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Synthesis and Properties of Polymers from Disubstituted Acetylenes with Chiral Pinanyl Groups

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ABSTRACT: Disubstituted acetylenes with chiral pinanyl groups, (−)-1-{4-[dimethyl(10-pinanyl)silyl]-phenyl}-2-phenylacetylene (**1**), (−)-1-{3-[dimethyl(10-pinanyl)silyl]phenyl}-2-phenylacetylene (**2**), (−)-1-{4-[dimethyl(10-pinanyl)silyl]phenyl}-1-propyne (**3**), and (−)-1-chloro-2-{4-[dimethyl(10-pinanyl)silyl]-phenyl}acetylene (**4**), polymerized with $NbCl_5$-, $TaCl_5$-, or $MoCl_5$-based catalysts to give high molecular weight polymers in good yields. Poly(**1**) and poly(**2**) showed intense circular dichroism (CD) effects in the UV−vis region and large optical rotations, which suggests that these polymers exist in helical conformations with an excess of one-handed screw sense. No significant decrease in the magnitude of CD effects of poly(**1**) and poly(**2**) with increasing temperature indicated the relatively high stability of their helical conformations. On the other hand, the intensities of CDs of poly(**3**) and poly(**4**) were approximately 1/10 those of poly(**1**) and poly(**2**), which means that introduction of two aromatic side groups into the repeating unit is favorable for the induction of helical conformation to disubstituted acetylene polymers. The free-standing membranes of poly(**1**), poly(**2**), and poly(**3**) exhibited characteristic properties as gas-permeable and optical resolution membranes.

Introduction

Synthesis of optically active polymers has been under intensive research because of their unique functions such as molecular recognition ability and catalytic activity for asymmetric synthesis.[1] Especially, chiral conjugated polymers are of great interest due to their potential benefits as asymmetric electrodes, polarization-sensitive electrooptical devices, nonlinear optical materials, and so on.[2] One such conjugated polymer is represented by polyacetylenes with chiral substituents, some of which are known to exhibit strong circular dichroism (CD) effects and large optical rotations based on the helical conformation.[3]

However, most of the optically active polyacetylenes are limited to those from monosubstituted acetylenes. This is simply because almost perfect stereoregularity (cis) is readily obtained from monosubstituted acetylenes by Rh or Fe catalysts[4] and because the stereoregular cis configuration is favorable for the induction of one-handed screw-sense conformation.[4] Despite these advantages, the chemical and thermal instability of polymers from monosubstituted acetylenes compared with those from disubstituted ones diminishes the utility of chiral polyacetylenes in the practical use. For example, the polymers from *n*- and *sec*-alkylacetylenes are readily oxidized in air, leading to the degradation of the backbone.[5] The polymers from monosubstituted arylacetylenes without bulky ortho substituents are more stable but still unstable in solution; a rapid decrease in molecular weight is often observed in solution.[6] In contrast, polymers from disubstituted acetylenes are thermally stable, and their excellent permeability of gases and liquids allows these polymers to be applied for separation membranes.[7] Therefore, synthesis of disubstituted acetylene polymers with optically active pendants is of great interest due to their potential utility as stable membranes for the resolution of racemic compounds.

It is unfortunate that there are so few studies on the polymerization of disubstituted acetylenes with chiral substituents, and no systematic information is available on their polymerization behavior, structure, and characteristics of the formed polymers. An example has been reported by authors for the polymerization of (−)-1-[dimethyl(10-pinanyl)silyl]-1-propyne (**5**).[8] This monomer undergoes polymerization in the presence of $TaCl_5-Ph_3Bi$ to give a high molecular weight polymer ($M_w = 15 \times 10^4$). Small but clear Cotton effects in the absorption region of polymer backbone suggest that the polymer takes helical conformations with an excess of single-screw sense. The free-standing membrane of this polymer achieves the optical resolution of various racemates such as tryptophan, 1,3-butanediol, phenylalanine, and valine. This finding stimulated us to study on the synthesis of a wide range of polymers from disubstituted acetylenes with chiral pendant groups and to clarify the relationship between the structure of the monomers and the conformation of the formed polymers.

This paper deals with the polymerization of disubstituted acetylenes with chiral pinanyl groups by using various transition-metal catalysts. The monomers employed are (−)-1-{4-[dimethyl(10-pinanyl)silyl]phenyl}-2-phenylacetylene (**1**), (−)-1-{3-[dimethyl(10-pinanyl)-silyl]phenyl}-2-phenylacetylene (**2**), (−)-1-{4-[dimethyl(10-

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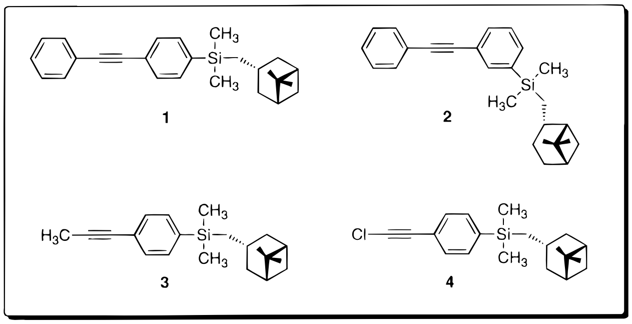
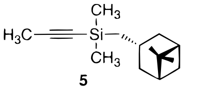
Chart 1





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pinanyl)silyl]phenyl}-1-propyne (**3**), and (−)-1-chloro-2-{4-[dimethyl(10-pinanyl)silyl]phenyl}acetylene (**4**) (Chart 1). Synthetic routes to these monomers are illustrated in Scheme 1. Both **1** and **2** were used for the examination of the effect of position of the chiral substituent on the conformation and permeability of the polymers. Monomers **3** and **4** were designed to investigate the influence of the size of substituents on the conformation of the polymers. The characteristics of the polymers as gas-permeable and chiral resolution membranes were also examined.

