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Synthesis, Chiroptical Properties, and High Gas Permeability of Poly(phenylacetylene) with Bulky Chiral Silyl Groups

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Since Sommer and co-workers succeeded in the optical resolution of methyl(1-naphthyl)phenylsilyl compounds[1] in 1959, many studies have been carried out on the stereochemistry of organosilicon compounds. In the field of polymer chemistry, for instance, Kawakami synthesized optically active silanes and siloxanes having functional groups such as allyl, propargyl, and vinyl groups by using methyl(1-naphthyl)phenylmenthoxysilane (**1**) as a starting material and further prepared stereoregular poly(carbosilanes)[2a] and poly(carbosiloxanes)[2a−c] from these silanes and siloxanes.

It is well-known that the main chain of some polyacetylenes with chiral substituents exists in the helical conformation with an excess of one-handed screw sense. For instance, the Rh-catalyzed polymerization of phenylacetylenes affords essentially perfect stereoregular (cis−transoidal structure) polymers, which leads to the induction of one-handed screw sense conformation in the presence of chiral substituents.[3] Despite this advantage, the helical conformation of monosubstitued acetylene polymers such as poly(phenylacetylenes) is thermally unstable,[4] so that their circular dichroism (CD) effects readily decrease when they are heated.

In our previous studies,[5] we found that, as the steric crowding around the polymer backbone increases, the thermal stability of the polymer improves. For example, the onset temperature of weight loss of poly(1-naphthylacetylene) is 330 °C, which is higher than that (250 °C) of poly(phenylacetylene). Furthermore, polyacetylenes with bulky spherical substituents tend to be highly permeable to gases. Especially, several polyacetylenes with silyl groups show very high gas permeability. Thus, the oxygen permeability coefficients (P_{O_2}) of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)][6] and poly[1-*p*-(trimethylsilyl)phenyl-2-phenylacetylene] [poly(TMSDPA)][7] are 6100 and 1100 barrers, respectively. Hence, it is expected that the polymerization of phenylacetylene with a bulky, chiral silicon-containing substituent (e.g., optically active methyl(1-naphthyl)phenylsilyl group) offers a thermally stable, helical, and further highly gas-permeable polymer.

Here we report on the polymerization of (+)-*p*-{[methyl(1-naphthyl)phenyl]silyl}phenylacetylene (MeNpPhSi*PA; $[\alpha]_D$ = 2.30°, *c* = 10 g/dL, in cyclohexane) with transition-metal catalysts and, further, the thermal properties, CD effects, and oxygen permeability of the resulting polymer.

Scheme 1 shows the process of the monomer synthesis: (−)-Methyl(1-naphthyl)phenylmenthoxysilane (**1**)[8] was employed as a starting compound, and chiral silanes **2**[9] and **3**[10] were prepared as intermediates to synthesize the present monomer.[11] [(nbd)RhCl]$_2$ (Aldrich) and WCl$_6$ (Kanto Chemicals) were used as purchased. Toluene, Et$_3$N, and Et$_3$SiH were distilled twice from CaH$_2$. The attempt to determine the optical purity of MeNpPhSi*PA by HPLC and ^{1}H NMR was unsuccessful. However, the melting point of MeNpPhSi*PA was very sharp (44−46 °C) and quite different from that (112−114 °C) of racemic MeNpPhSiPA. Thus, it is assumed that the optical purity of MeNpPhSi*PA is very high.

Scheme 1. Synthesis of (+)-1-*p*-{[Methyl(1-naphthyl)phenyl]silyl}phenylacetylene (MeNpPhSi*PA)

