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Synthesis, characterization, and oxygen permeability of homo- and copolymers from *p*-[tris(trimethylsilyl)silyl]-phenylacetylene

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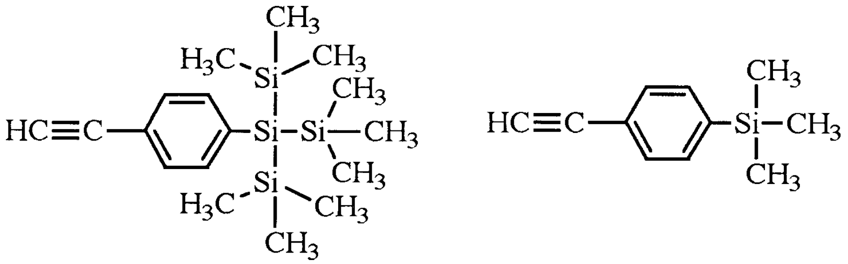
Summary

Homopolymerization of *p*-[tris(trimethylsilyl)silyl]phenylacetylene [*p*$(Me_3Si)_3$SiPA] by Rh catalyst provided insoluble polymer. On the other hand, copolymerization of *p*$(Me_3Si)_3$SiPA with *p*-(trimethylsilyl)phenylacetylene (*p*Me_3SiPA) at 80:20, 50:50, and 20:80 feed ratios afforded high molecular weight copolymers ($M_w > 1x10^6$), all of which were soluble in common solvents such as toluene and chloroform. The mole ratios of *p*$(Me_3Si)_3$SiPA to *p*Me_3SiPA unit in copolymers were close to those in the feeds. The oxygen permeability increased monotonously with increasing *p*$(Me_3Si)_3$SiPA content of copolymer in correspondence with fractional free volume; the value of the copolymer for the 80:20 feed ratio reached 770 baffers.

Introduction

A variety of silicon(Si)-containing polyacetylenes have been synthesized in our and other research groups. Some of the polymers are highly permeable to gases. In particular, disubstituted polyacetylenes having trimethylsilyl (Me_3Si) group have attracted much attention because of their extraordinarily high gas permeability. For instance, the oxygen permeability coefficients (Po_2) of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] [1] and poly[1-phenyl-2-(*p*-(trimethylsilyl)phenylacetylene] [poly(*p*Me_3SiDPA)] [2] reach 6100 and 1100 barrers, respectively. Their high permeability is considered to result from their high excess free volume. In ring-substituted poly(phenylacetylenes), the gas permeability increases with increasing number of Me_3Si group. For example, the Po_2 value (450 barrers) of poly[(*o,p*-bis(trimethylsilyl)phenylacetylene] is higher than that (170 barrers) of poly[*p*-(trimethylsilyl)phenylacetylene] [poly(*p*Me_3SiPA)] [3].

Polymerization of various para-substituted phenylacetylenes with Rh catalysts produces high molecular weight polymers in high yield, while it is more difficult to polymerize ortho-substituted counterparts with the same catalysts [4]. Recently, we have found that p-[{methyl(1-naphtyl)phenyl}silyl]phenylacetylene, which has an extremely bulky chiral substitutent at para position, provides high molecular weight (M_w 2.5x10^6) polymer in the presence of Rh catalysts [5].



$p(Me_3Si)_3SiPA$ pMe_3SiPA

Scheme 1. Monomer structure

In the present study, we investigated the homopolymerization of p-[tris(trimethylsilyl)silyl]phenylacetylene [$p(Me_3Si)_3SiPA$] and its copolymerization with p-(trimethylsilyl)phenylacetylene (pMe_3SiPA) (Scheme 1). Further, the resulting homo- and copolymers were characterized, and their oxygen permeability was examined.

Experimental

Materials

$[(nbd)RhCl]_2$ (Aldrich) and tris(trimethylsilyl)silane (Tokyo Kasei, Japan) were used as purchased. Toluene and Et_3N were distilled twice from CaH_2.