Results and Discussion

Polymerization. In general, group 5 transition metals represented by Ta(V) and Nb(V) are active for the polymerization of diphenylacetylenes.[4,7a] Especially, formation of high molecular weight polymers of diphenylacetylenes is possible by the systems composed of $TaCl_5$- and organometallic cocatalysts. Both **1** and **2** polymerized with the $TaCl_5$- or $NbCl_5$-based catalysts, and the results are summarized in Table 1. Poly(**1**) with extremely high molecular weight was obtained in good yield with $TaCl_5-n\text{-}Bu_4Sn$ catalyst. Increase in the monomer concentration improved both the yield and molecular weight of the polymer (runs 1 and 4). It was impossible to estimate the molecular weight of poly(**1**) by GPC measurement because its molecular weight exceeded the exclusion limit of the GPC columns. However, poly(**1**) possessed very high molecular weight beyond 1 million. Though the use of $NbCl_5$ as main catalyst also gave the polymer, both the yield and molecular weight decreased (run 6). Such a tendency is often observed in the polymerization of disubstituted acetylenes by group 5 transition metals.[4b] The yield of poly(**1**) increased with increasing polymerization temperature and showed a maximum value at 80 °C (runs 2−5). Both the yield and molecular weight of poly(**2**) were lower than those of poly(**1**) (runs 7−9). These results are consistent with the general feature of acetylene polymerization where meta-substituted diphenylacetylenes usually provide lower molecular weight polymers in lower yield than do para-substituted ones.[9]

Disubstituted acetylenes **3** and **4** also well polymerized with group 5 or 6 metal catalysts, and the results are listed in Table 2. Ta and Nb catalysts were found to be effective for the polymerization of **3**, giving the polymers in moderate to good yields (runs 1−4). The addition of Ph_3Bi as cocatalyst enabled the production of a polymer with molecular weight over 1 million (run 3). In contrast, a chlorine-containing monomer, **4**, polymerized with Mo catalysts (runs 5−10). Although the polymerization of **4** in the absence of any cocatalyst gave only oligomers (35%, run 5), combinations of $MoCl_5$ with organometallic cocatalysts such as $n\text{-}Bu_4Sn$, Ph_4Sn, and Et_3SiH were quite active for the polymerization of **4** (runs 7−9). $Mo(CO)_6-CCl_4-h\nu$ provided the polymer with the highest molecular weight (run 10).

All the polymers produced were soluble in various solvents including toluene, chloroform, heptane, cyclohexane, dichloromethane, THF, etc., and partly soluble in ether. The difference in the catalysts, i.e., Ta or Nb, caused no difference in solubility among poly(**1**), poly(**2**), and poly(**3**), although a little difference in solubility is observed in the case of poly(1-trimethylsilyl-1-propyne) by changing the catalyst.[10] Reflected by the high molecular weights, poly(**1**), poly(**2**), and poly(**3**) exhibited excellent film-forming ability; free-standing films were readily obtained by casting the polymers from toluene. Thermogravimetric analyses (TGA) in air showed the onset temperatures of weight loss (T_0) of poly(**1**) and poly(**2**) at 319 and 326 °C, respectively, which were about 70 °C higher than that of poly(phenylacetylene). Comparison of these T_0 values with that of poly[1-(4-trimethylsilyl)phenyl-2-phenylacetylene] (420 °C) indicates that the introduction of the pinanyl group reduces the thermal stability. Indeed, TGA displayed two stages on weight loss of poly(**1**) and poly(**2**); the first weight loss left ca. 65% of weight residue below 450 °C, which agreed well with the predicted value assuming that pinanyl group was lost first upon heating.

Conformation of Polymers in Solution. The polymers derived from **1** and **2** displayed very large optical rotations. For example, polymerization of **1** by $TaCl_5-n\text{-}Bu_4Sn$ gave a polymer with $[\alpha]_D$ of +2480° ($c = 4.3 \times 10^{-3}$ g/mL, $CHCl_3$), whereas the starting monomer, **1**, showed a much smaller $[\alpha]_D$ with opposite sign [−2.39° ($c = 1.0$ g/mL, $CHCl_3$)]. In a similar way, **2**, which has a quite small $[\alpha]_D$ [−1.21° ($c = 1.0$ g/mL, $CHCl_3$)], provided a polymer having a very large $[\alpha]_D$ [+1860° ($c = 4.3 \times 10^{-3}$ g/mL, $CHCl_3$)]. These values are approximately 3 orders larger than that of poly(**5**).[8] Both CD spectra of poly(**1**) and poly(**2**) also exhibited very large molar ellipticities $[\theta]$ in the UV−vis region in $CHCl_3$ (Figure 1). The magnitude of $[\theta]$ was comparable to that of poly(phenylacetylene) with chiral menthoxycarbonyl groups[3d] and about 1 order larger than that of poly(**5**).[9] Since the present Cotton effects are presumably attributable to the backbone $\pi-\pi^*$ transition, these results lead to the conclusions that the main chains of poly(**1**) and poly(**2**) exist in predominantly one screw sense and that the large optical rotations arise from the twisted conformation with an excess of one sense of the backbones.[11]

