)_2$), 0.19 (s, 9H, Si−$(CH_3)_3$).

Synthesis of (−)-[4-{Dimethyl(10-pinanyl)siloxy}phenylacetylene] (1). Potassium carbonate (0.339 g, 2.45 mmol) was added to a solution of **5** (9.42 g, 24.5 mmol) in methanol (150 mL) at room temperature. The solution was stirred for 18 h at room temperature. After the filtration of the mixture, the filtrate was concentrated to give an oily product. The crude product was purified with a silica gel column chromatography to give **1** as a colorless liquid. Yield: 61%. R_f = 0.59 (ethyl acetate:hexane = 1:9). $[\alpha]_D^{20}$ = −4.34° (*c* 0.031, $CHCl_3$). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.36 (d, 2H, aromatic protons), 6.77 (d, 2H, aromatic protons), 3.00 (s, 1H, H−C≡C), 2.23−0.66 (m, 11H, in pinanyl group), 1.18, 0.81 (2s, 6H, *gem*-$(CH_3)_2$), 0.22 (s, 6H, Si−$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 141, 133, 131, 122 (4C, aromatic carbons), 83.8, 77.4 (2C, C≡C), 49.2, 40.7, 39.6, 31.2, 27.0, 25.6, 24.8, 23.9, 23.0, 20.1 (10C, in pinanyl group), −1.76, −1.95 (2C, Si−$(CH_3)_2$). Anal. Calcd for $C_{20}H_{28}$-OSi: C, 76.86; H, 9.03. Found: C, 76.84; H, 9.01.

Synthesis of 4-(Ethoxycarbonyl)-1-(trimethylsilylethynyl)benzene (6). Trimethylsilylacetylene (19 mL, 13.7 mmol) was added dropwise to a solution of ethyl 4-iodobenzoate (25.0 g, 90.6 mmol), bis(triphenylphosphine)palladium(II) chloride (127 mg, 0.181 mmol), copper(I) iodide (863 mg, 0.453 mmol), and triphenylphosphine (119 mg, 0.453 mmol) in dry triethylamine (250 mL) at room temperature. The solution was stirred for 3 h at the reflux temperature. The formed salt was removed by filtration, and the solvent of the filtrate was evaporated to give an oily product. The crude product was purified by a silica gel column chromatography to give **6** as a yellow solid. Yield: 92%. R_f = 0.60 (ethyl acetate:hexane = 1:4). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.95, 7.49 (2d, 4H, aromatic protons), 4.36 (q, 2H, O−CH_2−CH_3), 1.39 (t, 3H, O−CH_2−CH_3), 0.26 (s, 9H, Si−$(CH_3)_3$).

Synthesis of 4-(Hydroxymethyl)-1-(trimethylsilylethynyl)benzene (7). Lithium aluminum hydride (0.950 g, 25

Scheme 2. Synthetic Routes to Pinanylsiloxy-Containing Phenylacetylenes (1 and 2)

