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Synthesis and gas permeation properties of various Si-containing poly(diarylacetylene)s and their desilylated membranes

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ABSTRACT

Diarylacetylene monomers having trimethylsilyl groups and other substituents (substituted biphenyl, **1a** and **1b**; trimethylsilylmethylphenyl, **1c**–**e**) were synthesized and polymerized with $TaCl_5$-*n*-Bu_4Sn catalyst to produce the corresponding poly(diarylacetylene)s (**2a**–**d**). Polymers **2a**–**c** had high molecular weights and were soluble in common organic solvents. Free-standing membranes of **2a**–**c** as well as previously reported **2f**–**h** were prepared by the solution-casting method. Desilylation of these Si-containing polymer membranes was carried out with trifluoroacetic acid to afford **3a**, **3b**, and **3f**–**h**. Upon desilylation, biphenyl-containing membranes became less permeable (**3a**, **b**), whereas fluorene-containing membranes became more permeable (**3f**–**h**). In particular, **3h** exhibited extremely high gas permeability ($PO_2 = 9800$ barrers), which is about the same as that of poly(1-trimethylsilyl-1-propyne). Desilylated membranes **3a** and **3f**–**h** showed different gas permeability from that of polymers **2i**–**k** which have the identical chemical structures and obtained directly by the polymerization of the corresponding monomers.

1. Introduction

Substituted polyacetylenes are attractive polymers from the viewpoints of their unique physical and chemical characteristics as well as their potential applications as functional materials in optoelectronics, sensing based on stimuli-responsiveness, membrane separation of gases, and other fields [1–6]. Membrane-based separation technology has attracted considerable attention in the past few decades. As an important category of gas separation membrane materials, substituted polyacetylenes, especially polymers derived from disubstituted acetylenes, are characterized by high gas permeability and high vapor/gas selectivity [7–10]. Unique permeation properties of these polymers are mainly attributed to their large excess free volume, which originates from their stiff main chain, bulky substituents, and low cohesive energy structure. For example, regarding poly(1-trimethylsilyl-1-propyne) [poly(TMSP)] which is one of the most gas-permeable polymers among all the existing polymers [11,12], many studies concerning its gas permeation properties have been reported to date [13–16]. Poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] exhibits both high gas permeability and excellent thermal stability; its oxygen permeability coefficient (PO_2) is as large as 1100 barrers, and the onset temperature of weight loss reaches 420 °C [17,18]. More recently we have developed indan-containing polyacetylenes that display gas permeability even higher than that of poly(TMSP) [19].

The design and synthesis of novel polymers as membrane materials are of great importance not only because some limitations of the existing polymers may be overcome but also because valuable information will be provided for membrane science and technology. We have previously reported that solvent-insoluble membranes of poly(diphenylacetylene) can be obtained through the desilylation of various silylated poly(diphenylacetylene)s, which cannot be obtained directly by the solvent-casting method owing to its insolubility [20,21]. Desilylation not only imparts chemical stability to the polymers but also affects their gas permeability. For example, the PO_2 of poly[1-β-naphthyl-2-(*p*-trimethylsilylphenyl)acetylene] is 3500 barrers, while the value of its desilylated derivative increases to 4300 barrers [22]. In contrast, the PO_2 of poly(TMSDPA) decreases from 1500 barrers to 910 barrers after desilylation [21]. It is presumed that molecular-scale voids are formed by the desilylation reaction in the solid state, and that the number/size of the formed microvoids is affected by the

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substituents. Further, the decrease of local mobility upon the loss of silyl group must also be considered. However, detailed studies of the effects of substituents on the gas permeability of desilylated polymer membranes are rather limited. Thus it is quite interesting to compare in detail the gas permeability of desilylated poly(diarylacetylenes) with that of silyl-containing precursor polymers and polymers having identical chemical structures which are synthesized directly by the polymerization of the corresponding monomers.

In the present study, several Si-containing poly(diarylacetylene)s were synthesized Scheme 1. Free-standing membranes were fabricated from several resultant polymers, and desilylation of the membranes was carried out with trifluoroacetic acid. Then, the solubility characteristics and thermal properties of the polymers were elucidated. Further, the gas permeation parameters of the polymer membranes were determined, and their diffusion and solubility coefficients were revealed.

2. Experimental section

2.1. Measurements

Molecular weights of polymers were estimated by gel permeation chromatography (GPC) on a Shimadzu PU/SPD-6A/UV-975 chromatograph equipped with polystyrene columns (Showa Denko Shodex K-805, K-806, and K-807) using $CHCl_3$ as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standard samples. NMR spectra were recorded on a JEOL EX-400 spectrometer. Elemental analysis of monomers was carried out at the Microanalytical Center of Kyoto University. Thermogravimetric analysis (TGA) was conducted in air with a Shimadzu TGA-50 thermal analyzer.