Similarly to the cases of **1** and **2**, the signs of $[\alpha]_D$ reversed after the polymerizations of **3** and **4**. However, $[\alpha]_D$ values of poly(**3**) and poly(**4**) were quite small compared with those of poly(**1**) and poly(**2**) (Table 2). For instance, when the phenyl group of **1** was changed to a small substituent (methyl group), the value of $[\alpha]_D$ was drastically reduced from +2480° to +11.0°. In a similar way, the Cotton effects of poly(**3**) and poly(**4**) were quite weak (Figure 2). It is probable that there is no significant difference in the geometrical structure among poly(**1**), poly(**2**), and poly(**3**) because they were prepared by the same catalyst. Therefore, the weak CD of poly(**3**) is not due to the difference in the geometrical

Scheme 1

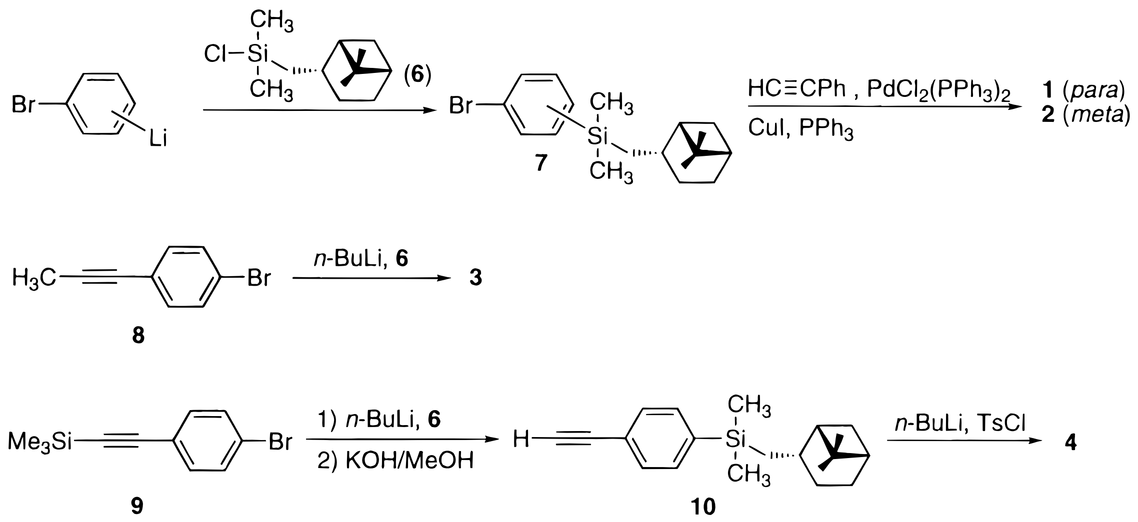

Table 1. Polymerization of 1 and 2[a]

run	monomer	$[M]_0$ (mol/L)	catalyst	temp (°C)	yield (%)[b]	$M_w/10^4$ [b,c]	$[\alpha]_D$ (deg)[d]
1	**1**[e]	0.10	$TaCl_5$–n-Bu_4Sn	80	63	>100	+2350
2		0.20	$TaCl_5$–n-Bu_4Sn	30	61	>190	+534
3		0.20	$TaCl_5$–n-Bu_4Sn	60	82	>110	+1750
4		0.20	$TaCl_5$–n-Bu_4Sn	80	90	>130	+2480
5[f]		0.20	$TaCl_5$–n-Bu_4Sn	120	69	>120	+2420
6		0.20	$NbCl_5$–n-Bu_4Sn	80	15	>160	+1970
7	**2**[g]	0.10	$TaCl_5$–n-Bu_4Sn	80	40	38	+1550
8		0.20	$TaCl_5$–n-Bu_4Sn	80	46	71	+1540
9[h]		0.10	$NbCl_5$–n-Bu_4Sn	80	5	42	+1860

[a] In toluene, 24 h, [cat.] = 10 mmol/L, [n-Bu_4Sn] = 20 mmol/L. [b] Methanol-insoluble part. [c] Estimated by GPC (PSt, $CHCl_3$). [d] $c = 4.0 \times 10^{-3}$ g/dL, $CHCl_3$. [e] $[\alpha]_D = -2.39°$ (c = 1.0 g/dL, $CHCl_3$). [f] In o-xylene. [g] $[\alpha]_D = -1.21°$ (c = 1.0 g/dL, $CHCl_3$). [h] 6 days.