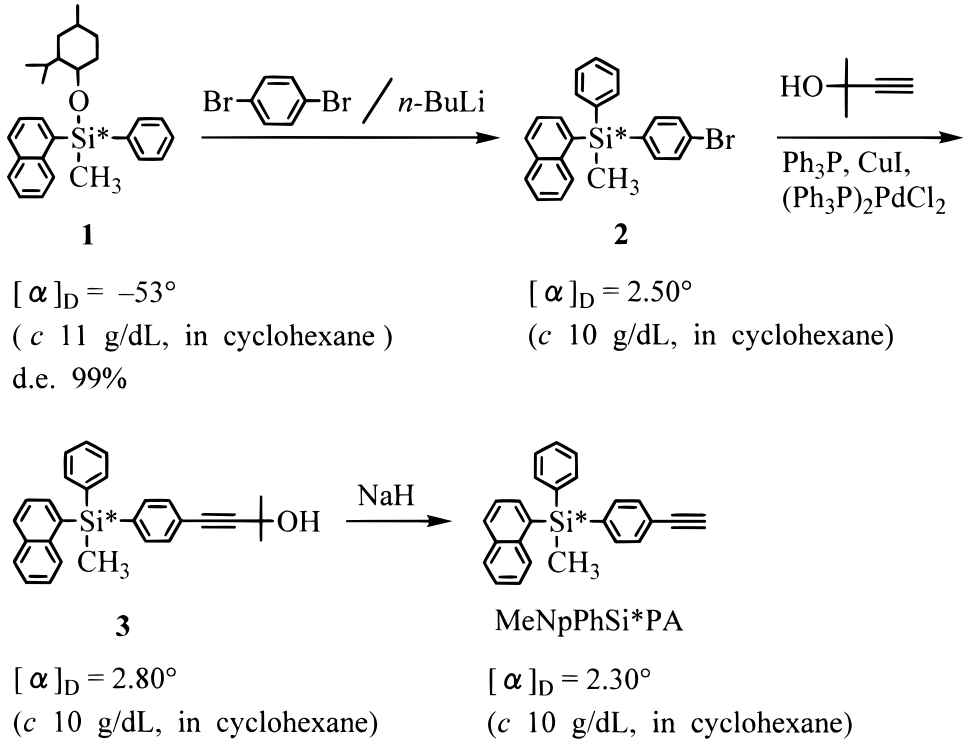

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Table 1. Polymerization of MeNpPhSi*PA

run	catalyst	temp (°C)	yield	$10^{-3}M_w$ (M_w/M_n)[a]	$[\alpha]_D$[b] (deg)
1[c]	$[(nbd)RhCl]_2-Et_3N$	25	95	2500 (2.5)	−150
2[d]	WCl_6-Et_3SiH	30	17	27 (2.8)	−52
3[d]	WCl_6-Et_3SiH	80	100	990 (1.4)	−42

[a] Determined by GPC. [b] $c = 0.11$ g/dL. [c] Polymerized with $[(nbd)RhCl]_2$-Et_3N in toluene for 1 h: $[M]_0 = 0.50$ M; [cat] = 1.0 mM; [cocat] = 2.0 mM. [d] Polymerized in toluene with WCl_6–Et_3SiH for 3 h: $[M]_0 = 1.0$ M; [cat] = 10 mM; [cocat] = 10 mM.

Table 1 shows the results of the polymerization of MeNpPhSi*PA. Polymerization by $[(nbd)RhCl]_2-Et_3N$ and WCl_6-Et_3SiH under suitable conditions gave polymers in high yields over 90%. The polymer obtained with $[(nbd)RhCl]_2-Et_3N$ possessed an especially high molecular weight (M_w) up to 2.5×10^6. Both yield and M_w of the present polymer formed with WCl_6-Et_3SiH increased with increasing polymeriztion temperature, and the M_w of the polymer obtained at 80 °C reached ca. 1.0×10^6. According to our previous studies, phenylacetylenes with bulky ortho substituents produce polymers with high M_w around 1×10^6 by using W catalysts,[12] whereas para-substituted phenylacetylenes do not even though the para substitutents are as bulky as admantyl and *tert*-butyl groups.[13] Thus, it is worth noting that an extremely bulky substituent, the *p*-methyl(1-naphthyl)phenylsilyl group, enhances the M_w of the W-based polymer up to ca. 1×10^6 like bulky ortho substituents.

The structure and properties of the resulting polymer were examined using mainly the Rh-based sample (Table 1, run 1). The IR spectrum of poly(MeNpPhSi*PA) exhibited no absorption at 3283 cm^{-1} ($\upsilon_{H-C\equiv}$) that was seen in the monomer. Anal. Calcd for $(C_{25}H_{20}Si)_n$: C, 86.19; H, 5.74. Found: C, 85.27; H, 5.59. The UV–vis spectrum of poly(MeNpPhSi*PA) showed two absorption maxima at $\lambda_{max} = 334$ nm (ϵ_{max} 7100 M^{-1} cm^{-1}) and 420 nm (ϵ_{max} 4500 M^{-1} cm^{-1}) and virtually no absorption above 490 nm ($\lambda_{\epsilon<50}$) (cf. Figure 1). On the other hand, the UV–vis spectra of the W-based poly(MeNpPhSi*PA)s (Table 1, runs 2 and 3) showed no absorption maximum (λ_{max}), and the cutoff wavelengths of their absorptions were longer (570–600 nm). These absorption spectra seem to correspond to the polymer colors; i.e., the Rh-based polymer is yellow, while the W-based polymers are brown.

