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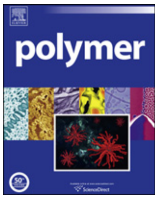

Synthesis of novel poly(diphenylacetylene)s with both trimethylsilyl and alkyl groups: The effect of desilylation on gas permeability

Aiko Takeda, Toshikazu Sakaguchi*, Tamotsu Hashimoto

Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan

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ABSTRACT

Diphenylacetylenes having both a trimethylsilyl group and an alkyl group at *para* positions [$Me_3SiC_6H_4C{\equiv}CC_6H_4R$; R = Et (**1a**), *n*-Bu (**1b**), *t*-Bu (**1c**), *n*-C_8H_{17} (**1d**)] and having only an alkyl group [$PhC{\equiv}CC_6H_4R$; R = *n*-Bu (**1B**), *n*-C_8H_{17} (**1D**)] were synthesized and then polymerized with $TaCl_5$/*n*-Bu_4Sn catalyst to provide the corresponding poly(diphenylacetylene)s (**2a**, **2b**, **2c**, **2d**, **2B**, and **2D**). The formed polymers except **2c** afforded tough free-standing membranes by casting from toluene solutions. Desilylation reaction of the Si-containing polymer membranes (**2a**, **2b**, **2d**) was carried out with trifluoroacetic acid, and the desilylated polymer membranes (**3a**, **3b**, **3d**) were obtained. The permeability to O_2, N_2, and CO_2 were determined for the obtained polymer membranes. All the desilylated membranes showed lower gas permeability than the Si-containing counterparts. To clarify the effects of the desilylation further, CO_2 diffusivity, CO_2 solubility, and fractional free volume (FFV) of the polymer membranes were investigated. The FFV and CO_2 diffusivity decreased upon desilylation, while CO_2 solubility hardly varied.

1. Introduction

A variety of poly(substituted acetylene)s with bulky spherical substituents along with stiff main chain composed of alternating double bond show extremely high gas permeability [1]. Poly(1-trimethylsilyl-1-propyne), for example, is the most gas-permeable polymer among all the known polymers [2]. Therefore, poly(substituted acetylene)s are promising materials for gas separation membranes. Various poly(substituted acetylene)s have been synthesized so far, and the gas permeability of their membranes has been investigated [1,3]. Poly(diphenylacetylene) is obtained in high yield by the polymerization of diphenylacetylene with $TaCl_5$/*n*-Bu_4Sn catalyst [4]. It is thermally very stable, and insoluble in any solvents. Therefore, its membrane cannot be prepared by solution-casting. On the other hand, the polymerization of 1-(*p*-trimethylsily)phenyl-2-phenylacetylene provides a soluble polymer in common organic solvents, and the tough free-standing membrane can be fabricated by solution-casting [5,6]. Teraguchi et al. successfully obtained a solvent-insoluble poly(diphenylacetylene) membrane through an indirect route, namely desilylation of poly[1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene] membrane [7]. Since then, insoluble membranes of poly(substituted acetylene)s have been synthesized by the desilylation method [8–12]. In such a desilylation reaction, it has been predicted that the spaces occupied by silyl groups are maintained in some level as microvoids because the mobility of polymer chain is restrained in a solid state. However, the details about the effect of desilylation in a solid state upon gas permeability have not been known yet.

In this study, the desilylation of membranes of poly(diphenylacetylene)s having both trimethylsilyl and various alkyl groups at *para* position of phenyl groups was performed, and the effect of desilylation on gas permeability was investigated in detail. The desilylation of the previous Si-containing poly(substituted acetylene)s gave insoluble polymers, while the desilylated polymers in this research are soluble in common solvents. Therefore, the polymer membranes with the same chemical structure could be prepared by three different routes (Scheme 1). First is the desilylation of Si-containing membranes, and second is solvent-casting method using the desilylated polymers. Final route is solvent-casting method using polymers synthesized directly by the polymerization of monomers without silyl group. The comparison of the permeability between such three types of membranes can reveal the effect of desilylation of the membrane on gas permeability. The membranes prepared by desilylation in a solid state exhibited the same or low permeability compared with the other two types of membranes without silyl group. The result indicates that the microvoids were not generated by desilylation of the membranes.

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* Corresponding author. Tel.: +81 776 27 9779; fax: +81 776 27 8767.
E-mail address: sakaguchi@matse.u-fukui.ac.jp (T. Sakaguchi).