2.2. Materials

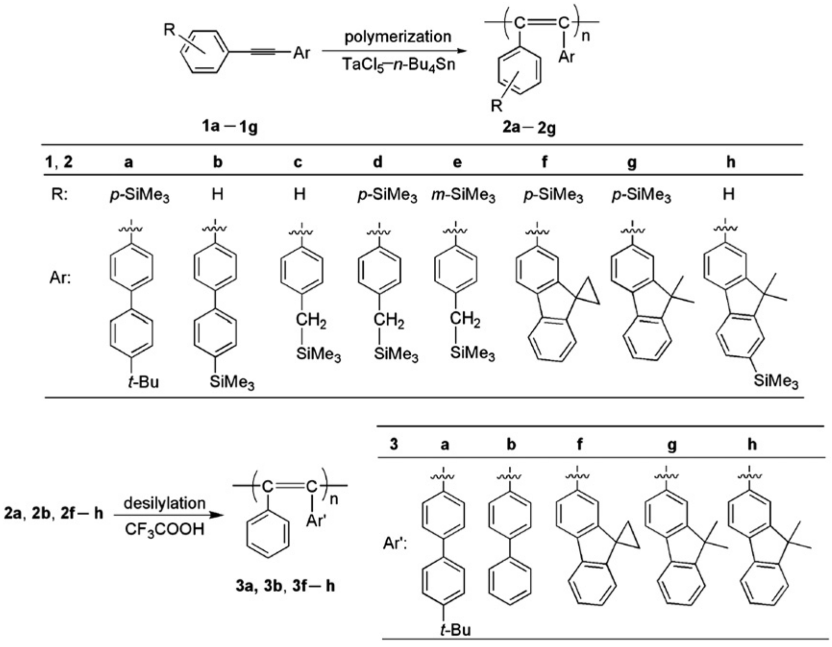
Tantalum (V) chloride ($TaCl_5$, Aldrich) was used without further purification. Tetra-*n*-butyltin (n-Bu_4Sn, Wako) was used after distillation. 4-(trimethylsilyl)phenylacetylene was donated by NOF Co. Ltd. Phenylacetylene (Aldrich), 4-bromo-4′-*tert*-butylbiphenyl (TCI), 4,4′-dibromobiphenyl, benzyltrimethylsilane, 1,3-dibromobenzene, trifluoroacetic acid (TFA), and common solvents (Wako Pure Chemical) were used without further purification except toluene as a polymerization solvent which was purified by the standard method.

2.3. Monomer synthesis

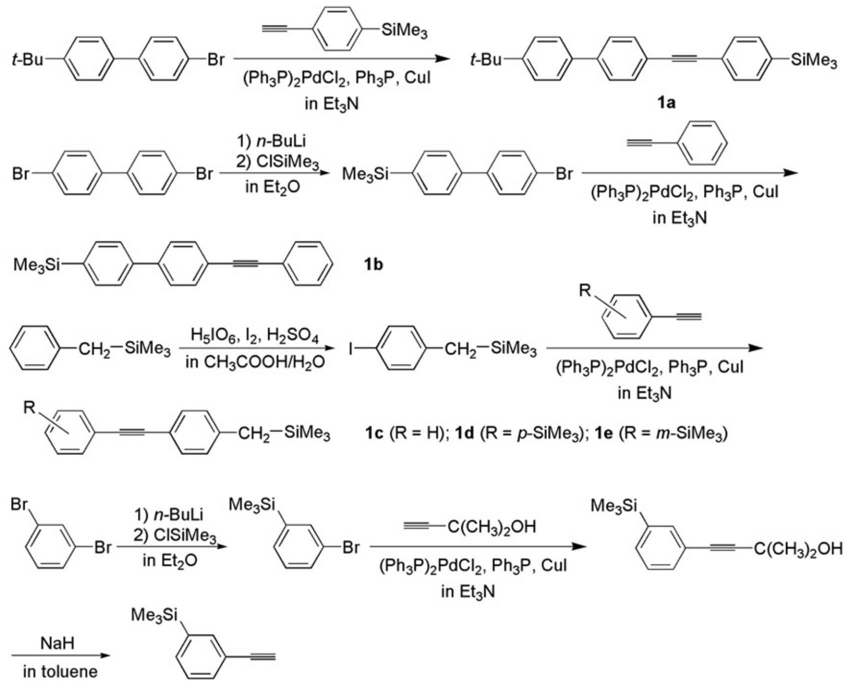
(4-Iodobenzyl)trimethylsilane, 4-bromo-4′-trimethylsilylbiphenyl, and 3-(trimethylsilyl)phenylacetylene were prepared according to the literature methods [23,24]. Monomers **1a**–**d** were synthesized referring to the literature of ethynylation reactions (Scheme 2) [25]. Monomers **1f**–**h** were synthesized as previously described [26].