Poly(MeNpPhSi*PA) was soluble in toluene, THF, and $CHCl_3$ but insoluble in hexane, ethyl acetate, DMF, DMSO, and methanol. A free-standing film could be fabricated by casting toluene solution of the polymer. The thermal stability of poly(MeNpPhSi*PA) was examined by the thermogravimetric analysis (TGA) in air. The weight loss began at ca. 320 °C, which is higher than the temperature (ca. 200 °C) for poly(phenylacetylene), and the weight residue of poly(MeNpPhSi*PA) was more than that of poly(phenylacetylene) at any temperature. Thus, the introduction of the very bulky para substituent onto poly(phenylacetylene) clearly improved the thermal stability. In the DSC of the present polymer, no significant peak was seen in the range from room temperature to its decomposition temperature.

The Rh-based poly(MeNpPhSi*PA) showed a very large optical rotation ($[\alpha]_D = -150°$, $c = 0.11$ g/dL in $CHCl_3$), whereas the $[\alpha]_D$ of the W-based ones (samples from Table 1, runs 2 and 3) were much smaller. The $[\alpha]_D$ value of the Rh-based polymer was smaller than that ($[\alpha]_D = -605°$, $c = 1.0$ g/dL in $CHCl_3$) of poly(phenylacetylene) with chiral menthoxycarbonyl groups.[4c] However, the CD spectrum of the Rh-based poly(MeNpPhSi*PA) exhibited very large molar ellipticities $[\theta]$ in the UV region in $CHCl_3$: $[\theta]_{max} = 7.1 \times 10^4$ deg cm^2 dmol^{-1} at 330 nm and -5.3×10^4 deg cm^2 dmol^{-1} at 370 nm (Figure 1). These $[\theta]_{max}$ values are about 1.5–2 times as large as those of poly(phenylacetylene) with chiral menthoxycarbonyl groups ($[\theta]_{max} = 3.7 \times 10^4$ deg cm^2 dmol^{-1} at 310 nm)[4c] and poly(diphenylacetylene) with chiral pinanyl groups ($[\theta]_{max} = 3.5 \times 10^4$ deg cm^2 dmol^{-1} at 320 nm).[14] Furthermore, the magnitude of the Cotton effect did not change in the temperature range of −30 to 20 °C. These results indicate that the helical conformation of the Rh-based poly(MeNpPhSi*PA) is sufficiently stiff and stable in solution at room temperature. In contrast, the W-based poly(MeNpPhSi*PA)s exhibited much weaker CD signals, which seems due to the trans-rich, rather irregular structure of the polymer backbone formed with this catalyst. The monomer was colorless above 300 nm and showed no CD signals above 300 nm.

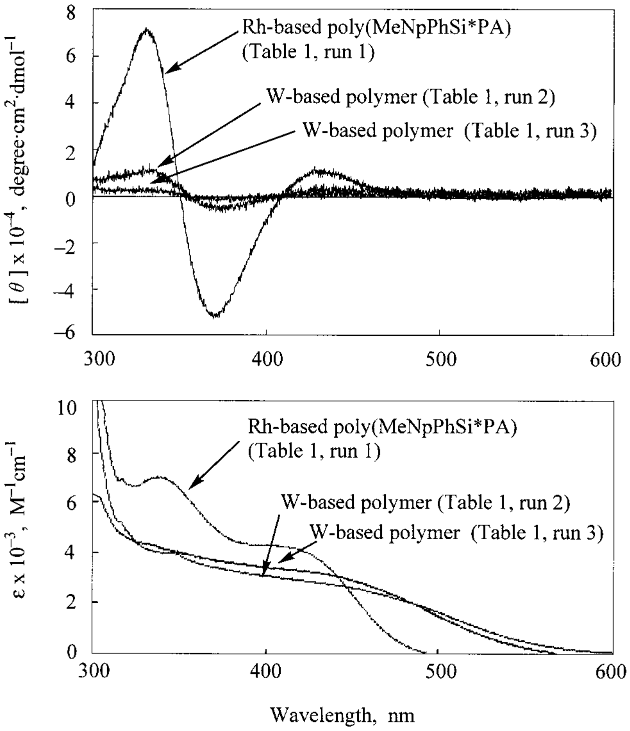

Figure 1. CD and UV–vis spectra of poly(NpMePhSi*PA) (in $CHCl_3$, 5.0×10^{-5} mol/L).