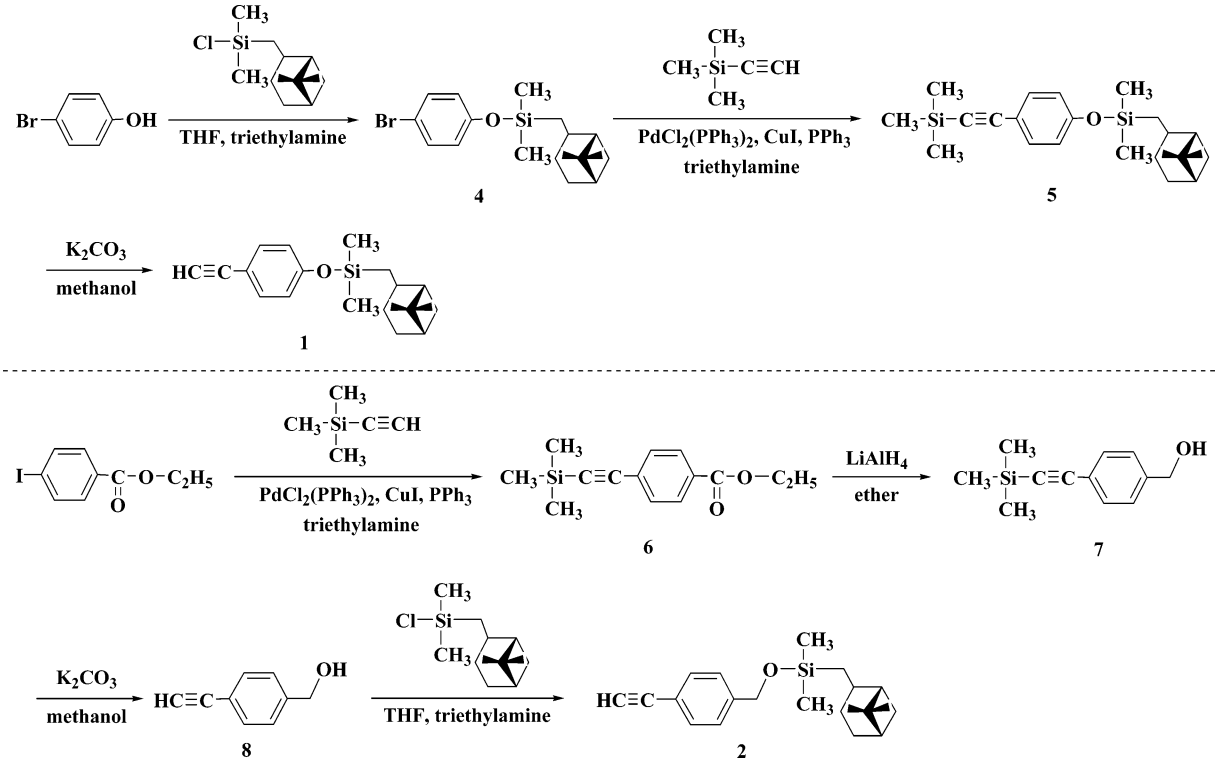


Table 1. (Co)polymerization of Pinanylsiloxy-Containing Phenylacetylenes[a]

	monomer (= M)		feed	(co)polymer					
no.	code[b]	$[\alpha]_D^{20}$ [c] (deg)	**3** (mol %)	**3** unit[d] (mol %)	yield (%)	$\bar{M}_w$[e] ($\times 10^5$)	cis[d] (%)	$[a]_D^{20}$ [c] (deg)	color
1	1	−1.80	0	0	82.8	9.50	78.8	−72.2	brown
2	2	−6.44	0	0	88.0	8.69	76.2	−40.6	yellow
3	1, 3		50	57	81.3	10.9	92.2	−131	brown
4	2, 3		50	55	89.8	14.9	95.2	−122	yellow
5	3	−2.85	100	100	85.6	16.1	96.4	−181	brown

[a] Polymerization by $[Rh(nbd)Cl]_2$ in toluene at room temperature for 4 h. [M] = 0.2 mol/L, [M]/[$[Rh(nbd)Cl]_2$] = 100, [triethylamine]/[$[Rh(nbd)Cl]_2$] = 100. [b] See Scheme 1. [c] In chloroform, *c* 0.012−0.032 g/dL. [d] Determined by ^{1}H NMR. [e] Determined by GPC correlating polystryrene standard; eluent: THF.

mmol) was added to a solution of **6** (20.6 g, 83.4 mmol) in dry diethyl ether (150 mL) under nitrogen at 0 °C. The solution was stirred for 2 h at room temperature. The reaction mixture was poured over ice water (100 mL) to quench the reaction. The ether solution was washed with brine (50 mL) and dried over Na_2SO_4. The solvent was evaporated to give an oily product. The crude product was purified by a silica gel column chromatography to give **7** as a colorless solid. Yield: 65%. R_f = 0.32 (ethyl acetate:hexane = 1:3). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.43, 7.26 (2d, 4H, aromatic protons), 4.66 (s, 2H, O−C*H*$_2$−OH), 1.85 (s, 1H, O−CH$_2$−O*H*), 0.24 (s, 9H, Si−$(CH_3)_3$).

Synthesis of 4-(Hydroxymethyl)phenylacetylene (8). Potassium carbonate (0.745 g, 5.39 mmol) was added to a solution of **7** (11.0 g, 53.9 mmol) in methanol (150 mL) at room temperature. The solution was stirred for 18 h at room temperature. After the filtration of the mixture, the filtrate was concentrated to yield an oily product. The crude product was purified by a silica gel column chromatography to give **8** as a slightly brown solid. Yield: 52%. R_f = 0.29 (ethyl acetate: hexane = 1:3). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.48, 7.31 (2d, 4H, aromatic protons), 4.71 (q, 2H, O−C*H*$_2$−OH), 3.07 (s, 1H, H−C≡C), 1.85 (s, 1H, O−CH$_2$−O*H*).