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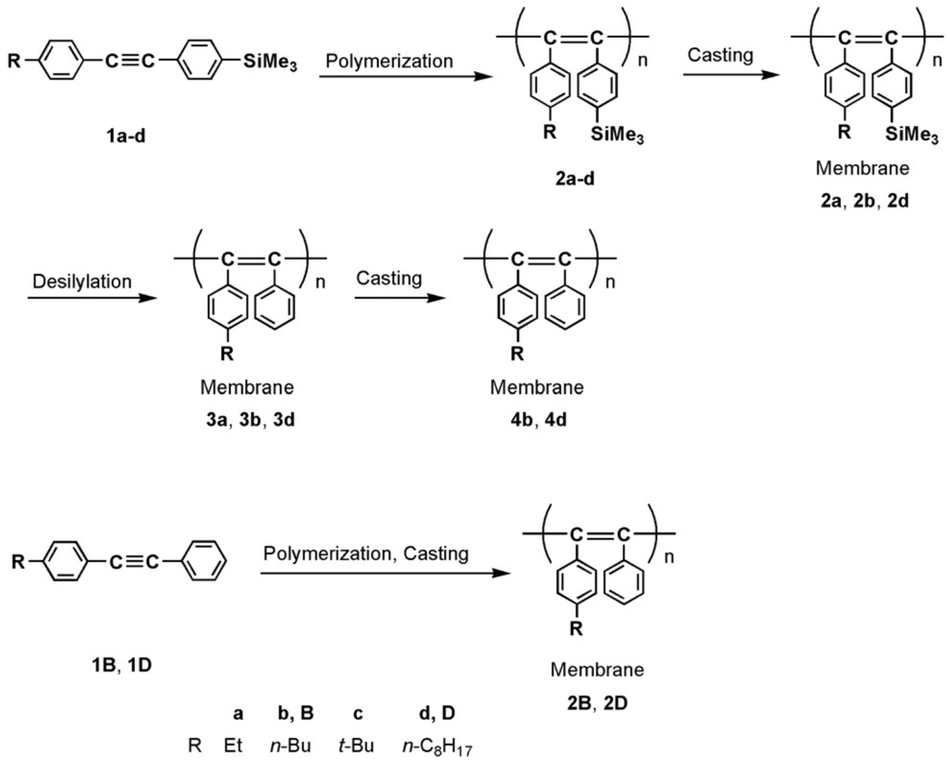


Scheme 1. Synthesis of polymers and preparation of polymer membranes.

2. Experimental

2.1. Measurements

The molecular weights and polydispersity ratios of polymers were estimated by gel permeation chromatography (tetrahydrofuran (THF) as eluent, polystyrene calibration) at 40 °C on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex KF-802.5 × 1 and A-80 M × 2) and a Shimadzu RID-6A refractive index detector. IR spectra were recorded on a Nicolet MAGNA 560 spectrometer. NMR spectra were obtained on a Jeol LA-500 spectrometer. Elemental analyses of monomers were performed at the Microanalytical Center of Kyoto University. A membrane thickness was measured using a micrometer, and it was estimated as an average amount of ten points on each membrane.

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C under 1 atm upstream pressure. The permeability coefficient P expressed in barrer unit (1 barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}) was calculated from the slope of the steady-state line. The D value was determined by the time lag method using the following equation:

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

here, l is the membrane thickness and θ is the time lag, which is given by the intercept of the asymptotic line of time-pressure curve to the time axis. The S value was calculated by using equation $S = P/D$.

2.2. Materials

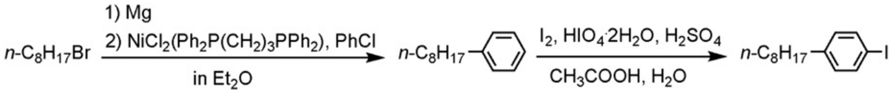
Toluene and cyclohexane as polymerization solvents were purified by distillation over calcium hydride. $TaCl_5$ as main catalyst was used without further purification, while n-Bu_4Sn as cocatalyst was purified by distillation. *p*-Ethyliodobenzene, *p*-*n*-butyliodobenzene, *p*-*t*-butyliodobenzene, 1-bromooctane, chlorobenzene, phenylacetylene, and common organic solvents were commercially obtained and used without further purification. *p*-Trimethylsilylphenylacetylene [13], 1-(*p*-*n*-butylphenyl)-2-phenyl-acetylene [14], and 1-(*p*-*n*-octylphenyl)-2-phenylacetylene [14] were synthesized according to the literatures. *p*-*n*-Octyliodobenzene was prepared as shown in Scheme 2, and the detailed procedure is as follows.

