



# Novel poly(diphenylacetylene)s with both alkyl and silyl groups as gas permeable membranes: Synthesis, desilylation, and gas permeability

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## ABSTRACT

Diphenylacetylenes having a dimethyloctylsilyl group and an alkyl group at *para* positions [ $\text{Me}_2n\text{-C}_8\text{H}_{17}\text{SiC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{R}$ ;  $\text{R} = \text{H}$  (**1a**), *i*-Pr (**1b**), *t*-Bu (**1c**), *n*-Bu (**1d**)] and having only an alkyl group [ $\text{PhC}\equiv\text{CC}_6\text{H}_4\text{R}$ ;  $\text{R} = i\text{-Pr}$  (**1B**), *t*-Bu (**1C**)] were synthesized and then polymerized with  $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$  catalyst to provide the corresponding poly(diphenylacetylene)s (**2a**, **2b**, **2c**, **2d**, **2B**, and **2C**). The formed polymers afforded tough free-standing membranes by casting from toluene solutions. Desilylation reaction of Si-containing membranes (**2a–d**) was carried out with trifluoroacetic acid to give the desilylated membranes (**3a–d**). The permeability of these membranes to  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  were determined. All the Si-containing membranes exhibited almost the same gas permeability. The desilylation of Si-containing membranes of **2a–c** resulted in large increase of gas permeability. No apparent increasing of gas permeability was observed in the desilylation of **2d**. To clarify the effects of desilylation,  $\text{CO}_2$  diffusivity ( $D(\text{CO}_2)$ ),  $\text{CO}_2$  solubility ( $S(\text{CO}_2)$ ), and fractional free volume (FFV) of the polymer membranes were investigated. The  $S(\text{CO}_2)$  values of desilylated membranes were much larger than that of Si-containing counterparts. The  $D(\text{CO}_2)$  and FFV of membranes of **2a–c** increased through desilylation. The desilylated membrane of **3d** had small  $D(\text{CO}_2)$  value and almost the same FFV compared with **2d**. Further, the comparison of the permeability between three types of membranes with the same chemical structure revealed that the microvoids were not generated by the desilylation of membranes of poly(diphenylacetylene)s containing alkyl groups.

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## 1. Introduction

Polyacetylenes with bulky spherical substituents show extremely high gas permeability. This is because both their stiff main chain composed of alternating double bonds and the steric repulsion of the bulky substituents make membranes sparse [1]. Therefore, poly(substituted acetylene)s are promising materials for gas separation membranes. A variety of poly(substituted acetylene)s have been synthesized so far, and the gas permeability of their membranes has been investigated [1–3]. Since a polymer membrane is usually prepared by casting its solution, the membrane of a solvent-insoluble polymer is not prepared directly by solution-casting. However, several membranes of insoluble poly(substituted acetylene)s have been prepared by an indirect method, namely desilylation of solvent-soluble membrane containing silyl groups [4]. In the desilylation reaction of polymer membrane, 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 [4–9]. However, the details about the effect of desilylation in a solid state upon gas permeability have not been known yet.

In the previous paper [10], we investigated the desilylation of membranes of poly(diphenylacetylene)s containing both trimethylsilyl and linear alkyl groups, and reported that additional microvoids in their membranes were not generated through desilylation. Linear alkyl groups are flexible pendant chains, and thus they are unsuitable to maintain a microvoid. However, poly(diphenylacetylene)s having both trimethylsilyl and branched alkyl groups such as *t*-butyl groups were insoluble in any solvents, and their membranes could not be prepared. Therefore, the effect of the branched alkyl groups versus the linear alkyl groups remains unknown. In order to solve the problem of insolubility, dimethyloctylsilyl groups were introduced to poly(diphenylacetylene)s instead of trimethylsilyl groups. This enabled us to investigate the effect of desilylation on gas permeability of poly(diphenylacetylene)s having branched alkyl groups for the first time.