Table 2. Polymerization of 3 and 4[a]

run	monomer	catalyst	yield (%)[b]	$M_w/10^4$ [b,c]	$[\alpha]_D$ (deg)[d]
1	**3**[e]	$TaCl_5$	48	33	+10.7
2		$TaCl_5$–n-Bu_4Sn	54	84	+11.0
3		$TaCl_5$–Ph_3Bi	79	132	+14.4
4		$NbCl_5$–n-Bu_4Sn	87	41	+16.5
5	**4**[f]	$MoCl_5$	0		
6		$MoCl_5$–n-Bu_4Sn	86	70	+6.7
7		$MoCl_5$–Ph_4Sn	84	61	+11.0
8		$MoCl_5$–Et_3SiH	96	71	+11.1
9		$MoCl_5$–Et_3SiH[g]	88	32	+8.3
10		$Mo(CO)_6$–CCl_4–$h\nu$	45	110	+9.8

[a] In toluene, 24 h, [cat.] = 10 mmol/L, [cocat.] = 20 mmol/L, 80 °C for **3**, 30 °C for **4**. [b] Acetone-insoluble part for poly(**3**) and methanol-insoluble part for poly(**4**). [c] Estimated by GPC (PSt, $CHCl_3$). [d] c = 0.1–0.13 g/dL, $CHCl_3$. [e] $[\alpha]_D = -2.85°$ (c = 1.0 g/dL, $CHCl_3$). [f] $[\alpha]_D = -2.50°$ (c = 1.0 g/dL, $CHCl_3$). [g] In anisole.

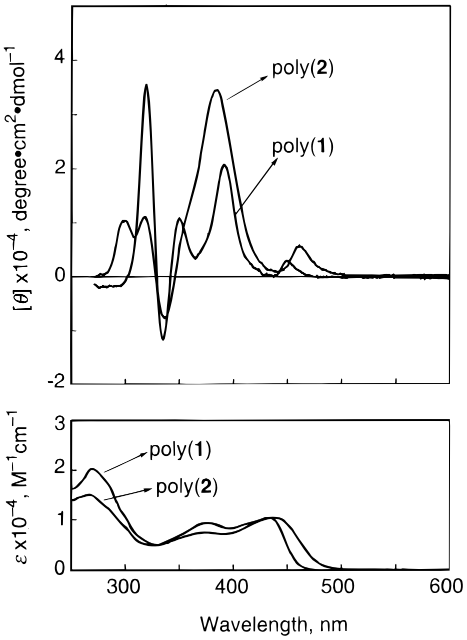

Figure 1. CD (top) and UV–vis (bottom) spectra of poly(**1**) and poly(**2**) prepared with $TaCl_5$–n-Bu_4Sn at 80 °C (in $CHCl_3$, 40 μg/mL, room temperature).

structure of the polymer. Although the decrease in the conjugation between the main chain and the pendants for poly(**3**) and poly(**4**) may be a reason for the weak CD, the absence of clear Cotton effects as well as the extremely small optical rotations of poly(**3**) indicates that the helical conformation is not satisfactorily induced to poly(**3**) and poly(**4**). In other words, introduction of two aromatic side groups into the repeating unit is favorable for the induction of helical conformation to disubstituted acetylene polymers.

It is worthy to note that, as the polymerization temperature was raised, the $[\alpha]_D$ of poly(**1**) progressively increased (Table 1). A similar tendency was recognized in the CD spectra of poly(**1**); the molar ellipticities of *all* Cottons increased with increasing polymerization temperature (Figure 3). Though there is no evidence at present, this phenomenon is presumably due to the change in the steric structure of polymer backbone (cis to trans and/or head-to-head to head-to-tail) with polymerization temperature.

In general, the magnitude of the Cotton effects and the specific rotation of a helical polymer tend to decrease as the measuring temperature is raised, which is

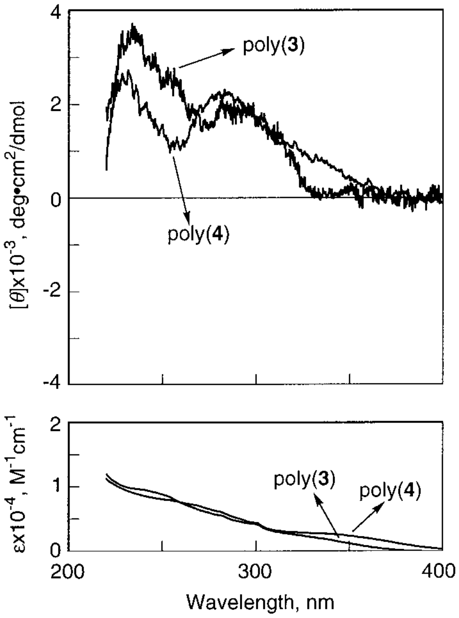

Figure 2. CD (top) and UV–vis (bottom) spectra of poly(**3**) prepared with $TaCl_5$–Ph_3Bi at 80 °C (in cyclohexane, 20 μg/mL, 25 °C) and poly(**4**) prepared with $MoCl_5$–Et_3SiH at 30 °C (in cyclohexane, 40 μg/mL, 25 °C).