2.2.1. *p-n-Octyliodobenzene*

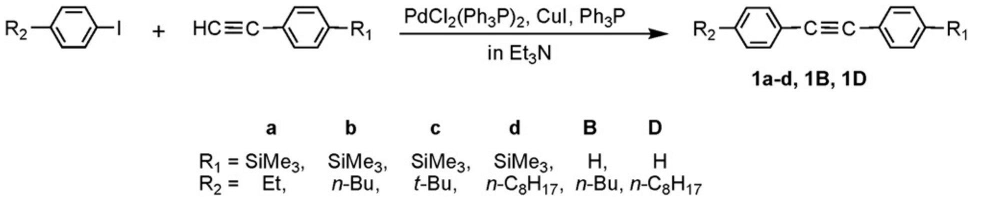
To prepare this reagent, two steps reaction were operated.

Step 1: 1-Bromooctane (70 g, 0.36 mol) was added dropwise to a mixture of magnesium (8.8 g, 0.36 mol) and ether (150 mL) at 0 °C, and the mixture was stirred overnight at room temperature. [1,3-Bis(diphenylphosphino)propane]dichloronickel (II) (0.49 g, 0.91 mmol) and chlorobenzene (41 g, 0.36 mol) were added dropwise at 0 °C, and the reaction mixture was heated at 40 °C for 4 h. Purification of the crude product by distillation provided *n*-octylbenzene (47 g, including hexadecane as by-product) as colorless liquid.

Step 2: A mixture of *n*-octylbenzene (7.1 g), iodide (3.0 g, 0.012 mol), orthoperiodic acid (1.4 g, 0.0062 mol), acetic acid (100 mL), water (20 mL), and sulfuric acid (3 mL) was stirred at 70 °C for 15 h. The reaction mixture was extracted with ether, and



Scheme 2. Synthesis of *p*-*n*-octyliodebenzene.



Scheme 3. Synthesis of monomers.

the organic solution was washed with aqueous sodium thiosulfate. The crude product was purified by silica gel column chromatography (eluent: hexane) to give the desired product (3.9 g, including hexadecane) as colorless liquid.

2.3. *Monomer synthesis*

Monomers were synthesized according to Scheme 3 with reference to the literature [9]. The synthesis procedures and analytical data of monomers are as follows.

2.3.1. *1-(p-Ethylphenyl)-2-(p-trimethylsilylphenyl)acetylene (**1a**)*

A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. Dichlorobis(triphenylphosphine) palladium (II) (0.029 g, 0.042 mmol), cuprous iodide (0.048 g, 0.25 mmol), and triphenylphosphine (0.044 g, 0.16 mmol) were placed in the flask. After the flask was flushed with nitrogen, *p*-ethyliodobenzene (4.9 g, 0.021 mol) and triethylamine (200 mL) were added, and then a solution of *p*-trimethylsilylphenylacetylene (3.7 g, 0.021 mol) in triethylamine (50 mL) was applied. The mixture was stirred for 2 h at room temperature. After the triethylamine was evaporated, ether (ca. 200 mL) was added, and the insoluble salt was filtered off. The solution was washed with HCl aq. (1.0 M) three times. The ethereal solution was dried over anhydrous sodium sulfate. After filtration, ether was evaporated, and the crude product was purified by silica gel column chromatography (eluent: hexane) to give the desired product (4.3 g, 74%) as white solid. ^{1}H NMR ($CDCl_3$, ppm): 7.51 (brs, 4H, Ar), 7.47 (d, $J = 8.3$ Hz, 2H, Ar), 7.19 (d, $J = 8.5$ Hz, 2H, Ar), 2.67 (q, $J = 7.6$ Hz, 2H, CH_2), 1.26 (t, $J = 7.6$ Hz, 3H, CH_2CH_3), 0.29 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 144.7, 140.7, 133.2, 131.6, 130.6, 127.9, 123.7, 120.4, 89.9, 88.9, 28.8, 15.4, −1.2. Anal. Calcd for $C_{19}H_{22}Si$: C, 82.0; H, 8.0; Si, 10.1. Found: C, 81.7; H, 8.1.

2.3.2. *1-(p-n-Butylphenyl)-2-(p-trimethylsilylphenyl) acetylene (**1b**)*

This monomer was prepared by the same method as for **1a** using *p*-*n*-butyliodobenzene instead of *p*-ethyliodobenzene. Yield 72%, colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.49 (brs, 4H, Ar), 7.45 (d, $J = 8.2$ Hz, 2H, Ar), 7.16 (d, $J = 8.3$ Hz, 2H, Ar), 2.62 (t, $J = 7.8$ Hz, 2H, $ArCH_2$), 1.60 (quint, $J = 7.7$ Hz, 2H, $ArCH_2CH_2$), 1.35 (sext, $J = 7.5$ Hz, 2H, $ArCH_2CH_2CH_2$), 0.93 (t, $J = 7.4$ Hz, 3H, $ArCH_2CH_2CH_2CH_3$), 0.27 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 143.4, 140.7, 133.2, 131.5, 130.6, 128.4, 123.7, 120.4, 89.9, 88.9, 35.4, 33.4, 22.3, 13.9, −1.2. Anal. Calcd for $C_{21}H_{26}Si$: C, 82.3; H, 8.6; Si, 9.2. Found: C, 82.4; H, 8.7.