Synthesis of (−)-4-{Dimethyl(10-pinanyl)siloxymethyl}-phenylacetylene (2). Chlorodimethyl(10-pinanyl)silane (7.10 mL, 28.2 mmol) was added dropwise to a solution of **8** (3.73 g, 28.2 mmol) in dry THF (80 mL) and triethylamine (12 mL) at 0 °C. The solution was stirred for 3 h at room temperature. The formed salt was removed by filtration, and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 and concentrated to yield an oily product. The crude product was purified by a silica gel column chromatography to give **2** as a slightly yellow liquid. Yield: 90%. R_f = 0.62 (ethyl acetate:hexane = 1:9). $[\alpha]_D^{20}$ = −6.44° (*c* 0.032, $CHCl_3$). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.47, 7.27 (2d, 4H, aromatic protons), 4.68 (s, 2H, −CH$_2$−O−), 3.05 (s, 1H, H−C≡C), 2.16−0.59 (m, 11H, in pinanyl groups), 1.17, 0.87 (s, 3H, *gem*-$(CH_3)_2$), 0.14 (s, 6H, Si−$(CH_3)_2$).^{13}C NMR ($CDCl_3$, δ, ppm): 141, 131, 126, 121 (4C, aromatic carbons), 83.7, 76.7 (2C, C≡C), 64.1 (1C, −CH$_2$−O−), 49.1, 40.7, 39.6, 30.5, 27.0, 25.5, 24.8, 24.5, 23.0, 20.1 (10C, in pinanyl group), −0.759, −0.957 (2C, Si−$(CH_3)_2$). Anal. Calcd for $C_{21}H_{30}OSi$: C, 77.24; H, 9.26. Found: C, 76.97; H, 9.30.

(Co)polymerization.[2a,f,g] The detailed (co)polymerization conditions are indicated in Table 1. The (co)polymers were isolated by reprecipitation into an excess of methanol.

Membrane Preparation.[2c,f] A 1−2 wt % (w/v) solution of a polymer in toluene was cast on a poly(tetrafluoroethylene) sheet, and the solvent was evaporated for 24 h at room temperature. The resulting solid membrane was detached from the sheet and dried in vacuo for 10 h. Thickness, 45−61 μm; area: (6.16−7.07) $\times 10^{-4}$ mm^2.

In-Situ Depinanylsilylation.[4] An original polymer membrane (poly(**1**), poly(**2**), or poly(**3**)) was immersed in a mixture of pure water/trifluoroacetic acid (volume rate 1:1) at room temperature for 72 h. The membrane was immersed in water for 48 h and washed with water to remove residual impurities including trifluoroacetic acid and dried at room temperature

for 48 h and in vacuo for 10 h to constant weight. The completion of depinanylsilylation was confirmed by the IR spectra of the membranes (de-poly(**1**), de-poly(**2**), or de-poly(**3**)) because the depinanylsilylated polymers were insoluble.

Measurements of Permeabilities.[2c] A disproportionate two-chamber cell, whose chamber volumes on the feed side and permeate sides were 150 and 20 mL, respectively, was used. The polymer membranes was placed between the chambers with silicone rubber packing. A solution of a racemate and solvent was supplied in the feed and permeate side chambers, respectively. The permeation experiment was carried out at room temperature with stirring. After a permeation period, the solvent of the permeate was removed by evaporation, and the resulting solute was weighed (q (g)). The normalized quantity (Q_c (g·m/m^2)) was calculated from $Q_c = qL/A$, where L and A are the thickness and area of the membrane. The permeation rate (P_c (g·m/(m^2·h))) was estimated from the slope of the Q_c vs permeation time ($t(h)$) plot. The permeability coefficient (P (m^2/h)) was calculated by dividing P_c by the difference in the concentration between the feed and permeate sides. The enantioselectivity in the permeation, i.e., the optical purity of the permeate (%ee), was directly determined by high-performance liquid chromatography (HPLC) with an optical resolution column (CROWNPAK CR or CHIRALCEL OD-H, Daicel Chemical Co.).

Instruments for Characterization. Relative molecular weights of polymers were determined by gel permeation chromatography (GPC; Hitachi 655A-11 with a GL A100M column using a UV detector, THF as eluent, polystyrene calibration). IR spectra were recorded on a Shimadzu FTIR-8100. NMR spectra were recorded on a JEOL GSX-270 at 270 MHz for ^{1}H and 67.5 MHz for ^{13}C. CD spectra were measured with a JASCO J-600 spectropolarimeter. Specific rotations were recorded with a HORIBA SEPA-200.

Results and Discussion

Synthesis and (Co)polymerization of Pinanylsiloxy-Containing Phenylacetylenes (**1** and **2**). Chiral phenylacetylenes containing pinanylsiloxy groups (**1** and **2**) were synthesized in good yields as shown in Scheme 2. Pinanylsilylphenylacetylene (**3**, Scheme 1) was also synthesized as a reference compound according to the method described in our previous report.[2f,g] The (co)-polymerizations of the three monomers were carried out using $[Rh(nbd)Cl]_2$ as an initiator to give yellow to brown polymers in good yields (Table 1). The polymers displayed much larger optical rotation values than the corresponding monomers. For example, $[\alpha]_D^{20}$ values of poly(**1**) and **1** were −72.2° (c 0.032, $CHCl_3$) and −1.80° (c 0.031, $CHCl_3$), respectively. In addition, the polymers showed large values of the molar ellipticity ($[\theta]$) in the UV−vis region which are assigned to absorption by the main chain (Figure 1), a fact leading to the conclusion that the polymers have a one-handed helical main chain. Since the $[\theta]$ values increase in the order of poly(**2**) < poly(**1**) ≪ poly(**3**), the polymers with longer spacers between the main chain and the chiral pendant group exhibit smaller $[\theta]$ values. The longer spacer presumably made it more difficult to induce chiral helicity in the backbone during polymerization. Similar observations were reported in our previous papers.[2f,g]