2.3.1. 1-(4-Trimethylsilylphenyl)-2-(4′-tert-butylbiphenyl-4-yl) acetylene (*1a*)

A 500 mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 4-bromo-4′-*tert*-butylbiphenyl (5.0 g, 17 mmol), bis(triphenylphosphine)palladium dichloride (250 mg, 0.35 mmol), cuprous iodide (390 mg, 2.1 mmol) and triphenylphosphine (360 mg, 1.4 mmol) were placed in the flask and dissolved in triethylamine (90 mL) at room temperature. Then, a solution of 4-(trimethylsilyl)phenylacetylene (3.0 g, 17.3 mmol) in triethylamine (20 mL) was added, and the reaction mixture was heated at reflux temperature for 5 h. Triethylamine in the reaction mixture was evaporated off, and then diethyl ether (200 mL) was added to the residual mass. Solvent-insoluble solid was filtered off, and the filtrate was washed with 2 M HCl aq. and then with water. The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give a white solid; yield 29%. ^1H NMR (400 MHz, δ, $CDCl_3$): 7.65–7.40 (m, 12H, Ar), 1.35 (s, 9H, CCH_3), 0.27(s, 9H, $SiCH_3$). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 150.7, 141.0, 140.8, 137.4, 133.2, 132.0, 130.6, 126.8, 126.6,



Scheme 1. Synthesis of poly(diarylacetylene)s.



Scheme 2. Synthesis of diarylacetylene monomers having trimethylsilyl moieties.

125.8, 123.6, 121.9, 90.1, 89.8, 34.6, 31.3, −1.2. Anal. Calcd. for $C_{27}H_{30}Si$: C, 84.76; H, 7.90; Si, 7.34. Found: C, 84.76; H, 7.90.

2.3.2. 1-Phenyl-2-(4′-trimethylsilylbiphenyl-4-yl)acetylene (*1b*)

A 500 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. After the flask was flushed with nitrogen, 4,4′-dibromobiphenyl (20 g, 64 mmol) and diethyl ether (100 mL) were added and cooled at 0 °C. At the same temperature, a hexane solution of *n*-butyllithium (42 mL, 1.58 M, 66 mmol) was added dropwise, and then the mixture was stirred for 1 h at room temperature. Then, a solution of trimethylchlorosilane (7.0 g, 64 mmol) in diethyl ether (50 mL) was added dropwise at 0 °C, and stirring was continued overnight at room temperature. A small amount of water was added at 0 °C, and the reaction mixture was extracted with diethyl ether. The organic phase was washed with water, and dried over anhydrous magnesium sulfate. After diethyl ether was evaporated, the crude product was purified by silica gel column chromatography (eluent: hexane) to give 4-bromo-4′-trimethylsilylbiphenyl.

Monomer **1b** was prepared by the same method as for monomer **1a** using 4-bromo-4′-trimethylsilylbiphenyl and phenylacetylene instead of 4-bromo-4′-*tert*-butylbiphenyl and 4-(trimethylsilyl) phenylacetylene to give a white solid; yield 36%. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.75−7.55 (m, 10H, Ar), 7.45−7.30 (m, 3H, Ar), 0.30 (s, 9H, Si*CH*$_3$). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 140.9, 140.7, 139.8, 133.9, 132.0, 131.6, 128.4, 128.3, 127.0, 126.3, 123.3, 122.2, 90.1, 89.3, −1.1. Anal. Calcd. for $C_{23}H_{22}Si$: C, 84.61; H, 6.79; Si, 8.60. Found: C, 84.76; H, 7.10.