It is known that the gas permeability of poly(TMSP) is enhanced by soaking it in nonsolvents such as methanol.[15] The oxygen permeability coefficient (P_{O_2}) of poly(MeNpPhSi*PA) membrane at 25 °C was 450 barrers ($P_{O_2}/P_{N_2} = 2.3$) when measured just after the film preparation by casting toluene solution of the polymer (solvent evaporation for several days and the subsequent vacuum-drying for 1 day). The P_{O_2} value, however, increased up to 900 barrers ($P_{O_2}/P_{N_2} = 2.0$) after the methanol conditioning (i.e., soaking in methanol for 24 h and the subsequent air-drying for several hours). This P_{O_2} value is comparable to that of poly(TMSDPA)[7] and is much larger than that (6.0 barrers) of poly(phenylacetylene).[16a] The P_{O_2} value of poly{[2,4,5-tris(trifluoromethyl)phenyl]acetylne} is 780 barrers,[16b,c] which was the largest among the values for conventional polymers from monosubstituted acetylenes, and that of poly{[2,4-

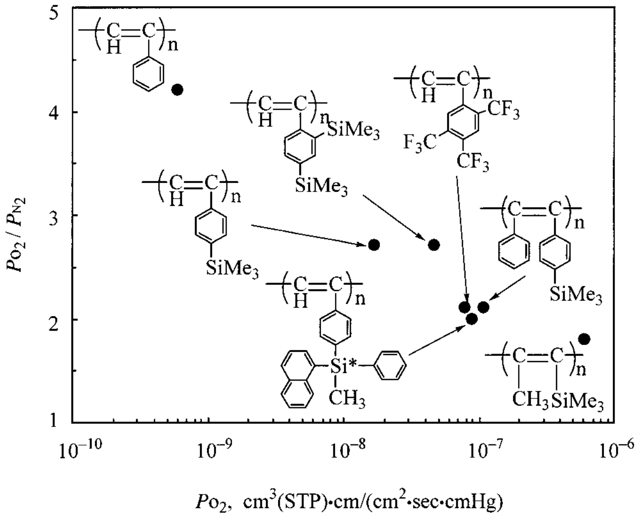

Figure 2. Plot of oxygen permeability coefficient (P_{O_2}) vs P_{O_2}/P_{N_2} of poly(NpMePhSi*PA) (sample from Table 1, run 1) and other substituted polyacetylenes (see refs 6, 7, and 16 for the P_{O_2} values).

bis(trimethylsilyl)phenyl]acetylne} is 470 barrers[16a,c] and the second largest (Figure 2). Thus, it is noteworthy that the P_{O_2} value of the present polymer is the largest among those ever reported for monosubstituted acetylene polymers. Furthermore, the present polymer has a possibility to be applied to optical resolution membrane.[3b,14]

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References and Notes

(1) Sommer, L. H.; Frye, C. L.; Parker, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

(2) (a) Kawakami, Y.; Imae, I. *Macromol. Chem. Phys.* **1999**, *200*, 1245. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592. (c) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 548.

(3) (a) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184. (b) Aoki, T.; Shinohara, K.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4192. (c) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861.

(4) (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 174. (b) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009.

(5) (a) Nanjo, K.; Karim, S. M. A.; Nomura, R.; Wada, T.; Sasabe, H.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 277. (b) Masuda, T.; Hamano, H.; Tsuchihara, K.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374.

(6) Masuda, T.; Isobe, E.; Higashimura, T. *J. Am. Chem. Soc.* **1983**, *105*, 7473.

(7) Tsuchihara, K.; Masuda, T.; Higashimura, T. *Macromolecules* **1992**, *25*, 5816.

(8) Synthesis of (−)-methyl(1-naphthyl)phenylmenthoxysilane (**1**): This compound was prepared according to the literature.[1] Its optical purity was >99% d.e. (by ^{1}H NMR).