In this paper, the desilylation of membranes of poly(diphenylacetylene)s having dimethyloctylsilyl and various alkyl groups, which contain linear and branched alkyl groups, at *para* position of phenyl groups was performed. The effect of

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desilylation on gas permeability was investigated in detail. The desilylated polymers in this study dissolve in common solvents, and the polymer membranes with the same chemical structure could be prepared by three different routes (Scheme 1). First method 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 which were prepared by desilylation in a solid state exhibited the same or low permeability compared with the other two types of membranes without silyl group. This indicates that the microvoids were not generated by the desilylation of the 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-80M × 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.

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 ( $1 \text{ barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Hg}^{-1}$ ) was calculated from the slope of the steady-state line. The  $D$  value was determined by the time lag method using the following equation:

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

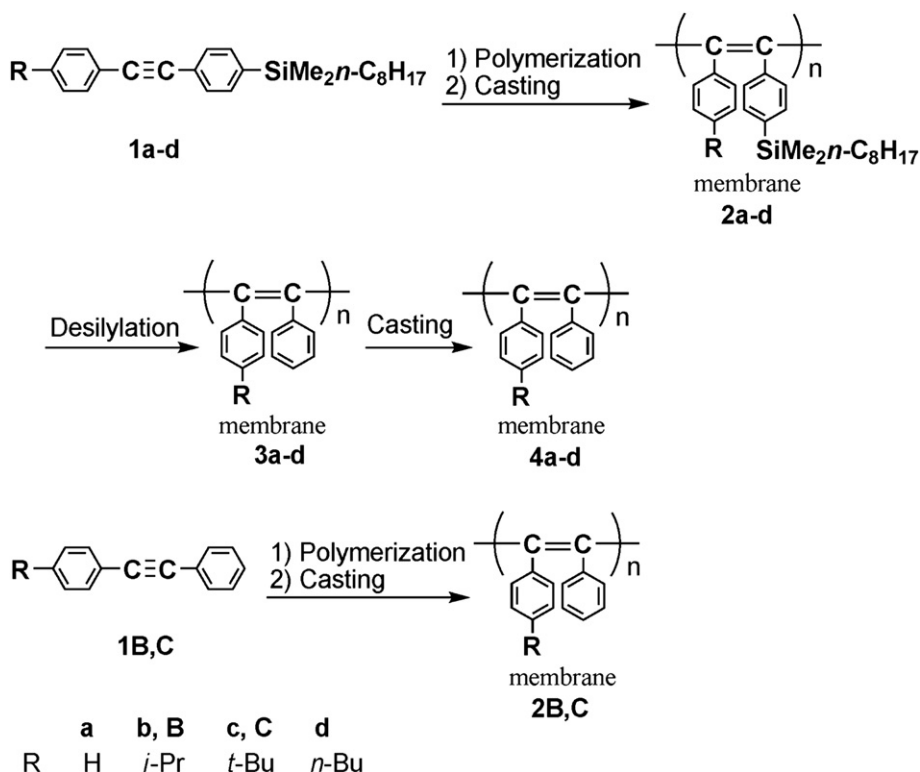
here,  $l$  is the membrane thickness and  $\theta$  is the time lag, which is given by the intercept of the asymptotic line of time-pressure curve to the time axis. The  $S$  value was calculated by using equation  $S = P/D$ .