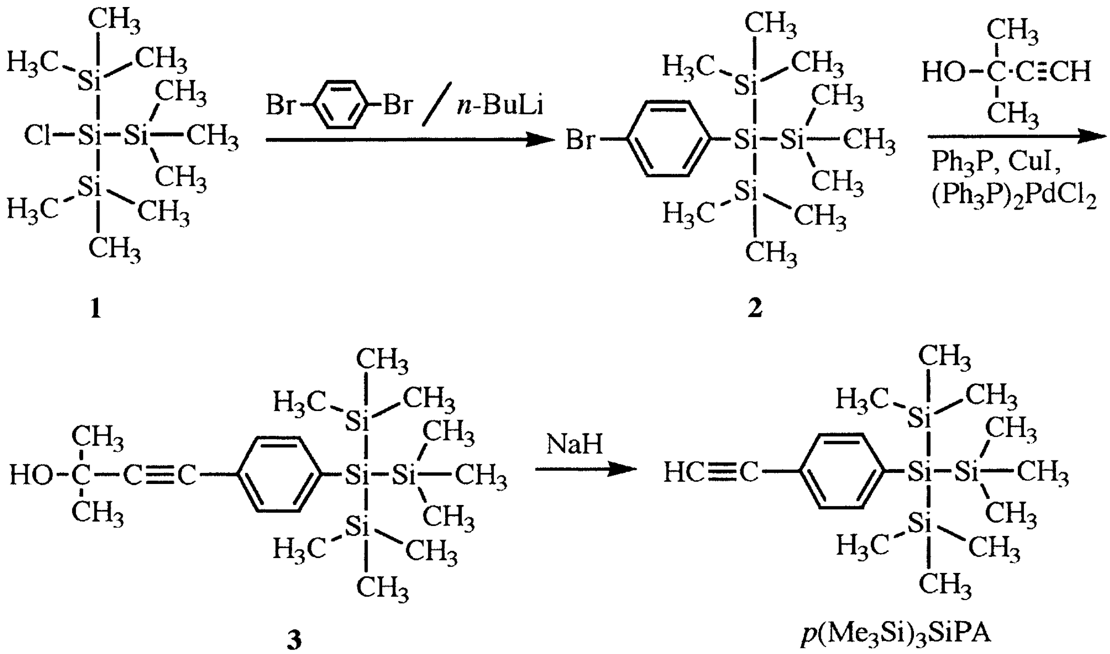
Synthesis

Tris(trimethylsilyl)chlorosilane (**1**) was prepared as follows [6]: A 100-mL round bottomed flask was equipped with a three-way stopcock and a dropping funnel. After the flask was flushed with nitrogen, tris(trimethylsilyl)silane (25 g, 100 mmol) and CCl_4 (30 mL) were placed in the flask, and the mixture was heated at 80 °C for 10 h. After the completion of the reaction had been confirmed by thin layer chromatography (TLC), CCl_4 was evaporated. The crude product was distilled under vacuum to give the desired product (yield 20 g, 70%) as colorless solid. Bp 71 °C / 0.5 mmHg (290 °C / 760 mmHg), ^1H NMR ($CDCl_3$): δ 0.51 (27H, $[Si(CH_3)_3]_3$) ppm.

Intermediates **2** and **3** and the $p(Me_3Si)_3SiPA$ monomer were synthesized according to scheme 2 by modifying the literature method [3a] with use of **1** as a starting material. Data of **2**, **3**, and $p(Me_3Si)_3SiPA$ are as follows: **2**: yield 50%, colorless liquid, ^1H NMR ($CDCl_3$): δ 7.48-7.33 (4H, aromatic) and 0.21 (27H) ppm. **3**: yield 35%, yellow liquid, ^1H NMR ($CDCl_3$): δ 7.52-7.38 (4H, aromatic), 2.02 (1H), 1.61 (6H), and 0.21 (27H) ppm. $p(Me_3Si)_3SiPA$: yield 60%, colorless liquid, IR (KBr): 3306, 2951, 1506, 1481, 1304, 1246, 1082, 1018, 835, 746, 688, 648, 623, 700, 660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45-7.32 (4H, aromatic), 3.10 (1H), and 0.21 (27H) ppm. ^{13}C NMR ($CDCl_3$): δ 138.2, 136.5, 131.1, 120.9, 83.9, 77.9, 0.5 ppm. ^{29}Si NMR ($CDCl_3$): δ -12.7 ($3SiMe_3$), -76.0 (SiC_6H_4-) ppm. Anal. Calcd for $C_{17}H_{32}Si_4$: C, 58.59; H, 9.18.

Found: C, 58.41; H, 9.09.

p-(Trimethylsilyl)phenylacetylene (*p*Me_3SiPA) was prepared according to the literature [3a].