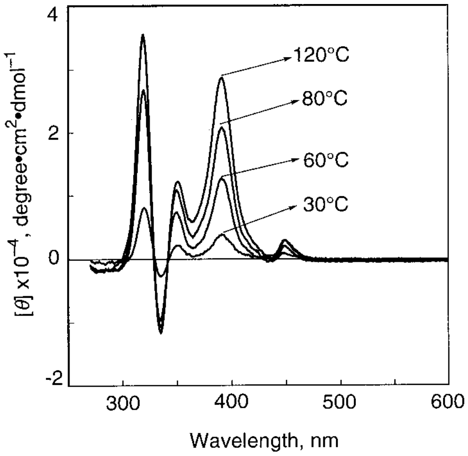

Figure 3. CD spectrum of poly(**1**) prepared with $TaCl_5$–*n*-Bu_4Sn at various temperatures (in $CHCl_3$, 40 μg/mL).

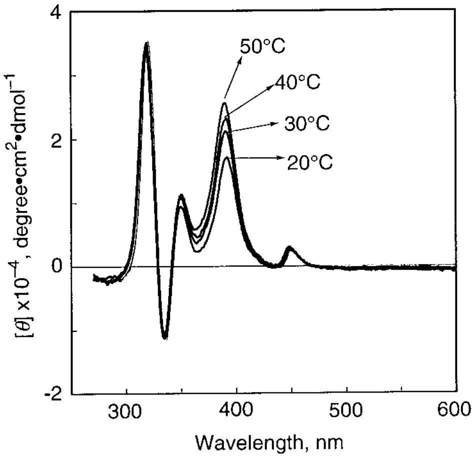

Figure 4. Variable temperature CD spectra of poly(**1**) prepared with $TaCl_5$–*n*-Bu_4Sn at 80 °C (in $CHCl_3$, 40 μg/mL).

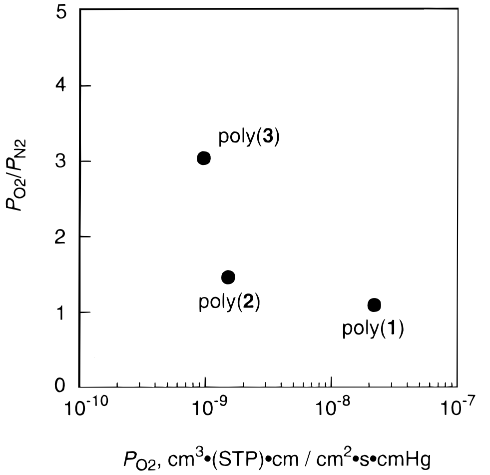

Figure 5. Plot of the separation factor against nitrogen (P_{O_2}/P_{N_2}) versus the oxygen permeability coefficients (P_{O_2}) for poly(**1**), poly(**2**), and poly(**3**).

explicable by helix-to-coil transformation. Contrary to expectation, the intensity of the Cotton effects of poly(**1**) increased as its solution was heated (Figure 4). Namely, as the measuring temperature was raised from 20 to 50 °C, the signal at 390 nm gradually increased from (+)1.7 × 10^4 to (+)2.7 × 10^4. This enhancement of intensity was reversible; i.e., decreasing the temperature resulted in the recovery of the original value. It should be noted that the intensities of other Cottons at 320, 340, 350, and 450 nm did not change significantly over the temperature range 20–50 °C. Such a phenomenon is unknown except for the following case: in the poly(phenylacetylene) with chiral menthoxycarbonyl groups at the para position produced with a W catalyst, the specific rotation dramatically increased from −497° to −772° upon heating the chloroform solution from 40 to 45 °C.[3d] On the other hand, the magnitudes of [θ] of poly(**3**) and poly(**4**) slightly decreased with increasing temperature from 20 to 75 °C, similarly to the cases of chiral polyacetylenes previously reported.[3a,b] For example, the [θ] of poly(**4**) at 280 nm decreased from (+)1900 at 20 °C to (+)1450 at 75 °C. These results suggest that the helical conformation of substituted poly(diphenylacetylenes) is appreciably stiff and stable in solution over the temperature range studied.

Permeability of the Polymers. Figure 5 plots the oxygen permeability coefficients (P_{O_2}) versus separation factor against nitrogen (P_{O_2}/P_{N_2}) for poly(**1**), poly(**2**), and poly(**3**). Like most substituted polyacetylenes, the present polymers exhibited fairly large oxygen permeability. The P_{O_2} of poly(**1**) is about 10 times larger than that of poly(**3**), which is consistent with the excellent gas permeability of poly(diphenylacetylene)s with round-shaped substituents. The para-substituted poly(**1**) exhibited a P_{O_2} value 10 times larger than that of the meta-substituted counterpart, poly(**2**). The P_{O_2} values of poly(**1**) and poly(**2**), however, were ca. 1 and 2 orders, respectively, lower than those of the corresponding poly(diphenylacetylene)s with trimethylsilyl groups and comparable to those of poly(diphenylacetylene)s having dimethylisopropylsilyl groups.[9a]

Poly(**1**), poly(**2**), and poly(**3**) had enantioselectivities in the permeation of racemic tryptophan as shown in Figure 6. The decreasing order of *P* is poly(**1**) > poly(**2**) > poly(**3**), while the decreasing order of α^R is poly(**3**) > poly(**2**) > poly(**1**). In other words, the selectivity increases with the decrease of the permeability in this enantiomer permeation. This behavior is the same as in the relationship between P_{O_2} and P_{O_2}/P_{N_2} (Figure 5).