2.3.3. 1-Phenyl-2-(4-trimethylsilylmethylphenyl)acetylene (*1c*)

A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. After the flask was flushed with nitrogen, benzyltrimethylsilane (8.7 g, 53 mmol), iodine (5.3 g, 21 mmol), and periodic acid (2.6 g, 11 mmol) were dissolved in aqueous acetic acid solution (52 mL, 80%) containing sulfuric acid (1.6 mL). The reaction mixture was stirred at 100 °C for 15 h. After H_2O (200 mL) was added, the solution was extracted with diethyl ether. The organic phase was washed first with 1 M $Na_2S_2O_3 \cdot 5H_2O$ aq (200 mL × 5) and then with H_2O (200 mL × 3). The ethereal solution was dried over anhydrous magnesium sulfate. After evaporating the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane) to give (4-iodobenzyl) trimethylsilane as a colorless liquid; yield 38%. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.49 (d, J = 8.0 Hz, 2H, Ar), 6.73 (d, J = 7.6 Hz, 2H, Ar), 2.01 (s, 2H, C*H*$_2$Si), −0.03 (s, 9H, Si*CH*$_3$). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 140.3, 137.0, 130.1, 88.2, 26.8, −2.0.

Monomer **1c** was prepared by the same method as for monomer **1a** using (4-iodobenzyl)trimethylsilane and phenylacetylene instead of 4-bromo-4′-*tert*-butylbiphenyl and 4-(trimethylsilyl) phenylacetylene to give a white solid; yield 80%. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.55−7.43 (m, 2H, Ar), 7.40−7.25 (m, 5H, Ar), 6.96 (d, J = 8.0 Hz, 2H, Ar), 2.10 (s, 2H, C*CH*$_2$Si), −0.01 (s, 9H, Si*CH*$_3$). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 141.4, 131.5, 131.4, 128.2, 128.0, 127.9, 123.6, 118.5, 89.8, 88.5, 27.5, −1.9. Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.76; H, 7.62; Si, 10.62. Found: C, 81.65; H, 7.62.

2.3.4. 1-(4-Trimethylsilylphenyl)-2-(4-trimethylsilylmethylphenyl)-acetylene (*1d*)

This monomer was prepared by the same method as for monomer **1a** using (4-iodobenzyl)trimethylsilane instead of 4-bromo-4′-*tert*-butylbiphenyl to give a white solid; yield 29%. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.47 (s, 4H, Ar), 7.38 (d, J = 8.0 Hz, 2H, Ar), 6.96 (d, J = 8.0 Hz, 2H, Ar), 2.10 (s, 2H, C*CH*$_2$Si), 0.26 (s, 9H, Si*CH*$_3$), −0.02 (s, 9H, Si*CH*$_3$). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 141.4, 140.5, 133.1, 131.4, 130.5, 127.9, 123.9, 118.5, 90.1, 88.6, 27.5, −1.2, −1.8. Anal. Calcd. for $C_{21}H_{28}Si_2$: C, 74.93; H, 8.38; Si, 16.69. Found: C, 74.64; H, 8.38.

2.3.5. 1-(3-Trimethylsilylphenyl)-2-(4-trimethylsilylmethylphenyl)-acetylene (*1e*)

This monomer was prepared by the same method as for monomer **1a** using (4-iodobenzyl)trimethylsilane and 3-(trimethylsilyl)phenylacetylene instead of 4-bromo-4′-*tert*-butylbiphenyl and 4-(trimethylsilyl)phenylacetylene to give a colorless liquid;

yield 63%. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.65 (s, 1H, Ar), 7.50–7.35 (m, 4H, Ar), 7.31 (t, $J = 7.6$ Hz, 1H, Ar), 6.96 (d, $J = 8.0$ Hz, 2H, Ar), 2.10 (s, 2H, C*CH$_2$*Si), 0.27 (s, 9H, Si*CH$_3$*), −0.02 (s, 9H, Si*CH$_3$*). ^{13}C NMR (100 MHz, δ, $CDCl_3$): 141.4, 140.7, 136.4, 132.7, 131.7, 131.5, 128.0, 127.6, 123.0, 118.6, 89.7, 88.8, 27.5, −1.2, −2.0. Anal. Calcd. for $C_{21}H_{28}Si_2$: C, 74.93; H, 8.38; Si, 16.69. Found: C, 75.12; H, 8.52.

2.4. Polymerization procedure

Polymerizations were performed using toluene as solvent in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations: $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. The formed polymers were isolated by precipitation into a large amount of methanol, and dried to constant weight. The polymer yields were determined by gravimetry.

2.5. Membrane fabrication and desilylation

The membranes (thickness ca. 80–120 μm) of polymers **2a**–**c** and **2f**–**g** were fabricated by casting from toluene solution of the polymer (concentration ca. 0.50–1.0 wt%) onto a flat-bottomed Petri dish. Then, the dish was covered with a glass vessel to slow solvent evaporation (ca. 3–5 days). After a membrane was formed, the membrane was peeled off, and it was immersed in methanol for 24 h and dried to constant weight at room temperature for 24 h. With reference to the method described in the literature [20,27], the desilylation reaction of polymer membranes was carried out using trifluoroacetic acid. A typical procedure of the desilylation reaction is as follows; a polymer membrane was immersed in a mixture of TFA and water (volume ratio 9:1) at room temperature for 24 h. The membrane was immersed in water for 24 h, then washed with water to remove residual impurities, and dried at room temperature for 24 h and in vacuo for 5 h to constant weight.