2.3.3. *1-(p-t-Butylphenyl)-2-(p-trimethylsilylphenyl)acetylene (**1c**)*

This monomer was prepared by the same reaction as for **1a** using *p*-*t*-butyliodobenzene instead of *p*-ethyliodobenzene. Yield 93%, white solid. ^{1}H NMR ($CDCl_3$, ppm): 7.50 (brs, 4H, Ar), 7.47 (d, $J = 8.4$ Hz, 2H, Ar), 7.37 (d, $J = 8.6$ Hz, 2H, Ar), 1.33 (s, 9H, CCH_3), 0.28 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 151.5, 140.8, 133.2, 131.4, 130.6, 125.3, 123.8, 120.3, 89.9, 88.9, 34.8, 31.2, −1.2. Anal. Calcd for $C_{21}H_{26}Si$: C, 82.3; H, 8.6; Si, 9.2. Found: C, 81.5; H, 8.5.

2.3.4. *1-(p-n-Octylphenyl)-2-(p-trimethylsilylphenyl)acetylene (**1d**)*

This monomer was prepared by the same method as for **1a** using *p*-*n*-octyliodobenzene instead of *p*-ethyliodobenzene. Yield 79%, colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): 7.50 (brs, 4H, Ar), 7.46 (d, $J = 8.2$ Hz, 2H, Ar), 7.17 (d, $J = 8.2$ Hz, 2H, Ar), 2.62 (t, $J = 7.7$ Hz, 2H, $ArCH_2$), 1.62 (quint, $J = 7.7$ Hz, 2H, $ArCH_2CH_2$), 1.30 (m, 10H, $ArCH_2CH_2(CH_2)_5$), 0.89 (t, $J = 7.0$ Hz, 3H, $ArCH_2CH_2(CH_2)_5CH_3$), 0.29 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 143.4, 140.7, 133.2, 131.5, 130.6, 128.4, 123.8, 120.4, 90.0, 88.9, 35.9, 31.9, 31.2, 29.4, 29.3, 22.7, 14.1, −1.2. Anal. Calcd for $C_{25}H_{34}Si$: C, 82.8; H, 9.5; Si, 7.8. Found: C, 82.9; H, 9.6.

2.4. *Polymerization*

Polymerization was carried out in a glass tube equipped with a three-way stopcock under dry nitrogen. Unless otherwise specified, the reaction was carried out at 80 °C for 24 h under the following conditions: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, and $[n\text{-}Bu_4Sn] = 40$ mM. A detailed procedure of polymerization is as follows: The monomer solution was prepared in a glass tube. Another glass tube was charged with $TaCl_5$, n-Bu_4Sn, and toluene; this catalyst solution was aged at 80 °C for 10 min, and then monomer solution was added to it. Polymerization was run at 80 °C for 24 h, which was quenched with a small amount of methanol. The resulting polymer was isolated by precipitation into a large excess of methanol, and its yield was determined gravimetrically.

2.5. *Membrane fabrication and desilylation*

Membranes (thickness ca. 20–100 μm) of polymers (**2a**, **2b**, **2d**, **2B**, and **2D**) were fabricated by casting their toluene solutions (conc. 0.30–0.80 wt%) into Petri dishes. The dish was covered with a glass vessel to slow solvent evaporation (3–5 days). After a membrane was formed, the membrane was peeled off, and it was further dried at 25 °C for 24 h. Then, it was immersed in methanol for 24 h and dried to constant weight at room temperature. The desilylation of membranes of **2a**, **2b**, and **2d** was carried out using trifluoroacetic acid [7]. A detailed procedure is as follows: The polymer membranes of **2a** and **2b** were immersed in trifluoroacetic acid at room temperature for 24 h. To remove residual impurities in the polymer matrix, the membrane was immersed in acetone followed by methanol at room temperature for 24 h. It was dried at room temperature under atmospheric pressure for 24 h. The desilylation of membrane of **2d** was carried out by the same method using a mixture of trifluoroacetic acid/hexane (9/1 volume ratio). The completion of desilylation was confirmed by the comparison between IR spectra of the polymer membranes before and after the reaction.