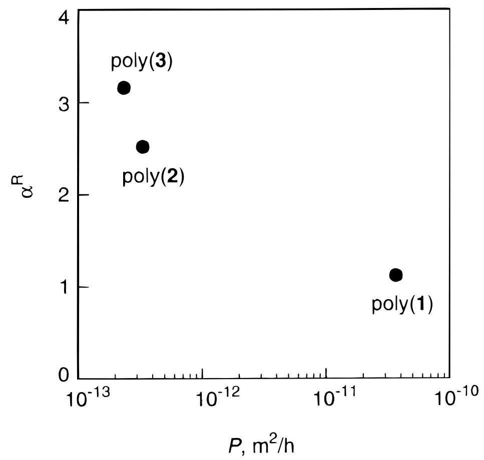

Figure 6. Plot of enantioselectivities (α^R) versus total permeability coefficients (P) in concentration-driven permeation of 0.5 wt % tryptophan (aqueous) for poly(**1**), poly(**2**), and poly(**3**).

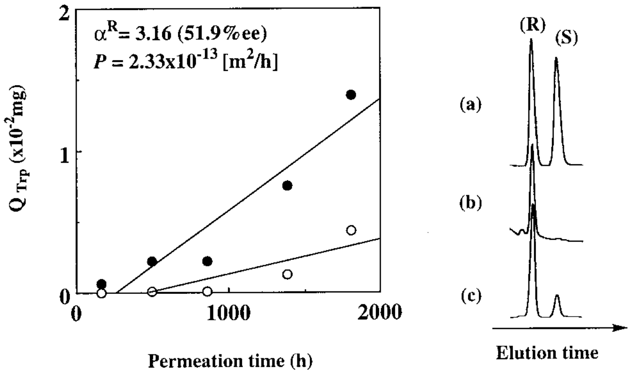

Figure 7. (left) Plots of quantity (Q_{Trp}) of permeated (●) R−(+)- and (○) *S*-(−)-tryptophan (Trp) from 0.50 wt % racemic aqueous solution vs permeation time through a poly(**3**) membrane in concentration-driven permeation. (right) HPLC chromatogram of Trp: (a) racemic Trp (feed); (b, c) Trp in the permeate at an initial period (160−497 h) and at a later period (862−1385 h), respectively. Column, CROWNPAK-CR; eluent, $HClO_4$(aq).

Among the three disubstituted acetylene polymers, poly(**3**) displayed the highest selectivity ($\alpha^R = 3.16$), which is comparable to that of poly(**5**).[8] The enantiomeric excess (% ee) increased from 0% ee to 51.9% ee after an initial period in the permeation of the racemic tryptophan solution through a poly(**3**) membrane. (See the solid lines in the left graph and the right chromatogram (a) and (c) in Figure 7.) Furthermore, a complete optical resolution was achieved at the initial period of the permeation. (See the right chromatogram (b) in Figure 7.)

Although poly(**3**) had much smaller [θ] and $[\alpha]_D$ values than poly(**1**) and poly(**2**), the former showed the best enantioselectivity. This is probably because poly(**1**) and poly(**2**) possess a stiffer structure than poly(**3**). Namely, compared with poly(**3**), both poly(**1**) and poly(**2**) are stiff owing to their bulky substituents and higher extents of helical conformation, so that the membranes of poly(**1**) and poly(**2**) may have more and larger molecular-scale voids. Indeed, the membranes of poly(**1**) and poly(**2**) were more brittle than that of poly(**3**). Hence, high gas permeability and essentially no permselectivity were obtained when poly(**1**) and poly(**2**) were employed. Similarly, the presence of many molecular-scale voids in the membranes of poly(**1**) and poly(**2**) may achieve high permeation of the racemate and reduce the effect of the helical conformations. In other words, chiral environment originating from the helical conformations of polymers does not seem to improve the enantioselectivity if the polymer membranes have many molecular-scale voids.

In summary, we have demonstrated a new example for the synthesis of disubstituted acetylene polymers having chiral pendant groups. Satisfactorily high molecular weight polymers with excellent solubility as well as good film-forming ability were readily accessible by the polymerization of diphenylacetylenes with chiral pinanyl groups. The polymers showed quite large optical rotations and intense CDs, which suggests helical conformations with an excess of one-handed screw sense. Increase in the temperature caused no decrease in the intensity of the Cotton effects of poly(**1**) and poly(**2**), which means that the present poly(diphenylacetylene)s exist in fairly stable helical conformations. The produced polymers achieved enantioselective permeation of racemic tryptophan. The authors believe that appropriate design of chiral pendants of diphenylacetylenes offers advanced polymeric membranes for the separation of racemic compounds.

Experimental Section

Materials. All the solvents used were distilled by the standard procedures. $TaCl_5$, $NbCl_5$, $MoCl_5$, Ph_3Bi, and $Mo(CO)_6$ were used as received. *n*-Bu_4Sn and Et_3SiH were distilled by the usual manners and used as toluene solutions (200 mmol/L). All the reagents in monomer synthesis were used as purchased without further purification unless specified. (−)-Chlorodimethyl(10-pinanyl)silane (**6**) was prepared by the reported manner.[8,12] 1-(4-Bromophenyl)-1-propyne (**8**)[13] and 1-(4-bromophenyl)-2-trimethylsilylacetylene (**9**)[14] were prepared by the Pd-catalyzed coupling of 4-iodo-1-bromobenzene with propyne and 1-trimethylsilylacetylene, respectively, with reference to the reported methods.