2.6. Measurement of gas permeability

Gas permeability coefficients (P) of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus equipped with an MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated to 0.3 Pa, while the upstream side was filled with a gas at about 1 atm (10^5 Pa), and the increase of pressure in a downstream receiving vessel was measured. The P values were calculated from the slopes of time–pressure curves in the steady state where Fick's law held.

The gas diffusion coefficients (D) were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

Here, l is membrane thickness, and θ is time lag, which is given by the intercept of the asymptotic line of the time–pressure curve to the time axis. The membrane thickness was controlled so that the time lag would be in the range 10–300 s, preferably 30–150 s. When the time lag was <10 s, the error of measurement became relatively large. If the time lag was, on the contrary, >300 s, the error based on baseline drift became significant. The gas solubility coefficients (S) were calculated by using equation $S = P/D$.

3. Results and discussion

3.1. Polymerization

The polymerization of diarylacetylene monomers (**1a**–**e**) was examined by using $TaCl_5$-n-Bu_4Sn catalyst, whose results are summarized in Table 1. It has been reported that $TaCl_5$-n-Bu_4Sn is an effective catalyst for the polymerization of sterically crowded disubstituted acetylenes including diphenylacetylene derivatives to provide polymers having high molecular weights [4,5], which is essential for fabrication of free-standing membranes. The polymerization of monomers **1a** and **1b** having both biphenyl and trimethylsilyl groups afforded polymers **2a** and **2b** in high yields (65% and 78%, respectively), whose weight-average molecular weights (M_w) exceeded 6.0×10^6. Monomer **1c** containing a trimethylsilylmethyl group also polymerized to give a polymer with somewhat lower M_w (6.6×10^5) in 55% yield. When cyclohexane was used as polymerization solvent, both M_w and yield of the polymer increased. Similar results have been observed in the polymerization of other diarylacetylenes in our previous studies [22]. On the other hand, polymer **2d** obtained from monomer **1d**, which has a trimethylsilyl substituent on the *para*-position of a phenyl ring, was insoluble in any organic solvents. The *meta*-counterpart **2e** did not polymerize under the same conditions, which should be due to steric hindrance. Thus, the monomer structure significantly affects polymerization behavior and polymer solubility.

3.2. Fabrication and desilylation of polymer membranes

Free-standing membranes could be fabricated by casting polymers **2a**–**c** from their toluene solution, whereas the membrane of **2d** could not be prepared due to its insolubility. The formed membranes were sufficiently tough and transparent. The membranes from **2f**–**g** were also fabricated to prepare their desilylated membranes. The desilylation reaction of polymer membranes **2a**, **2b**, and **2f**–**h** was carried out in a trifluoroacetic acid/H_2O mixture (9:1 volume ratio) at room temperature for 24 h. The completion of desilylation of **2b**, **2f** and **2h** was confirmed by the IR spectra and TGA curves of the polymers. Fig. 1 shows the IR spectra of membranes **2b** and **3b**. The absorption peaks at 1250, 1120, and 860 cm^{-1} indicating the presence of the trimethylsilyl groups in **2b** disappeared in **3b**. Just the same changes were observed in the cases of **2f**, **2h**, **3f**, and **3h**. Because of overlapping of the absorption peaks between t-butyl and trimethylsilyl groups, the complete removal of trimethylsilyl groups could not be confirmed by IR spectroscopy in the case of **3a**, for which TGA was used to confirm the practically complete desilylation (Fig. 2). In the cases of **3a**, **3b**, **3f**, and **3h**, no SiO_2 residue was detected when the polymers were heated above 700 °C, which confirms that the desilylation reactions proceeded quantitatively. On the other hand, desilylation of polymer **2g** did not reach completion under the same reaction conditions; the result of TGA indicates that about 85% of the silyl groups of **2g** were removed under the above-stated conditions.

Table 1
Polymerization of monomers **1a**–**e** by $TaCl_5$-n-Bu_4Sn catalyst[a].