2.6. *Fractional free volume (FFV) of polymer membranes*

The densities of membranes were determined by hydrostatic weighing using a Mettler Toledo balance and a density determination kit. In this method, a liquid with known density (ρ_0) is needed, and the membrane density (ρ) is given by the following equation:

$$\rho = \rho_0 \times M_A/(M_A - M_L)$$

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. An aqueous sodium nitrate was used as the auxiliary liquid. FFV is calculated by the following equation:

$$\mathrm{FFV} = (v_{sp} - v_0)/v_{sp} \approx (v_{sp} - 1.3v_w)/v_{sp}$$

where v_{sp} is the polymer specific volume, and v_0 is the occupied volume of the polymer. The occupied volume is typically estimated as 1.3 times the van der Waals volume (v_w), which is calculated using the group contribution method [15].

3. Results and discussion

3.1. Polymerization

The polymerizations of monomers having both a trimethylsilyl group and an alkyl group (**1a–d**) were carried out by using $TaCl_5$/*n*-Bu_4Sn catalyst in toluene or cyclohexane at 80 °C. The polymerizations of monomers without trimethylsilyl group (**1B** and **1D**) were also performed with $TaCl_5$/*n*-Bu_4Sn in toluene. Table 1 summarizes the results.

The polymerization of the ethyl group-containing monomer **1a** produced a polymer **2a** with high molecular weight in good yield (M_w 2.53×10^6, yield 75%) (Run 1). Such a high molecular weight is essential for fabrication of free-standing polymer membranes. Monomers **1b** and **1c** (having a *n*-butyl and a *t*-butyl group, respectively) also polymerized under the same conditions to give polymers **2b** and **2c** as methanol-insoluble products (Runs 2 and 3). Their molecular weights could not be measured by GPC, because polymer **2b** was insoluble in THF and chloroform (eluents for GPC), and polymer **2c** was insoluble in any solvents. The polymerization of the *n*-octyl group-containing monomer **1d** under the same conditions gave a polymer **2d** (Run 4), whose molecular weight was considerably lower than that of **2a**. The relatively low molecular weight of **2d** would be caused by steric hindrance of two large substituents (*n*-C_8H_{17} and $SiMe_3$) of the monomer **1d**. A free-standing membrane of **2d** suitable for the permeability measurement could not be prepared. When cyclohexane was used as a polymerization solvent, the molecular weight of **2d** slightly increased to 0.709×10^6 (Run 5). However, it was still low, so that a free-standing membrane of **2d** was brittle. The polymer **2d** isolated by precipitation from acetone had higher molecular weight (Run 6), and formed a relatively tough free-standing membrane. This can be explained by the idea that the oligomers which were hardly soluble in methanol were removed through precipitation from acetone. Monomers **1B** and **1D** without a trimethylsilyl group were polymerized in the same way as **1a** to give polymers **2B** and **2D** with high molecular weights (M_w 3.60×10^{-6} and 0.933×10^{-6}, respectively) (Runs 7 and 8).

Table 1
Polymerizations of monomers.[a]

Run	Monomer	Solvent	Yield[b] [%]	$M_w \times 10^{-6}$ [c]	M_w/M_n[c]
1	**1a**	toluene	75	2.53	4.52
2	**1b**	toluene	78	Insoluble[d]	
3	**1c**	toluene	46	Insoluble[e]	
4	**1d**	toluene	51	0.651	5.28
5	**1d**	cyclohexane	58	0.709	6.46
6	**1d**	cyclohexane	42[f]	0.815	4.58
7	**1B**	toluene	78	3.60	4.65
8	**1D**	toluene	66	0.933	3.89

[a] At 80 °C for 24 h; $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, [*n*-Bu_4Sn] = 40 mM.
[b] Methanol-insoluble product.
[c] Measured by GPC.
[d] Insoluble in $CHCl_3$ and THF.
[e] Insoluble in any solvent.
[f] Acetone-insoluble product.

Table 2
Solubility of polymers.[a]

Solvent	2a	2b	2c	2d	2B	2D	3a	3b	3d
hexane	+	+	−	+	−	+	−	−	+
CCl_4	+	+	±	+	+	+	±	+	+
toluene	+	+	−	+	+	+	−	+	+
Et_2O	+	±	−	+	±	+	−	±	+
$CHCl_3$	+	±	−	+	+	+	±	+	+
THF	+	±	−	+	+	+	±	+	+
acetone	−	−	−	−	−	−	−	−	−
DMF	−	−	−	−	−	−	−	−	−
DMSO	−	−	−	−	−	−	−	−	−

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

3.2. Fabrication and desilylation of membranes

The solubility of the polymers is summarized in Table 2. Polymers **2a**, **2d**, and **2D** showed good solubility in relatively low polarity solvents including hexane, CCl_4, toluene, diethyl ether, chloroform, and THF. Polymer **2b**, which has both trimethylsilyl and *n*-butyl groups, completely dissolved in common solvents such as hexane, CCl_4, and toluene. It was partly soluble in diethyl ether, chloroform, THF. Polymer **2c** containing trimethylsilyl and *t*-butyl groups showed poor solubility, and it was partly soluble in CCl_4. Polymer **2B** having *n*-butyl group dissolved in CCl_4, toluene, chloroform, and THF, and it was partly soluble in diethyl ether. Polymer **2B** exhibited somewhat less solubility than **2D** which has longer alkyl side chain. All the present polymers were insoluble in polar solvents such as acetone, DMF, and DMSO.