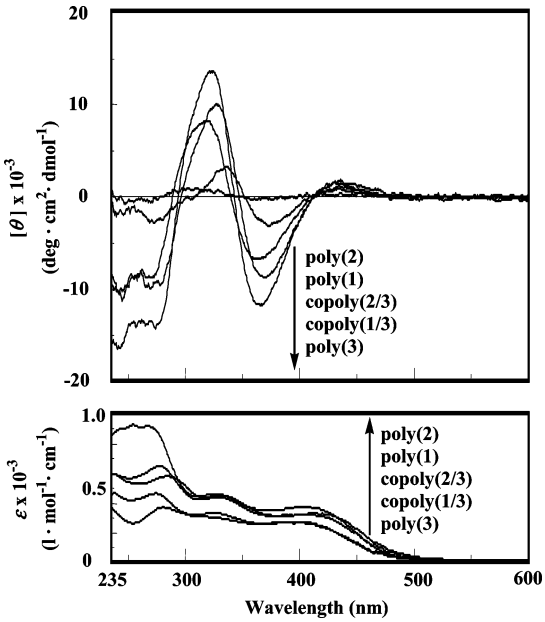


Figure 1. CD (top) and UV−vis (bottom) spectra of (co)poly-(pinanylsiloxy-containing phenylacetylene)s in chloroform. The codes in Figure correspond to those in Table 1.

Fabrication of Self-Supporting Membranes from Chiral Helical Pinanylsiloxy-Containing Poly-(phenylacetylene)s. Since the polymers obtained above had a very high molecular weight and also good solubility in various solvents such as THF, chloroform, toluene, and triethylamine (TEA) (Table 2), self-supporting membranes were readily obtained by the solvent-casting method we used previously with substituted polyacetylenes.[2]

Fabrication of Self-Supporting Membranes Containing Chiral Helical Main-Chain and Hydroxyl Groups without the Coexistence of Any Other Chiral Moieties by in-Situ Depinanylsilylation of Preformed Pinanylsiloxy-Containing Membranes. We reported recently that membranes prepared by complete depinanylsilylation of poly(diphenylacetylene)s having chiral pinanylsilyl groups in an in-situ membrane state retained the original chiral helicities.[4] In the present study, we were interested to observe the effect of using a poly(phenylacetylene) having a more flexible backbone. Since poly(phenylacetylene) derivatives can be synthesized more easily than poly(diphenylacetylene)s, the application of the method to poly-(phenylacetylene)s is important. Depinanylsilylation of the membrane polymers described above according to our previous method[4] proceeded quantitatively using trifluoroacetic acid while maintaining the membrane strength (Scheme 1). The completion of the reactions was confirmed by taking IR spectra of the membranes before and after the reaction (Figure 2) because the resulting membranes were insoluble in $CDCl_3$ (Table 2). Thus, absorptions at 3300 cm^{-1} ($\nu_{s,O-H}$) appeared in the

Table 2. Change in Solubility of the Membranes by in-Situ Depinanylsilylation of (Co)poly(pinanylsiloxy- or pinanylsilyl-containing phenylacetylene)s[a]

code[b]	hexane	chloroform, triethylamine, toluene	THF	DMF	methanol
poly(**1**), copoly(**1/3**)	+	+	+	−	−
de-poly(**1**), de-copoly(**1/3**)	−	−	+	+	+
poly(**2**), copoly(**2/3**)	+	+	+	−	−
de-poly(**2**), de-copoly(**2/3**)	−	−	−	−	−
poly(**3**)	+	+	+	−	−
de-poly(**3**)	−	+	+	+	−

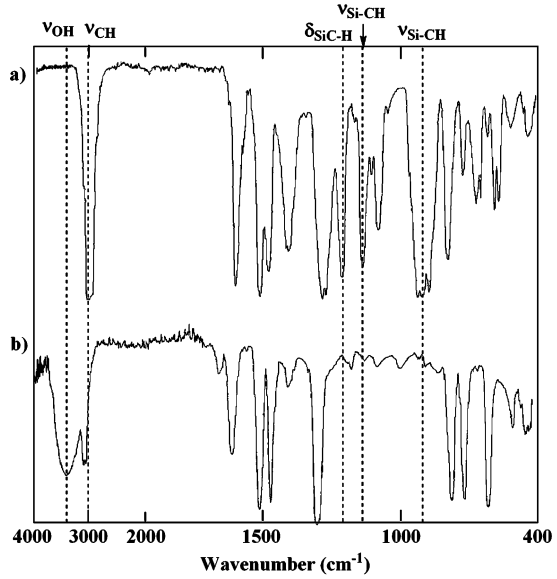


Figure 2. IR spectra of the membranes of (a) poly(**1**) and (b) de-poly(**1**).