(9) Synthesis of (+)-*p*-[methyl(1-naphthyl)phenylsilyl]bromobenzene (**2**): A 300 mL round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After the flask was flushed with nitrogen, *p*-dibromobenzene (12.5 g, 52.4 mmol) and diethyl ether (100 mL) were placed in the flask at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (35 mL, 1.5 M, 52.4 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. A solution of compound **1** (15.6 g, 38.6 mmol) in diethyl ether (50 mL) was added dropwise, and stirring was continued for 24 h. After removal of insoluble salts by filtration, the product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane:benzene 5:1) to give the desired product (yield 12.0 g, 77%) as a colorless liquid. $[\alpha]_D = 2.50°$ (c = 10 g/dL, in cyclohexane). ^{1}H NMR ($CDCl_3$): δ 7.94−7.30 (16H, aromatic) and 1.00 (3H) ppm.

(10) Synthesis of (+)-4-*p*-{[methyl(1-naphthyl)phenyl]silyl}-phenyl-2-methyl-3-butyn-2-ol (**3**): A 300 mL round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Triethylamine (100 mL), $(Ph_3P)_2PdCl_2$ (100 mg, 0.14 mmol), CuI (154 mg, 0.81 mmol), PPh_3 (142 mg, 0.54 mmol), 2-methyl-3-butyn-2-ol (3.9 mL, 39 mmol), and compound **2** (12 g, 29.7 mmol) were placed in the flask, and the mixture was stirred for 3 h at 80 °C. After the completion of reaction had been confirmed by thin-layer chromatography (TLC), triethylamine was evaporated. Diethyl ether (ca. 200 mL) was added, and insoluble salts were removed by filtration. The solution was washed with 2 N hydrochloric acid and then with water. The organic phase was dried over anhydrous sodium sulfate, and diethyl ether was evaporated. The crude product was purified by flash column chromatography (eluent, hexane:ethyl acetate 4:1) to give the desired product (yield 8.3 g, 69%) as a pale yellow liquid. $[\alpha]_D = 2.80°$ (c = 10 g/dL, in cyclohexane). ^{1}H NMR ($CDCl_3$): δ 7.94−7.30 (16H, aromatic), 2.05 (1H), 1.61 (6H), and 1.02 (3H) ppm.

(11) Synthesis of (+)-*p*-{[methyl(1-naphthyl)phenyl]silyl}phenylacetylene (MeNpPhSi*PA): A 300 mL round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Toluene (100 mL), NaH (110 mg, 4.58 mmol), and compound **3** (8.3 g, 20.4 mmol) were placed in the flask, and the mixture was stirred for 3 h at 90 °C. After the completion of reaction had been confirmed by TLC, insoluble salts were removed by filtration, and toluene was evaporated. The crude product was purified by flash column chromatography (eluent, hexane:benzene 10:1) to give the desired product (yield 6.0 g, 84%) as a white solid. Mp 43−45 °C, $[\alpha]_D = 2.30°$ (c = 10 g/dL, in cyclohexane). IR (KBr): 3283, 1506, 1429, 1383, 1259, 1143, 1101, 981, 825, 796, 785, 734, 716, 700, 660 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.94−7.30 (16H, aromatic), 3.12 (1H), and1.02 (3H) ppm. ^{13}C NMR ($CDCl_3$): δ 137.1, 137.0, 136.6, 136.0, 135.3, 135.1, 133.4, 131.6, 130.9, 130.6, 129.5, 128.9, 128.3, 128.0, 125.7, 125.5, 125.1, 123.1, 84.0, 78.1, −2.8 ppm.

(12) (a) Masuda, T.; Hamano, T.; Higashimura, T.; Ueda, T.; Muramatsu, H. *Macromolecules* **1988**, *21*, 281. (b) Masuda, T.; Hamano, Tsuchihara, K.; T.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374.

(13) Fujita, Y.; Misumi, Y.; Tabata, M,; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 3157.

(14) Aoki, T.; Kobayashi, Y.; Kaneko, T.; Oikawa, E.; Yamamura, Y.; Fujita, Y.; Teraguchi, M.; Nomura, R.; Masuda, T. *Macromolecules* **1999**, *32*, 79.

(15) (a) Shimomura, H.; Nakanishi, K.; Odani, H.; Kurata, M.; Masuda, T.; Higashimura, T. *Kobunshi Ronbunshu* **1986**, 43, 747. (b) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Saboca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970. (c) Nagai, K.; Higuchi, A.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 289.

(16) (a) Aoki, T.; Nakahara, H.; Hayakawa, Y.; Kokai, M.; Oikawa, E. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 849. (b) Hayakawa, Y.; Nishida, M.; Aoki, T.; Muramatsu, H. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 873. (c) Masuda, T. In *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 32.

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