Monomer	Solvent	Polymer[b]		
		Yield (%)	$M_w \times 10^{-3}$[c]	M_w/M_n[c]
1a	toluene	65	>6000	–
1b	toluene	78	>6000	–
1c	toluene	55	660	4.7
1c	cyclohexane	74	1000	5.3
1d	toluene	52	–[d]	–[d]
1e	toluene	0	–	–

[a] Polymerization at 80 °C for 24 h; $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM.
[b] Methanol-insoluble product.
[c] Determined by GPC eluted with $CHCl_3$ (polystyrenes as standards).
[d] Insoluble in any solvents.

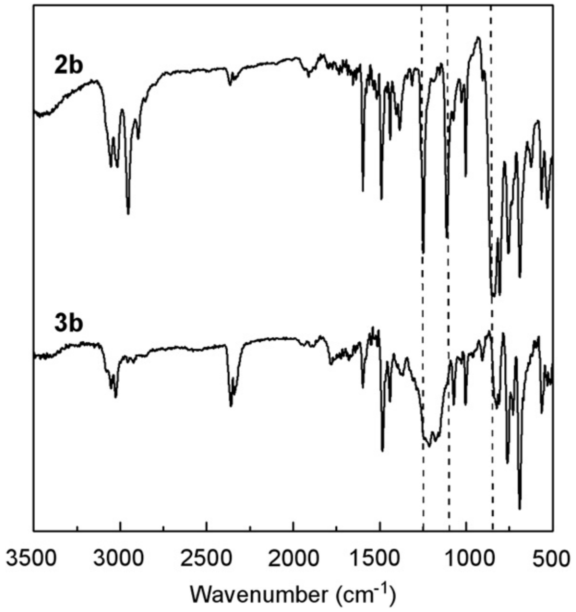


Fig. 1. IR spectra of polymer **2b** and its desilylated product **3b** (films).

3.3. Solubility and thermal stability of the polymers

The solubility of the formed polymers was examined for various solvents (Table 2). Si-containing polymers **2a–c** and **2f–h** are readily soluble in common organic solvents including toluene, $CHCl_3$, and THF. In contrast, polymer **2d** having two similar side groups in size are insoluble, which has also been observed with other polyacetylene derivatives [13]. Desilylated polymers **3a**, **3f**, and **3h** showed practically the same solubility as that of **2i** [28], **2j** [26], and **2k** [26] (Chart 1), respectively, which have the identical chemical structures and were obtained directly by the polymerization of the corresponding monomers. These results indicate that the desilylation reaction did not affect the solubility of the polymers. The thermal stability of polymers **2a–c**, **3a**, **3b**, and **3f–h** was examined by TGA in air (Fig. 2). Except **2c**, the onset temperatures of weight loss of the present polymers were above 400 °C, indicating excellent thermal stability.

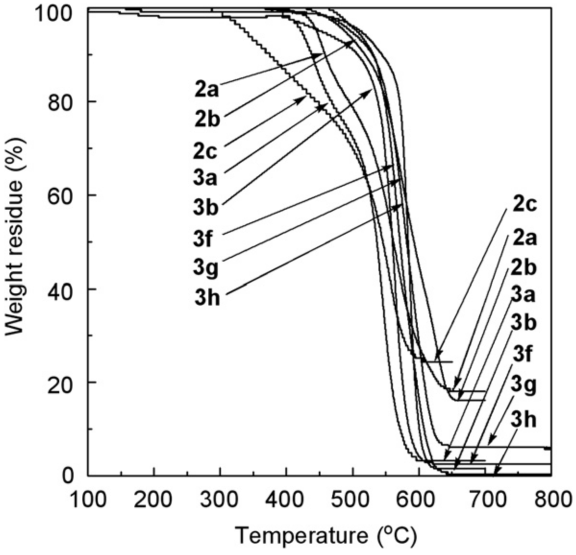


Fig. 2. TGA curves of the polymers (in air, heating rate 10 °C/min).

Table 2
Solubility of polymers[a].

	2a–c	**2d**	**2f**	**2g**	**2h**	**2i**	**2j**	**2k**	**3a**	**3b**	**3f**	**3g**	**3h**
Hexane	−	−	−	−	+	−	−	−	−	−	−	−	−
Cyclohexane	±	−	+	−	+	±	−	−	−	−	−	±	−
Toluene	+	−	+	+	+	+	+	+	+	−	+	+	+
$CHCl_3$	+	−	+	+	+	+	+	+	+	−	+	+	+
THF	+	−	+	+	+	+	+	+	+	−	+	+	+
Methanol	−	−	−	−	−	−	−	−	−	−	−	−	−
DMF	−	−	−	−	−	−	+	+	−	−	+	+	+
DMSO	−	−	−	−	−	−	−	−	−	−	−	−	−

[a] Symbols: +: soluble; ±: partly soluble; −: insoluble.