IR spectra of de-poly(**1**), de-poly(**2**), de-copoly(**1/3**), and de-copoly(**2/3**) membranes, and absorptions at 3010 ($\nu_{s,aliphaticC-H}$), 1210 ($\delta_{s,SiC-H}$), 1150 ($\nu_{as,\ Si-CH_3}$), 925 ($\nu_{as,Si-CH_3}$), and 900 cm^{-1} ($\nu_{s,Si-CH_3}$) in the IR spectra of poly(**1**), poly(**2**), copoly(**1/3**), copoly(**2/3**), and poly(**3**) membranes, indicating the presence of pinanylsilyl groups, completely disappeared. In addition, the weight loss of the membranes upon depinanylsilylation supported the completion of the reaction. For example, poly(**1**): 60.9 mg; de-poly(**1**): found 22.7 mg, calcd 22.6 mg.

In addition, all these membranes maintained strength enough to use as separation membranes. Unlike the depinanylsilylated poly(diphenylacetylene)s described in our previous report[4] and de-ploy(**3**), the depinanylsilylated polymers (de-ploy (**1**), de-ploy (**2**), de-copoly(**1/3**), and de-copoly(**2/3**)) contained hydroxyl groups. Since most of the phenylacetylenes polymerize with rhodium complexes to yield very high molecular weight polymers, some of them, in particular monomers containing hydroxyl or other polar groups, tend to produce insoluble polymers which cannot be fabricated into a membrane. Therefore, this technique revealed a new preparation method for hydroxyl-group-containing poly(phenylacetylene) membranes having good membrane strength.

Table 2 summarizes the solubilities of the polymers obtained. The solubilities of the pinanylsiloxy- or pinanylsilyl-containing polymers (poly(**1**), poly(**2**), copoly(**1/3**), and copoly(**2/3**)) were very different from those of the resulting depinanylsilylated polymers (de-poly(**1**), de-poly(**2**), de-copoly(**1/3**), and de-copoly(**2/3**)). The former were soluble in nonpolar solvents such as hexane, toluene, and chloroform and insoluble in polar solvents such as *N*,*N*-dimethylformamide (DMF) and methanol, while the latter were insoluble in hexane, toluene, and chloroform and soluble in DMF and methanol except for de-poly(**2**) and de-copoly(**2/3**), which were insoluble in all polar and nonpolar solvents tested. Therefore, de-poly(**2**) and de-copoly(**2/3**) membranes can be used for separation membranes even when organic solvents were used.

To measure circular dichroism (CD) spectra of the depinanylsilylated products, membranes prepared from a toluene solution cast on a quartz plate were treated as described previously.[4c] Figure 3 shows CD and UV−vis spectra of polymer membranes before and after in situ depinanylsilylation. The de-poly(**1**) and de-poly(**2**) membranes showed CD signals similar to those of the original polymer (poly(**1**) and poly(**2**), respectively) in the UV−vis region. This finding indicates that the depinanylsilylated polymers retain the same preferential one-handed helical conformation as those in the original polymers. These findings indicate that a more flexible poly(phenylacetylene) was also able to maintain the chiral conformation, similar to that seen with poly(diphenylacetylene)s, without the presence of chiral pendant groups in the membranes. This is the first method of synthesizing such chiral helical poly(phenylacetylene)s without the coexistence of any other chiral moieties, except for our recent report on helix-sense-selective polymerization of a phenylacetylene derivative.[5a,b]

Effect of Depinanylsilylation on the Enantioselective Permeabilities of the Membranes. a. Confirmation of the Contribution of the Chiral Helical Main Chain to Enantioselective Permeation. Figure 4 shows the normalized quantity (*Q*) of permeated (*R*)- and (*S*)-phenylalanine (Phe) vs permeation time through poly(**1**) and de-poly(**1**) membranes in concentration-driven permeation when an aqueous solution of racemic Phe was supplied. The results of the permeation through all the depinanylsilylated membranes and the corresponding original membranes are summarized in Table 3. All the original polymer membranes were able to enantioselectively separate racemic Phe of an aqueous solution to give an (*R*)-isomer-enriched permeate. The order of increasing enantioselective permeability, i.e., enantiomeric excesses (%ee) of the permeate, was poly(**2**) < poly(**1**) < copoly(**2/3**) < copoly(**1/3**) < poly(**3**). The order corresponds exactly to the order of increasing molar ellipticity ([θ]) of the polymers (Table 3, Figure 1), a fact suggesting the contribution of the chiral main chain. But, since this ordering also corresponds exactly to the order of the increasing content of pinanylsilyl groups (Pi%) (Table 3), the origin of the enantioselectivity was not clear.