Scheme 2. Synthesis of *p*$(Me_3Si)_3$SiPA

Polymerization

A solution of $[(nbd)RhCl]_2$ (0.90 mg, 0.2 µmol) and Et_3N (0.040 mg, 0.4 µmol) in toluene (1 mL) was added to a solution of a monomer (1 mmol) or comonomers (1 mmol in total) in toluene (4 mL) at 25 °C under nitrogen. The solution was kept at 25 °C for 4 h. The polymerization mixture was diluted with toluene (ca. 10 mL) and poured into a large excess of methanol to precipitate polymer. The polymer was filtered with a sintered glass (G3) and dried under reduced pressure.

Film preparation and characterization

Homogenious films (thickness 35-80 µm) of copolymers were prepared by the solution casting method using toluene as solvent. Film thicknesses were determined with a digital micrometer readable to ±1 µm. Film samples were weighed on an analytical balance, and their volumes were calculated from the area and thickness of films. Film densities were calculated from their weight and volume at ambient conditions. The fractional free volume (FFV) was estimated from

$$\mathrm{FFV} = \frac{V - 1.3V_w}{V}$$

where V is the specific volume of polymer (reciprocal of density) and V_w is the specific van der Waals volume estimated from van Krevelen's group contribution method [7].

Measurments

The weight- and number-average molecular weights (M_w and M_n, respectively) of polymers were determined by gel permeation chromatography (GPC); eluent $CHCl_3$, Shodex K-805, K-806, and K-807 polystylene gel columns (Showa Denco, Co., Japan), polystyrene calibration. ^1H NMR spectra were measured in $CDCl_3$ solution at 25 °C on a JEOL EX-400 spectrometer. Gas permeability coefficients were measured with a Rikaseiki K-315 gas permeability apparatus. The measurements of thermogravimetric analysis (TGA) were conducted with a Perkin-Elmer TGA-7 analyzer in air at a heating rate of 10 °C/min. IR and UV-visible spectra were measured on Shimadzu FTIR-8100 and Shimadzu UV-2200 specrophotometers (KBr pellet and $CHCl_3$ solution), respectively.

Results and discussion

Polymerization

Table 1 shows results for the polymerization of *p*$(Me_3Si)_3SiPA$ and its copolymerization with *p*Me_3SiPA. Homopolymerization of *p*$(Me_3Si)_3SiPA$ with Rh catalyst provided polymer in very high yield of 95%. However, the homopolymer was insoluble in any organic solvents. On the other hand, the copolymerization of *p*$(Me_3Si)_3SiPA$ with *p*Me_3SiPA (feed mole ratios: 80:20, 50:50, and 20:80) afforded high molecular weight ($M_w > 1x10^6$) copolymers, all of which showed very good solubility to organic solvents such as chloroform and toluene. When the *p*$(Me_3Si)_3SiPA$ content of the feed was over 90 mol%, the copolymerizations gave insoluble copolymers. The mole ratios of *p*$(Me_3Si)_3SiPA$ to *p*Me_3SiPA unit in copolymers, which were calculated from the results of elemental analysis [8] for copolymers, were 84:16, 50:50. 21:79, and close to those in the feeds. This is reasonable because the polymer yields were virtually quantitative.

Table 1. Copolymerization of *p*$(Me_3Si)_3SiPA$ (M_1) with *p*Me_3SiPA (M_2) at various feed ratios

run	M_1 in feed	polymer [a]					
	mol%	name	yield wt%	M_1 unit mol% [b]	$M_w/10^3$ [c]	$M_n/10^3$ [c]	color
1	100	poly[*p*$(Me_3Si)_3SiPA$]	95	100	— [d]	— [d]	dark orange
2	80	copoly(80:20)	96	84	1800	780	dark orange
3	50	copoly(50:50)	96	50	1500	630	orange
4	20	copoly(20:80)	97	21	1300	510	yellow
5	0	poly(*p*Me_3SiPA)	95	0	1000	290	light yellow

[a] Polymerized with $[(nbd)RhCl]_2–Et_3N$ in toluene for 4 h: $[M]_0 = 0.20$ M; [cat] = 0.40 mM; [cocat] = 0.80 mM. [b] Determined by elemental analysis. [c] Determined by GPC. [d] Insoluble in any solvent.