3.4. Gas permeation properties

The gas permeability of membranes **2a–c**, and desilylated membranes **3a**, **3b**, and **3f–h** to various gases was measured at 25 °C. As seen from Table 3, **2a** having both trimethylsilyl and *p-tert*-butylbiphenyl groups showed the oxygen permeability coefficients (PO_2) of 620 barrers, which is obviously lower than that of poly(TMSDPA) (1500 barrers). This result may be due to the presence of the planar biphenyl group which may stack with each other, leading to the decrease of microvoids. When spacers (phenyl and methylene for **2b** and **2c**, respectively) were inserted between the silicon atom and the phenyl ring of poly(TMSDPA), the gas permeability decreased. Thus, the PO_2 value of **2b** was 390 barrers which is about a quarter that of poly(TMSDPA), and polymer **2c** having trimethylsilylmethyl groups exhibited the lowest permeability among **2a–c** (PO_2 = 140 barrers). It is considered that incorporation of flexible or planar spacers reduces the stiffness of polymer chain, resulting in the decrease of microvoids, and in turn, gas permeability. Similar results have been reported in previous studies; namely, the introduction of flexible groups in polymer results in a decrease of gas permeability; e.g., the PO_2 value of poly[1-(4-methylphenyl)-2-(4-*tert*-butyldimethylsiloxylphenyl)acetylene] is 230 barrers, while that of poly[1-(4-ethylphenyl)-2-(4-*tert*-butyldimethylsiloxylphenyl)acetylene] is 140 barrers [29].

The desilylation reaction affected the gas permeability of the polymers in different ways when they have different substituents. For example, the PO_2 values of the desilylated membranes **3a** and **3b** having biphenyl groups were 260 and 180 barrers, respectively, which are lower than their Si-containing precursors **2a** and **2b**. On the other hand, the gas permeability of the fluorenyl-containing polymers increased to 1.5–2 times after desilylation. Thus, the PO_2

Table 3
Gas permeability coefficients (P) of polymer membranes.

Polymer	P (barrer[a])						PO_2/PN_2
	He	H_2	O_2	N_2	CO_2	CH_4	
2a	560	1200	620	250	3300	730	2.5
2b	370	810	390	160	2200	450	2.4
2c	240	420	140	44	640	120	3.2
2f[b]	840	1900	1000	540	4100	1500	1.9
2g[b]	480	980	440	190	1900	500	2.3
2h[b]	3400	8500	5400	3400	18000	10000	1.6
3a	260	580	260	95	1600	260	2.7
3b	200	440	180	65	1300	170	2.8
3f	1100	2500	1300	870	4900	2300	1.5
3g	890	2000	830	420	3400	940	2.0
3h	8800	19000	9800	8100	24000	19000	1.2
2i[c]	170	330	130	46	840	120	2.8
2j[b]	600	1400	660	300	3200	810	2.2
2k[b]	3200	8100	4800	3300	17000	9100	1.5

[a] At 25 °C in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (=1 barrer).
[b] Data from Ref. [26].
[c] Data from Ref. [28].

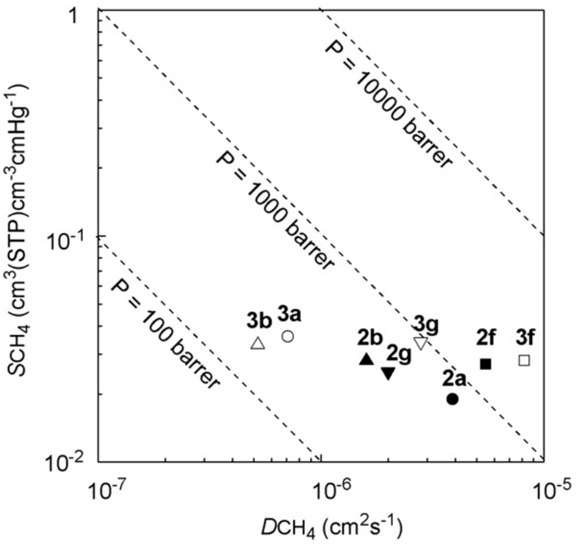


Fig. 3. Plot of diffusion coefficient (*D*) vs solubility coefficient (*S*) of the polymers before and after desilylation in methane permeation.

values of **3f** and **3g** were 1300 and 830 barrers, respectively, and higher than those of **2f** and **2g** (1000 and 400 barrers). It is quite interesting that membrane **3h** exhibited extremely high gas permeability; for instance, its PO_2 value was 9800 barrers, which is much higher than that of **2h** (5400 barrers) and is about the same as that of poly(TMSP) (~10,000 barrers). These results indicate or imply the following things: (i) the desilylation of diarylacetylene derivatives increases or decreases gas permeability depending on the chemical structure of the starting polymer, (ii) the variation of gas permeability upon desilylation in the solid state is considered to be mainly governed by the increase or decrease of microvoids and the decrease of local mobility, and (iii) the increase or decrease of microvoids should lead to the increase or decrease of excess free volume, and in turn, gas permeability, while the decrease of local mobility based on the loss of the silyl group will lead to the decrease of permeability [30,31].