Tough free-standing membranes could be fabricated by casting polymers **2a**, **2b**, **2d**, **2B**, and **2D** from their toluene solutions, whereas it was impossible to prepare a membrane of polymer **2c** by solution-casting because of its insolubility. The desilylation of membranes of **2a** and **2b** was carried out in trifluoroacetic acid at room temperature for 24 h to give desilylated membranes. Although the desilylation reaction of membrane of **2d** could not be achieved by the same method, it could be accomplished by using a trifluoroacetic acid/hexane (9/1 volume ratio) mixture. Since a hexane solvent swelled the membrane of **2d**, the desilylation reaction proceeded smoothly. The completion of desilylation was confirmed by IR spectra of the polymer membranes. Fig. 1 shows the IR spectra of membranes of **2b**, **3b**, and **2B**. The absorptions at 1250 cm^{-1} derived from stretching of SiC–H bonds and at 1120 cm^{-1} derived from vibration of Si–C completely disappeared in the spectrum of membrane of **3b**. The spectrum of **3b** agreed well with that of **2B** which was obtained directly by the polymerization of the monomer without a trimethylsilyl group. After desilylation, weights of the polymer membranes decreased to the values anticipated for desilylation, which also suggested the completion of the reaction. The solubility of the desilylated polymers was examined (Table 2). Desilylation of ethyl group-containing polymer **2a** produced practically insoluble polymer **3a** in any solvents. The desilylated polymer **3b** containing *n*-butyl groups dissolved in CCl_4, toluene, chloroform, and THF, and it was insoluble in hexane. Polymer **3d** having *n*-octyl groups exhibited the similar solubility to the Si-containing polymer **2d**. Desilylated polymers **3b** and **3d** have the identical chemical structures to **2B** and **2D**, respectively, which have been obtained directly by the polymerizations of the

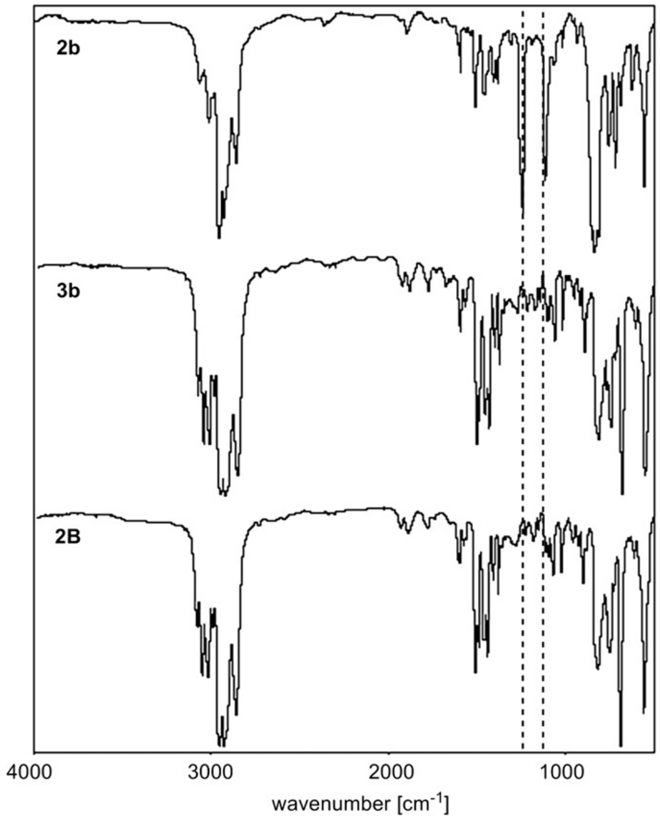


Fig. 1. IR spectra of membranes before and after desilylation (**2b**, **3b**, and **2B**).

corresponding monomers **1B** and **1D**. The difference of preparation method, desilylation and polymerization, did not affect the solubility of the polymers. It is the first example that the solvent-soluble desilylated polymer was obtained. Thus, the molecular weight of the desilylated polymer can be measured. The M_w and M_w/M_n of the desilylated polymer **3d** are 719,000 and 4.89, respectively. These values are almost the same as those of polymer **2d**, which indicates that the polymer main chain was not decomposed by the desilylation reaction.