Polymer characterization

The IR specta of the homo- and copolymers exhibited no absorption around 3200 cm^{-1} ($\upsilon_{H\text{-}C}$) that was seen in both monomers. The UV-visible spectra of poly(*p*Me$_3$SiPA), copoly(20:80), copoly(50:50), and copoly(80:20) showed three absorption maxima around λ_1 = 266-272 nm, λ_2 = 328-335 nm, and λ_3 = 407-440 nm (Figure 1);see Table 1 for the names of the copolymers. The cutoff wavelengths of their absorptions were 488, 516, 529, and 553 nm, respectively. These absorption spectra seem to correspond to their respective colors, i.e., light yellow, yellow, orange, and dark orange.

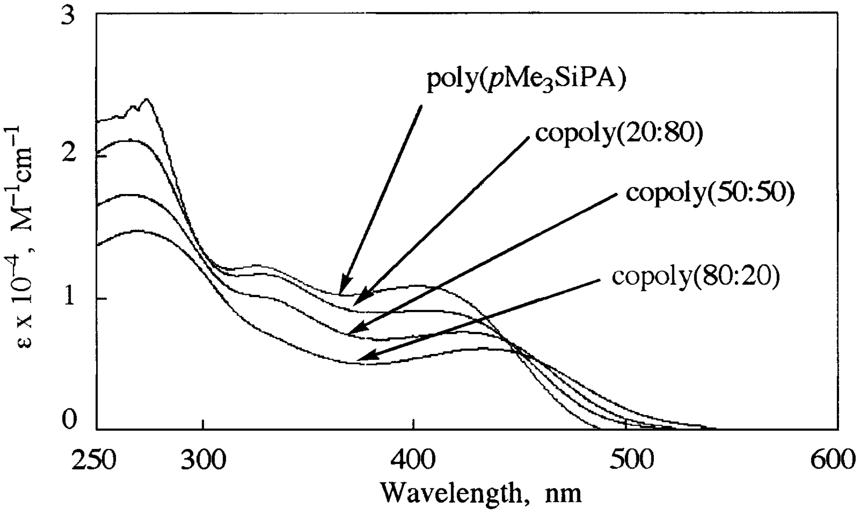


Fig. 1. UV-visible spectra of poly(*p*Me$_3$SiPA) and copolymers (in CHCl$_3$, 5.0x10^{-5} mol/L).

Figure 2 shows the TGA curves of poly[*p*(Me$_3$Si)$_3$SiPA], copolymers, and poly(*p*Me$_3$SiPA) measured in air. As seen from this Figure, the onset temperatures of weight loss (T_0) of these polymers are 250-270 °C, and hardly different from one another. The weight residue of poly[*p*(Me$_3$Si)$_3$SiPA] is, however, more than that of poly(*p*Me$_3$SiPA) at any temperature. The more the *p*(Me$_3$Si)$_3$SiPA content of copolymer, the more the weight residue after complete decomposition. The observed weight residues after decomposition agreed well with

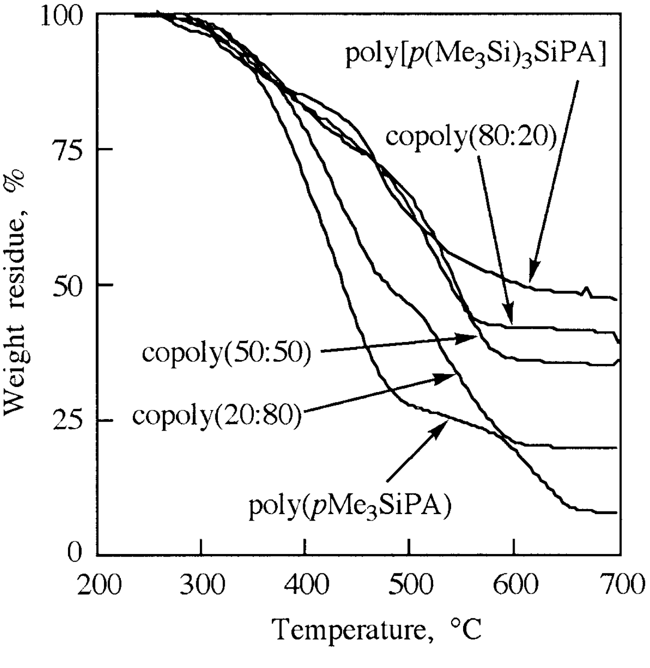


Fig. 2. TGA curves of the homo- and copolymers (heating rate 10 °C/min, in air).

the values calculated by assuming the formation of SiO_2 as ash.