In a fashion similar to the original polymer membranes, all the depinanylsilylated polymer membranes showed (*R*)-isomer enantioselectivity in permeation (Table 3, Figure 4). This result directly indicates that the chiral main chain contributes to the enantioselective permeability, and the depinanylsilylated polymers retained the same preferential one-handed helical conformations as those in the original polymers. Although the enantioselectivities through the depinanylsilylated polymer membranes were lower than the original polymers, we found that depinanylsilylated polymer membranes from polymeric membranes having a more flexible poly(phenylacetylene) backbone did show enantioselective permeabilities. Therefore, the importance of the contribution of the chiral main chain on enantioselective permeation was confirmed. This is the first confirmation because we have obtained chiral helical poly(phenylacetylene) membranes without the coexistence of any other chiral moieties for the first time in this study.

b. Enhancement of Permeation Rates by in-Situ Depinanylsilylation, i.e., Making Molecular-Scale Pores. The permeation coefficients (*P*) of all the depinanylsilylated membranes were higher than those of the original polymer membranes (Table 3). This method is very promising to improve low *P* which most enan-

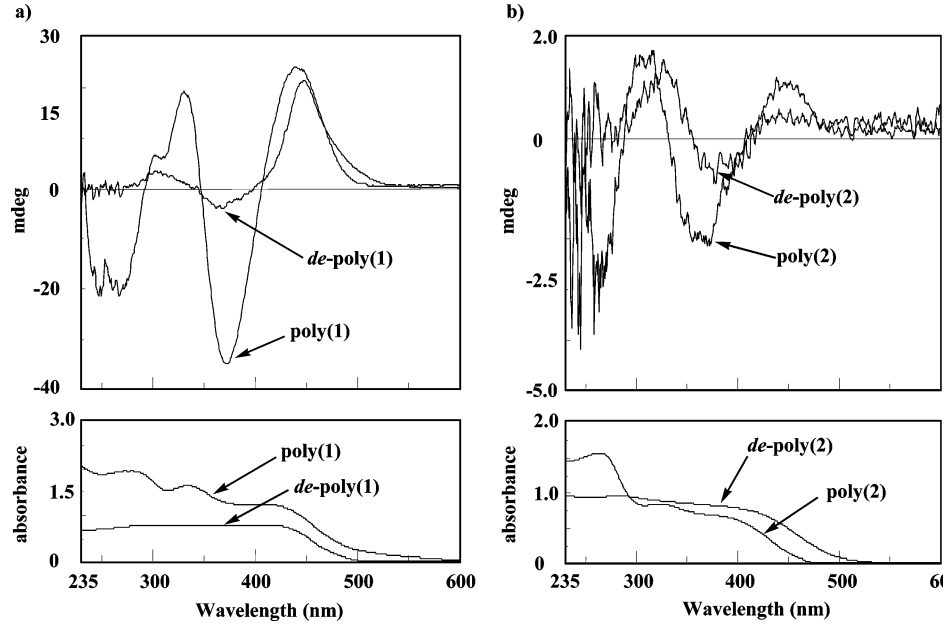


Figure 3. CD (top) and UV−vis (bottom) spectra of the polymer membranes before and after in situ depinanylsilylation: (a) poly(**1**) and de-poly(**1**); (b) poly(**2**) and de-poly(**2**).

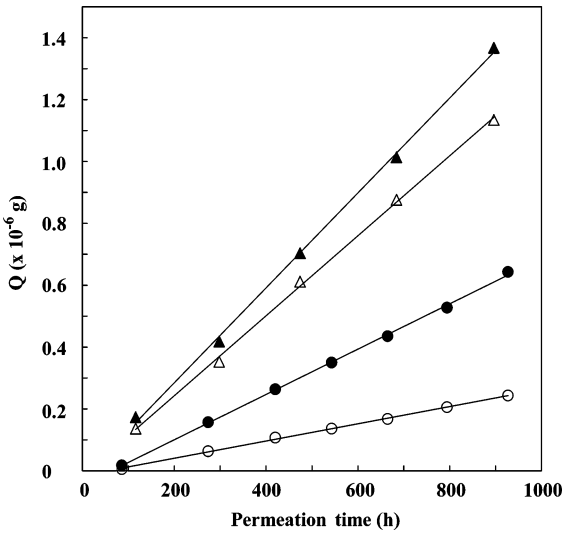


Figure 4. Plots of quantity (Q) of permeated (R)- and (S)-phenylalanine vs permeation time through poly(**1**) and de-poly(**1**) membranes. Feed: 0.50 wt % racemic aqueous solution. (●, ○) (R)- and (S)-isomer through poly(**1**) membrane, respectively; (▲, △) (R)- and (S)-isomer through de-poly(**1**) membrane, respectively.