3.3. *Gas permeability*

The permeability of Si-containing polymer membranes (**2a**, **2b**, **2d**) and desilylated membranes (**3a**, **3b**, **3d**) to various gases was examined at 25 °C (Table 3). Oxygen permeability coefficients ($P(O_2)$) of **2a**, **2b**, and **2d** were 430, 200, and 31 barrers, respectively. The polymer membrane having longer alkyl chains showed lower oxygen permeability. With regard to nitrogen and carbon dioxide, the same tendency was observed; i.e., the membrane of **2a** was the most permeable among the Si-containing polymers. The membrane densities of **2a**, **2b**, and **2d** were 0.918, 0.957, and 0.966 g/cm^3, respectively. The membrane density increased with increase in length of the alkyl substituent on the side chain. The FFV of the polymer membranes was calculated from the membrane density, and it is one of important factors for their permeability. The FFV values of the membranes of **2a**, **2b**, and **2d** were 0.255, 0.212, and 0.185, respectively. It was found that the FFV became smaller as the alkyl side chain became longer. Such a trend has been reported for different types of substituted acetylene polymers [16,17]. Spherical bulky substituents tend to generate free volume due to its steric repulsion, and stiff main chain such as polyacetylenes maintains free volume in some level [1]. Consequently, polyacetylenes with spherical bulky substituents exhibit high gas permeability. However, long alkyl groups seem to occupy the free volume generated by spherical bulky groups such as a trimethylsilyl group because of the flexibility of long alkyl chain.

The $P(O_2)$ of the desilylated membrane of **3a** was 46 barrers, which was smaller than that of the Si-containing membrane of **2a**. The gas permeability coefficients of the desilylated polymer membranes of **3b** and **3d** were also smaller than those of the Si-containing counterparts. Decrease of gas permeability through desilylation was due to the elimination of spherical bulky silyl groups. The FFV of the desilylated membranes, in fact, showed small values compared to the corresponding Si-containing membranes. Desilylation of the polymer membrane having octyl groups (**2d**) led to significant decline in FFV. As the length of alkyl group becomes shorter, an extent of decline in FFV through desilylation became smaller. This fact indicates that the effect of linear alkyl group on polymer chain packing was more conspicuous in desilylated membranes rather than Si-containing membranes. The decrease in FFV of membrane having long alkyl groups through desilylation affects gas permeability less effectively. This is because the flexibility of long alkyl chain supports the diffusion of gas molecules in polymer matrix.

3.4. *CO_2 diffusivity and solubility*

The CO_2 diffusion coefficients ($D(CO_2)$) and CO_2 solubility coefficients ($S(CO_2)$) were measured by time lag method (Table 3). Unfortunately, the time lags on oxygen and nitrogen permeability measurement were so small that $D(O_2)$ and $D(N_2)$ could not be calculated. In the Si-containing membranes, the CO_2 diffusivity decreased with increasing alkyl length. After desilylation, the CO_2 diffusivity decreased in every polymer. The *D* value of the desilylated membrane of **3a** was, for instance, much smaller than those of **2a**, **2b**, and **2d**, although the FFV of **3a** was even larger than those of **2b** and **2d**. The high *D* values of **2a**, **2b**, and **2d**, therefore, can be accounted for by the large local mobility of the trimethylsilyl groups [18,19], because gas diffusivity of polymer membranes was mainly determined by not only free volume of membrane but also local mobility of substituents. In the case of the desilylated membranes (**3a**, **3b**, and **3d**), the membrane having longer alkyl

Table 3
Gas permeability coefficients (*P*),[a] CO_2 diffusivity (*D*),[b] CO_2 solubility (*S*),[c] density, and FFV of Si-containing and desilylated polymers.

	2							**3**						
	$P(O_2)$ [barrer]	$P(N_2)$ [barrer]	$P(CO_2)$ [barrer]	$D(CO_2)\times10^8$	$S(CO_2)\times10^3$	Density [g/cm^3]	FFV	$P(O_2)$ [barrer]	$P(N_2)$ [barrer]	$P(CO_2)$ [barrer]	$D(CO_2)\times10^8$	$S(CO_2)\times10^3$	Density [g/cm^3]	FFV
a	430	180	1900	650	28	0.918	0.255	46	11	240	61	40	1.00	0.226
b	200	84	1000	560	18	0.957	0.212	38	11	190	94	20	1.05	0.172
d	31	9.0	130	230	5.8	0.966	0.185	11	3.2	50	98	5.1	1.05	0.136

[a] Measured at 25 °C. 1 barrer = 1×10^{-10} cm^3(STP) cm/(cm^2 s cmHg).
[b] Measured by the 'time lag' method. In the units of cm^2/s.
[c] Calculated from the equation '$S = P/D$. In the units of cm^3(STP)/(cm^3 cmHg).