Oxygen permeability

It is known that the gas permeability of polyacetylenes such as poly(TMSP) is enhanced by soaking it in non-solvents such as methanol [9]. Thus, we measured the oxygen permeability of membranes prepared by the solution casting method (solvent evaporation for several days), and the subsequent methanol conditioning (soaking in methanol for 24 h and air drying for several hours). The oxygen permeabilities of the three copolymers and poly(*p*Me_3SiPA) were as follows: copoly(80:20), Po_2 = 770 barrers; copoly(50:50), 450; copoly(20:80), 380; poly(*p*Me_3SiPA), 230. Figure 3 plots the oxygen permeability of copolymer against coploymer composition. It is noteworthy that the oxygen permeability increases monotonously with increasing *p*$(Me_3Si)_3$SiPA content of copolymer.

The geometric densities of the films of the three copolymers, i.e., copoly(80:20), copoly(50:50), and copoly(20:80), and poly(*p*Me_3SiPA) were 0.77 ± 0.02, 0.80 ± 0.04, 0.89 ± 0.02, and 0.97 ± 0.02, respectively. From these densities and elemental analysis values [8], the values of FFV were calculated as 0.30, 0.28, 0.22, and 0.17, respectively. Figure 4 shows that the FFV of copolymer increases practically linearly with its

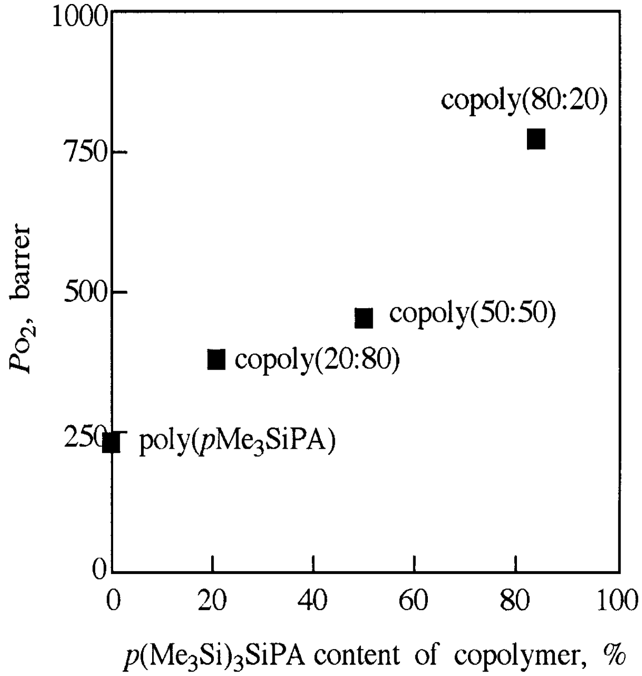


Fig. 3. Plot of oxygen permeability (Po_2) vs. *p*$(Me_3Si)_3$SiPA content of copolymer.

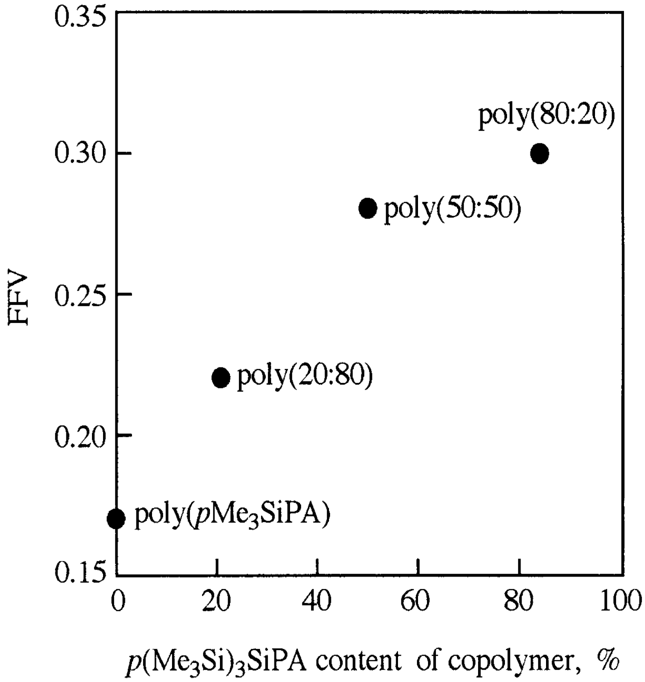


Fig. 4. Plot of fractional free volume (FFV) vs. *p*$(Me_3Si)_3$SiPA content of copolymer.

p($Me_3Si)_3$SiPA content, and consequently corresponds well with oxygen permeability.

Acknowledgment

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