### 2.2. Materials

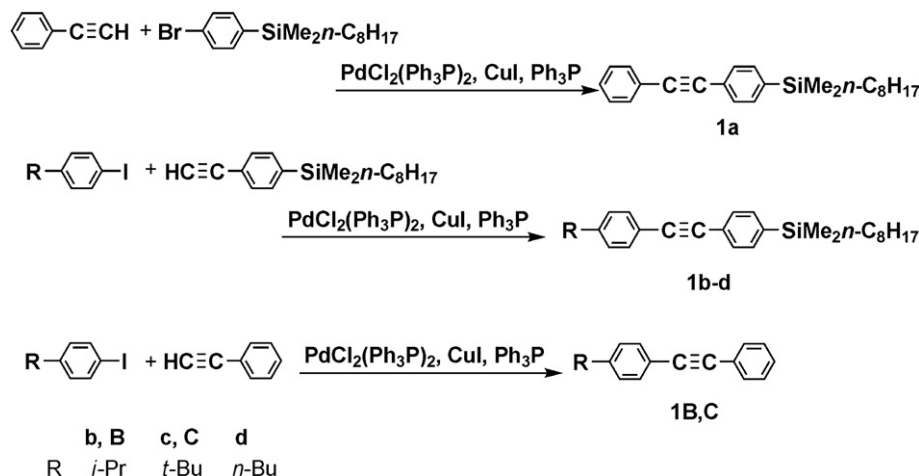
Toluene as polymerization solvent was purified by distillation over calcium hydride.  $\text{TaCl}_5$  as main catalyst was commercially supplied by Aldrich and used without further purification, while  $n\text{-Bu}_4\text{Sn}$  as cocatalyst was purified by distillation. Phenylacetylene,  $p$ -iodo- $i$ -propylbenzene,  $p$ - $t$ -butyliodobenzene,  $p$ - $n$ -butyliodobenzene and common organic solvents were commercially obtained and used without further purification.  $p$ -Dimethyloctylsilylphenylacetylene were synthesized referring to the literature [11]. 1-( $p$ -Dimethyloctylsilyl)phenyl-2-phenylacetylene (**1a**), 1-( $p$ - $i$ -propyl)phenyl-2-phenylacetylene (**1b**), and 1-( $p$ - $t$ -butyl)phenyl-2-phenylacetylene (**1c**) were synthesized according to the literatures [5,12]. Synthesis and properties of poly[1-( $p$ - $n$ -butyl)phenyl-2-phenylacetylene] (**2d**) have been reported in our previous paper [10], and the data of **2d** were used in this study to compared with **3d**.

### 2.3. Monomer synthesis

Monomers were synthesized according to Scheme 2 with reference to the literature [13]. The synthesis procedures and analytical data of monomers are as follows.



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



Scheme 2. Synthesis of monomers.

### 2.3.1. 1-(*p*-dimethyloctylsilyl)phenyl-2-(*p*-*i*-propyl)phenylacetylene (**1b**)

A 500 mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar. Dichlorobis(triphenylphosphine) palladium (0.030 g, 0.043 mmol), cuprous iodide (0.065 g, 0.34 mmol), and triphenylphosphine (0.052 g, 0.20 mmol) were placed in the flask. After the flask was flushed with nitrogen, *p*-iodoisopropylbenzene (5.0 g, 20 mmol) and triethylamine (200 mL) were added, and then a solution of *p*-dimethyloctylsilylphenylacetylene (5.5 g, 20 mmol) 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 (5.6 g, 71%) as colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.47 (m, 6H, Ar), 7.19 (d,  $J = 8.0$  Hz, 2H, Ar), 2.90 (sept,  $J = 6.9$  Hz, 1H, ArCH), 1.25 (m, 12H,  $\text{SiCH}_2(\text{CH}_2)_6$ ), 1.24 (d,  $J = 6.9$  Hz, 6H,  $\text{ArCH}(\text{CH}_3)_2$ ), 0.87 (t,  $J = 7.1$  Hz, 3H,  $\text{SiCH}_2(\text{CH}_2)_6\text{CH}_3$ ), 0.73 (t,  $J = 7.8$  Hz, 2H,  $\text{SiCH}_2$ ), 0.25 (s, 6H,  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 149.2, 140.1, 133.4, 131.6, 130.6, 126.4, 123.7, 120.6, 90.0, 88.9, 34.1, 33.6, 31.9, 29.3, 23.8, 23.8, 22.7, 15.6, 14.1,  $-3.1$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{38}\text{Si}$ : C, 83.0; H, 9.8; Si, 7.2. Found: C, 83.0; H, 9.9.