Measurements. The molecular weights of the polymers were estimated by gel permeation chromatography ($CHCl_3$ as an eluent, polystyrene calibration). IR and UV−vis spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer and a Shimadzu UV-2200 spectrophotometer, respectively. NMR spectra were obtained by using JEOL GSX-270 and JNM-LA500 spectrometers. Thermogravimetric analyses (TGA) were conducted in air on a Perkin-Elmer TGA7 thermal analyzer. CD spectra were measured with a Jasco J-600 spectropolarimeter. Specific rotations were recorded with a Jasco V-530 spectropolarimeter.

Syntheses of 1 and 2. A hexane solution of *n*-BuLi (1.53 M, 58.8 mL) was added slowly to a solution of 1,4-dibromobenzene (21.2 g, 90.0 mmol) in dry Et_2O(60 mL) at 0 °C. After stirring for 1.5 h at 0 °C, **6** (20.8 g, 90.0 mmol) was added dropwise, and the solution was stirred for 3 h at 0 °C. The formed salt was removed by filtration, and the filtrate was washed with water. The organic layer was dried over Na_2SO_4, concentrated, and distilled at 135−138 °C (0.5 mmHg) to yield (−)-1-[dimethyl(10-pinanyl)silyl]-4-bromobenzene (**7**, 16.8 g, 53.2%). A solution of **7** (4.42 g, 12.6 mmol) in dry Et_3N (20 mL) was added to a mixture of triphenylphosphine (77 mg, 0.29 mmol), dichlorobistriphenylphosphinepalladium (34 mg, 0.048 mmol), and cuprous iodide (46 mg, 0.24 mmol) in Et_3N (80 mL). To this mixture was added phenylacetylene (1.4 mL, 13 mmol). The mixture was heated at 90 °C and refluxed for 4 h. The resulting mixture was filtered and concentrated. The product was purified by a flash column chromatography (SiO_2, hexane) to give **1** as a white solid in a 42% yield based on **7**. All the above procedures concerning reactions were performed in nitrogen. Mp 43−47 °C. ^1H NMR ($CDCl_3$): δ 7.60−7.28 (m, 5H), 7.49 (2d, 4H), 2.20−0.62 (m, 11H), 1.14 (s, 3H), 0.76 (s, 3H), 0.28 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 140.9, 133.4, 131.6, 130.6, 128.3, 128.2, 123.3, 89.7, 89.6, 49.2, 40.6, 39.5, 31.1, 26.9, 25.5, 24.7, 23.9, 23.0,20.0, 1.9, 2.0; IR (KBr): 3072, 3036, 2988, 2224, 1600, 1500, 1252, 1102 cm^{-1}. Anal. Calcd for $C_{26}H_{32}Si$: C, 83.81; H, 8.66. Found: C, 83.66; H, 8.76. **2** (viscous liquid) was prepared from 1,3-dibromobenzene instead of 1,4-dibromobenzene in a similar manner. Yields: 41% (based on the meta isomer of **7**) and 15% (based on 1,3-dibromobenzene). ^{1}H NMR ($CDCl_3$): δ 7.68−7.28 (m, 9H), 2.20−0.65 (m, 11H), 1.15 (s, 3H), 0.77 (s, 3H), 0.29 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 140.6, 136.6, 133.2, 131.73, 131.67, 131.6, 128.3, 128.2, 127.6, 127.5, 123.4, 122.6, 89.8, 89.2, 49.2, 40.6, 39.5, 31.1, 26.9, 25.6, 24.8, 23.8, 20.0, 1.8, 2.0; IR (neat): 3064, 2912, 2868, 2224, 1602, 1496, 1252, 1112 cm^{-1}. Anal. Calcd for $C_{26}H_{32}Si$: C, 83.81; H, 8.66. Found: C, 82.20; H, 8.79.

Synthesis of 3. 1-(4-Lithiophenyl)-1-propyne was prepared by adding 35.2 mmol of *n*-BuLi (22 mL of a 1.60 M solution in hexane) to a solution of 6.40 g of **8** (33.0 mmol) in dry Et_2O at −78 °C under nitrogen. After 1 h, a solution of **6** (7.65 mL, 32.5 mmol) in dry Et_2O (80 mL) was added dropwise to the solution of 1-(4-lithiophenyl)-1-propyne at −78 °C, and the solution was gradually warmed to room temperature. After stirring for 5 h, water was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined ether layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by a flash column chromatography (SiO_2, cyclohexane) to give **3** as a colorless liquid. Yield (based on **8**): 37%. ^{1}H NMR ($CDCl_3$): δ 7.40 (d, 2H, $J = 7.81$ Hz), 7.34 (d, 2H, $J = 7.81$ Hz), 2.04 (s, 3H), 1.13 (s, 3H), 0.74 (s, 3H), 0.63−2.15 (m, 11H), 0.245 (s, 3H), 0.242 (S, 3H); ^{13}C NMR ($CDCl_3$): δ 139.8, 133.3, 130.5, 124.1, 86.1, 79.8, 49.2, 40.6, 39.4, 31.1, 26.8, 25.5, 24.7, 23.8, 22.9, 19.9, 4.3, −1.9, −2.1; IR (neat): 3065, 2980, 2247, 1250, 1107, 837, 820 cm^{-1}. Anal. Calcd for $C_{21}H_{30}Si$: C, 81.21; H, 9.73. Found: C, 81.46; H, 9.84.