tioselective permeable membranes have as a defect. Similarly to our previous report,[4c] the highest P value was observed for de-copoly(**1/3**) which has the highest content of pinanyl groups in the corresponding original copolymer, except for de-poly(**3**) which has no hydroxyl groups. These observations show that molecular-scale voids generated by depinanylsilylation were retained and effective in enhancing the P values. If the sizes of the pores had been much larger than a molecular scale, the enantioselectivities would have disappeared. This is the first example of preparing such enantioselective polymer membranes. Only chiral helical poly(diphenylacetylene) membranes were reported by our group,[4c] but they have no hydroxyl groups.

c. Effect of the Hydroxyl Groups on the Enantioselective Permeability. The increment of P for Phe by depinanylsilation was higher for hydroxyl-containing membranes (de-ploy (**1**), de-ploy (**2**), and so on) than that for non-hydroxyl-containing membranes, i.e., de-poly(**3**) (Table 3). This may be because a small amount of swelling occurred when an aqueous solution was supplied to the hydroxyl-containing membranes. As far as selectivity was concerned, we could not discern any advantage that we could attribute to the presence of hydroxyl groups in the polymer at present.

Comparisons of the Performance of the Depinanylsilylated Membranes with those of the Previously Reported Membranes. The P and %ee values of these membranes for Phe in this study were a little lower than those of the membranes from poly(phenylacetylene)s containing chiral oligopinanylsiloxanes as pendant groups.[2g] The siloxane-containing polymers may be suitable for the separation membranes because of their flexible nature.

As compared with the depinanylsilylated poly(diphenylacetylene) membranes for tryptophan we previously reported,[4c] the P and %ee values of these membranes for Phe in this study were a little lower. Although there were no data for the same permeant, the rigid backbone of the depinanylsilylated poly(diphenylacetylene)s may be more effective to keep molecular-scale pores.

Enantioselective Permeation of Organic Solution of a Racemate. Since most of organic polymers including poly(phenylacetylene)s swell or are soluble in hydrophobic solvents such as toluene, we should employ hydrophobic liquids such as water or methanol as solvents when using them for separation membranes.[2] On the other hand, because the depinanylsilylated polymeric membranes (de-ploy (**1**) and de-ploy (**2**)) were insoluble in toluene, hydrophobic racemates which cannot be dissolved in water can be used as a permeant.

The results of permeation of a toluene solution of racemic *trans*-stilbene oxide through the depinanylsilylated membranes in concentration-driven permeation are summarized in Table 4. Since the de-poly(**3**) membrane was soluble in toluene, it could not be used. All the depinanylsilylated polymer membranes could separate racemic *trans*-stilbene oxide enantioselectively in permeation to give an (*S*,*S*)-isomer-enriched permeate.

Table 3. Enantioselective Permeation of Phenylalanine[a] through the Original and Depinanylsilylated Polymer Membranes

	original membrane				P ($\times 10^{-14}$ m^2/h)[e]		selectivity (%ee)[e]	
no.	code[b]	$[\theta] \times 10^{-3}$ (deg cm^2 dmol^{-1})	Pi[c] (wt %)	OH[d] (wt %)	original membrane	depinanylsilylated membrane	original membrane	depinanylsilylated membrane
1	poly(**1**)	2.36	43.9	14.4	2.90	11.0	44.4	8.52
2	poly(**2**)	0.455	42.0	12.9	3.02	10.7	34.8	6.05
3	copoly(**1/3**)	8.87	45.3	6.19	3.94	13.1	60.4	16.6
4	copoly(**2/3**)	6.90	44.4	5.81	3.90	12.6	55.3	13.8
5	poly(**3**)	11.8	46.3	0	4.34	9.60	77.4	21.1

[a] A 0.50 wt % aqueous solution of the racemate of phenylalanine was fed. [b] See Scheme 1. [c] Weight percent of pinanyl group. [d] Weight percent of hydroxy group in depinanylsilylated polymer. [e] Permeation coefficient (P) and enantiomeric excess of the permeate was determined by HPLC with an optical resolution column (CROWNPAK CR(+); eluent, aqueous $HClO_4$, pH = 2.0).

Table 4. Enantioselective Permeation of a Toluene Solution of *trans*-Stilbene Oxide[a] through the Depinanylsilylated Polymer Membranes

no.	code[b]	P ($\times 10^{-13}$ m^2/h)[c]	selectivity (%ee)[c]
1	de-poly(**1**)	5.64	5.28
2	de-poly(**2**)	5.26	4.69
3	de-copoly(**1/3**)	7.32	8.37
4	de-copoly(**2/3**)	7.16	7.69

[a] A 0.50 wt % toluene solution of the racemate of *trans*-stilbene oxide was fed. [b] See Scheme 1. [c] Permeation coefficient (P) and enantiomeric excess of permeate were determined by HPLC with an optical resolution column (CHIRALCEL OD-H; eluent, *n*-hexane/2-PrOH = 9:1 (v/v).