Table 4
Comparison of membrane properties between polymers without Si-group.

	$P(O_2)$[a]	$P(O_2)/P(N_2)$	$D(CO_2)$[b] $\times 10^8$	$S(CO_2)$[c] $\times 10^3$	FFV
3b	38	3.4	94	20	0.172
4b	35	3.5	110	15	0.187
2B	89	3.0	198	22	0.202
3d	11	3.4	98	5.1	0.136
4d	10	3.6	83	5.3	0.144
2D	8.9	3.4	55	7.7	0.161

[a] Measured at 25 °C. In the unit of barrer.
[b] Measured by the 'time lag' method. In the units of cm^2/s.
[c] Calculated from the equation '$S = P/D$'. In the units of $cm^3(STP)/(cm^3\ cmHg)$.

groups exhibited lower FFV, while these membranes had nearly the same CO_2 diffusivity. This can be also explained by the large local mobility of long alkyl groups.

In both the Si-containing and desilylated membranes, the CO_2 solubility became lower as the alkyl groups became longer. The CO_2 solubility of the desilylated membrane of **3a**, which has ethyl groups, was higher than that of the Si-containing membrane of **2a**. In the case of the membranes containing *n*-butyl and *n*-octyl groups, the desilylated membranes of **3b** and **3d** exhibited the similar solubility to the Si-containing counterparts.

3.5. *Comparison of three types of membranes*

Polymer membranes of **4b** and **4d** were fabricated by re-casting using toluene solutions of the desilylated polymers. The other kind of membranes without trimethylsilyl groups were fabricated from **2B** and **2D**, which were obtained directly by the polymerization of the corresponding monomers **1B** and **1D**. That is to say, the membranes of **3b**, **4b**, and **2B** have an identical chemical structure, but they were prepared by different methods. The O_2 permeability coefficients, permselectivity, CO_2 diffusivity, CO_2 solubility, and FFV of membranes without trimethylsilyl group (**3b**, **3d**, **4b**, **4d**, **2B**, and **2D**) are listed on Table 4. The $P(O_2)$ of membranes of **3b** and **4b** were 38 and 35 barrers, respectively, which were similar to each other. On $P(O_2)/P(N_2)$ and FFV, there were no obvious difference between **3b** and **4b**. Gas permeation properties of **3d** were also almost the same as those of **4d**. These results suggest that excess free volume was not generated by desilylation in a solid state. The $P(O_2)$ values of **2B** and **2D** were 89 and 8.9 barrers, respectively. The oxygen permeability of **2D** was similar to those of **3d** and **4d**, but the membrane of **2B** showed somewhat high oxygen permeability compared to **3b** and **4b**. The difference of permeability between **2B** and **4b** would be attributed to the difference of geometric structure of the polymer main chain. Generally, the metathesis polymerization of substituted acetylene produces the poly(acetylene) main chain composed of a mixture of cis-form and trans-form [20]. The geometric structure is mainly dependent on a monomer structure. Therefore, geometric structure of **2B** and **4b** should not be identical.

The CO_2 solubility coefficients ($S(CO_2)$) of **3b**, **4b**, and **2B** were 20, 15, and $22 \times 10^{-3}\ cm^3(STP)/(cm^3\ cmHg)$, respectively, which were almost the same. Membrane of **2B** exhibited roughly twice the diffusivity coefficient ($198 \times 10^{-8}\ cm^2/s$) compared to **3b** and **4b** (94 and $110 \times 10^{-8}\ cm^2/s$, respectively). Membrane of **4d** showed the similar diffusivity and solubility to **3d**. Membrane of **2D** had somewhat lower diffusivity and slightly higher solubility than those of **3d**.

4. Conclusion

Novel poly(diphenylacetylene)s having both trimethylsilyl and various alkyl groups were synthesized, and these free-standing membranes were fabricated by solution-casting. The desilylation of these membranes was carried out, and the solvent-soluble desilylated membranes were successfully obtained. The desilylation of membranes caused decreases in gas permeability and FFV. The gas diffusivity was also decreased upon desilylation due to the decrease of FFV and elimination of silyl groups. The desilylated membranes showed almost the same gas permeability as membranes prepares by re-casting of the desilylated polymers. This indicates that microvoid was not generated by the elimination of silyl groups even in a solid state on poly[1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene] with liner alkyl groups.

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