Synthesis of 4. 9 was lithiated by the slow addition of a 1.60 M solution of *n*-BuLi in hexane (25 mL, 40.0 mmol) into a dry Et_2O solution of **9** (9.2 g, 36 mmol) at −78 °C under nitrogen, which was followed by the additional stirring for 1 h. Into the solution was added dropwise **6** (8.6 mL, 36 mmol) in dry Et_2O (80 mL), and the reaction mixture was gradually warmed to room temperature over 2 h. Quenching with water and ethereal working up gave the crude product which was subjected to desilylation by treating with KOH (ca. 2 g) in methanol (10 mL) at room temperature for 30 min. This solution was concentrated with a rotary evaporator, and the residue was dissolved in Et_2O. The ether layer was washed with brine and then water, dried over $MgSO_4$, concentrated, and purified by a flash column chromatography (SiO_2, hexane) to give (−)-4-[dimethyl-(10-pinanyl)silyl]-1-ethynylbenzene (**10**) as a colorless liquid (8.5 g, 94%). Into a dry Et_2O solution (70 mL) of **10** (8.5 g, 29 mmol) was added dropwise a 1.60 M solution of *n*-BuLi in hexane (18 mL, 29 mmol) at −78 °C, and the solution was stirred for an additional 1 h. Into this solution, *p*-toluenesulfonyl chloride (6.6 g, 35 mmol) in dry Et_2O (30 mL) was slowly added, and then the cooling bath was removed. After stirring for 4 h, the reaction was quenched by adding water. Ethereal working up and purification by a flash column chromatography (SiO_2, hexane) gave **4** as a colorless liquid (3.3 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, 2H, $J = 7.35$ Hz), 7.34 (d, 2H, $J = 7.35$ Hz), 1.13 (s, 3H), 0.74 (s, 3H), 0.63−2.14 (m, 11H), 0.252 (s, 3H), 0.249 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 141.4, 133.4, 130.9, 122.2, 69.5, 68.2, 49.1, 40.5, 39.4, 31.0, 26.8, 25.5, 24.7, 23.7, 22.9, 19.9, −1.9, −2.2; IR (neat): 3067, 2980, 2220, 1250, 1103, 837, 818 cm^{-1}. Anal. Calcd for $C_{20}H_{27}SiCl$: C, 72.58; H, 8.22; Cl, 10.71. Found: C, 72.30; H, 8.25; Cl, 11.00.

Polymerization. Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under nitrogen. Transition-metal catalysts and organometallic cocatalysts were used as purchased. The detailed polymerization conditions were indicated in Tables 1 and 2. The polymers were isolated by reprecipitation into an excess of methanol or acetone, and the yields were determined by gravimetry.

Membrane Preparation. A 1−2 wt % (w/v) solution of a polymer in chloroform 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 24 h. Thickness, 15.2−54.8 μm; area, 3.14 × 10^{-4} m^2 for air permeation, 5.72 × 10^{-4} or 6.15 × 10^{-4} m^2 for tryptophan solution permeation.

Measurements of Permeabilities. Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: cm^3 (STP) cm/cm s cmHg) were measured by the gas chromatographic method using a YANAKO GTR-10 apparatus. Concentration-driven enantioselective permeations of aqueous tryptophan solution were measured by using a disproportionate two-chamber glass cell at 25 °C. To maintain constant the difference of the concentration (0.5 wt %) between the feed and permeate sides, the solution in the permeate side chamber was exchanged by pure water before more than 1% of the solute in the feed had permeated. The permeated quantity was determined by analyzing aliquots on a HPLC equipped with a CROWNPAK CR column (diameter 4 mm, length 15 cm; Daicel Chemical Co). Enantiomer permeability coefficients (P_R and P_S) were estimated from the slope of the permeated quantity permeation time. Enantioselectivities (α^R) and total permeability coefficients (P) were calculated from $\alpha^R = P_R/P_S$ and $P = P_R + P_S$, respectively.

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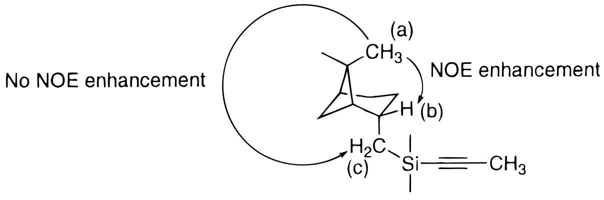
(12) The stereochemistry of the monomers was determined by the NOE enhancement in the ^{1}H NMR of **5** as shown below. Irradiation of the methyl protons (a) at 0.82 ppm caused an NOE enhancement of the signal attributable to the proton (b) at 2.19 ppm, whereas no NOE enhancement was detected for the methylene protons (c) at 0.52−0.69 ppm.



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