This method is promising to expand kinds of pemeants which can be separated by membranes. The order of increasing enantiomeric excesses (%ee) for the polymer membranes was de-poly(**2**) < de-poly(**1**) < de-copoly(**2/3**) < de-copoly(**1/3**). This order corresponds to the order of the increasing molar ellipticity for the original polymers (Table 3, Figure 1). This result reinforces again the idea that enantioselective permeability depends on the main chain being chiral.

Conclusions

We synthesized two new chiral helical poly(hydroxyl-containing phenylacetylene) membranes by complete in-situ depinanylsilylation of preformed chiral helical poly(pinanylsiloxy-containing phenylacetylene) membranes. The chiral helicities of the polymers after removing the chiral pendant groups were confirmed by measuring the CD spectra of the membranes. This is the first method to synthesizing such chiral poly(phenylacetylene)s, except for the helix-sense-selective polymerization by chiral catalyst we reported recently.[5a] Since the membranes maintained their ability to be self-supporting, they could be used as separation membranes. These membranes showed enantioselectivity in permeation that depended on the presence of chiral helicity. The importance of the contribution of the chiral main chain on enantioselective permeation was directly confirmed for the first time. The permeation rates of such membranes were higher than those of the corresponding original chiral helical poly(pinanylsiloxy-containing phenylacetylene) membranes. This observation suggested that molecular-scale pores may have formed in the membrane. These results confirm that it is possible to synthesize chiral helical polymers without the presence of any other chiral moieties for poly(phenylacetylene)s other than poly(diphenylacetylene)s by the method. This method is also useful for making hydroxyl-group-containing poly(phenylacetylene) membranes that are otherwise difficult to fabricate because they tend to be insoluble. In addition, since the depinanylsilylated membranes did not swell and were insoluble in organic solvents, it was possible to use them for enantioselective permeation of a toluene solution.

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References and Notes

(1) Aoki, T. *Prog. Polym. Sci.* **1999**, *24*, 951.
(2) (a) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009. (b) Shinohara, K.; Aoki, T.; Oikawa, E. *Polymer* **1995**, *36*, 2403. (c) Aoki, T.; Shinohara, K.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4192. (d) Aoki, T.; Oshima, M.; Shinohara, K.; Kaneko, T.; Oikawa, E. *Polymer* **1997**, *38*, 235. (e) Aoki, T.; Kobayashi, Y.; Kaneko, T.; Oikawa, E.; Yamamura, Y.; Fujita, Y.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules* **1999**, *32*, 79. (f) Shinohara, K.; Aoki, T.; Kaneko, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1689. (g) Aoki, T.; Fukuda, T.; Shinohara, K.; Kaneko, T.; Teraguchi, M.; Yagi, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4502.
(3) (a) Maruyama, A.; Adachi, N.; Takatsuki, T.; Torii, M.; Sanui, K.; Ogata, N. *Macromolecules* **1990**, *23*, 2748. (b) Kakuchi, T.; Yokota, T.; Yokota, K. *Polym. J.* **1990**, *22*, 199. (c) Higuchi, A.; Ishida, Y.; Nakagawa, T. *Desalination* **1993**, *90*, 127. (d) Lakshmi, B. B.; Martin, C. R. *Nature (London)* **1997**, *388*, 758. (e) Lee, S. B.; Mitchell, D. T.; Trofin, L.; Nevanen, T. K.; Soderlund, H.; Martin, C. R. *Science* **2002**, *296*, 2198. (f) Skolaut, A.; Retey, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2960. (g) Higuchi, A.; Higuchi, Y.; Furuta, K.; Yoon, B. O.; Hara, M.; Maniwa, S.; Saitoh, M.; Sanui, K. *J. Membr. Sci.* **2003**, *221*, 207. (h) Yang, H.; Zhang, S.; Yang, W.; Chen, X.; Zhuang, Z.; Xu, J.; Wang, X. *J. Am. Chem. Soc.* **2004**, *126*, 4054.
(4) (a) Teraguchi, T.; Masuda, T. *Macromolecules* **2002**, *35*, 1149. (b) Sakaguchi, T.; Kwak, G.; Masuda, T. *Polymer* **2002**, *43*, 3937. (c) Teraguchi, M.; Suzuki, J.; Kaneko, T.; Aoki, T.; Masuda, T. *Macromolecules* **2003**, *36*, 9694.
(5) (a) Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346. (b) Sato, T.; Aoki, T.; Teraguchi, M.; Kaneko, T.; Kim, S.-Y. *Polymer* **2004**, *45*, 8109.
(6) The influence of birefringence on the solid-state CD spectra could be ignored because the CD spectra hardly changed when changing the measuring conditions.

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