The PO_2 values of desilylated membranes **3a**, **3f**, and **3h** were about twice those of **2i** [28], **2j** [26], and **2k** [26] (130 barrers, 660 barrers, and 4800 barrers, respectively; Table 3), which have the identical chemical structures and obtained by solution-casting method using the polymers synthesized directly by the polymerization of the corresponding monomers. In contrast, **3g** obtained by desilylation showed much lower gas permeability than **2k**, although they have the identical chemical structure to each other. Sakaguchi and coworker have reported that desilylation of the poly[1-*p*-*n*-alkylphenyl-2-(*p*-trimethylsilyl)phenylacetylene] membranes reduce gas permeability, while the desilylated polymers show gas permeability similar to that of the same polymers obtained by direct polymerization [32]. The following reasons are possible for the finding that desilylated polymers and the corresponding polymers obtained directly by polymerization show different gas permeability: (i) they may have different geometric and/or regio structures, (ii) the polymers desilylated in the solid state may have less relaxed structures, and so forth.

The permeability of the membranes to other gases such as He, H_2, N_2, CO_2, and CH_4 showed similar tendencies. The separation factors of oxygen against nitrogen (PO_2/PN_2) of the present polymers were in a range of 1.2–3.2. A tradeoff relationship is observed between permeability and permselectivity, namely, more permeable polymers are generally less permselective and vice versa [33].

The gas permeability coefficients (*P*) of the polymers before and after desilylation were inspected in more detail by separating them into the gas diffusion coefficients (*D*) and gas solubility coefficients (*S*). The calculation method was explained in the experimental section. Fig. 3 shows the plot of *D* and *S* values of the methane permeability of the present polymers. The time lag in the permeation of **3h** was too small to calculate the *D* value.

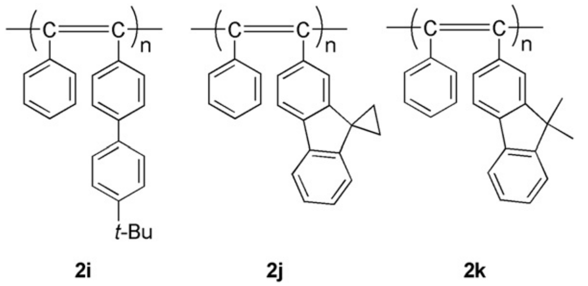


Chart 1. Poly(diarylacetylene)s having the identical chemical structures to those of desilylated polymers (**3a**, **3f**, and **3h**) and obtained directly by the polymerization of the corresponding monomers.

The SCH_4 values of the polymers hardly changed upon desilylation, while the DCH_4 values of the polymers with different substituents showed different tendencies. The gas diffusivity of polymer membranes should depend not only on the free volume of membrane but also on the local mobility of substituents. For instance, the DCH_4 significantly decreased in the biphenyl-containing membranes **3a** and **3b** by desilylation, which suggests the strong effect of the decrease of local mobility. On the other hand, the *D* values of **3f** and **3g** were larger than those of **2f** and **2g**, which is attributable to the formation of microvoids in **3f** and **3g** at the location where silyl groups were present in **2f** and **2g**. A more detailed study is underway.

4. Conclusion

In the present study, poly(diarylacetylene) derivatives having trimethylsilyl groups were synthesized by the polymerization of the corresponding monomers with $TaCl_5$-*n*-Bu_4Sn catalyst. Polymers **2a**–**c** had high molecular weights, and showed good solubility in common organic solvents and film-forming ability. Desilylation of trimethylsilyl-containing polymer membranes **2a** and **2b**, along with previously reported **2f**–**h**, was achieved with trifluoroacetic acid to give membranes **3a**, **3b**, and **3f**–**h**. Biphenyl-containing membranes **3a**, **3b** showed decreases in gas permeability upon desilylation, whereas fluorene-bearing counterparts **3f**–**h** exhibited increases in gas permeability. These desilylated membranes showed different gas permeability from that of membranes prepared by solution-casting of the polymers having the identical chemical structures and obtained directly by the polymerization of the corresponding monomers.

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