### 2.3.2. 1-(*p*-*t*-butyl)phenyl-2-(*p*-dimethyloctylsilyl)phenylacetylene (**1c**)

This monomer was prepared by the same method as for **1b** using *p*-*t*-butyliodobenzene instead of *p*-iodoisopropylbenzene. Yield 54%, colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.50 (m, 6H, Ar), 7.38 (d,  $J = 8.3$  Hz, 2H, Ar), 1.34 (s, 9H,  $\text{CCH}_3$ ), 1.33 (m, 12H,  $\text{SiCH}_2(\text{CH}_2)_6$ ), 0.90 (t,  $J = 6.7$  Hz, 3H,  $\text{SiCH}_2(\text{CH}_2)_6\text{CH}_3$ ), 0.76 (t,  $J = 7.8$  Hz, 2H,  $\text{SiCH}_2$ ), 0.27 (s, 6H,  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 151.5, 140.1, 133.4, 131.3, 130.6, 125.3, 123.7, 120.3, 89.9, 88.9, 34.8, 33.6, 31.9, 31.2, 29.2, 23.8, 22.7, 15.6, 14.1,  $-3.1$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{40}\text{Si}$ : C, 83.1; H, 10.0; Si, 6.9. Found: C, 82.9; H, 10.2.

### 2.3.3. 1-(*p*-*n*-butyl)phenyl-2-(*p*-dimethyloctylsilyl)phenylacetylene (**1d**)

This monomer was prepared by the same method as for **1b** using *p*-*n*-butyliodobenzene instead of *p*-iodoisopropylbenzene. Yield 79%, colorless liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.50 (m, 6H, Ar), 7.18 (d,  $J = 8.2$  Hz, 2H, Ar), 2.64 (t,  $J = 7.6$  Hz, 2H,  $\text{ArCH}_2$ ), 1.62 (quint,  $J = 7.7$  Hz, 2H,  $\text{ArCH}_2\text{CH}_2$ ), 1.38 (sext,  $J = 7.5$  Hz, 2H,  $\text{ArCH}_2\text{CH}_2\text{CH}_2$ ),

1.29 (m, 12H,  $\text{SiCH}_2(\text{CH}_2)_6$ ), 0.95 (t,  $J = 7.3$  Hz, 3H,  $\text{Ar}(\text{CH}_2)_3\text{CH}_3$ ), 0.90 (t,  $J = 6.8$  Hz,  $\text{SiCH}_2(\text{CH}_2)_6\text{CH}_3$ ), 0.76 (t,  $J = 7.9$  Hz, 2H,  $\text{SiCH}_2$ ), 0.28 (s, 6H,  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 143.3, 140.0, 133.4, 131.5, 130.5, 128.4, 123.7, 120.4, 89.9, 88.9, 35.6, 33.6, 33.4, 31.9, 29.3, 23.8, 22.7, 22.3, 15.6, 14.1, 14.0,  $-3.1$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{40}\text{Si}$ : C, 83.1; H, 10.0; Si, 6.9. Found: C, 82.9; H, 9.8.

## 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:  $[\text{M}]_0 = 0.20$  M,  $[\text{TaCl}_5] = 20$  mM, and  $[n\text{-Bu}_4\text{Sn}] = 80$  mM. A detailed procedure of polymerization is as follows: The monomer solution was prepared in a glass tube. Another glass tube was charged with  $\text{TaCl}_5$ ,  $n\text{-Bu}_4\text{Sn}$ , 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  $\mu\text{m}$ ) of polymers (**2a**, **2b**, **2c**, **2d**, **2B**, and **2C**) were fabricated by casting their toluene solutions (conc. 0.30–0.80 wt%) into Petri dishes at room temperature. 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 immersed in methanol for 24 h and dried to constant weight at room temperature. As shown in the literature, the desilylation of membranes of **2a–d** was carried out using trifluoroacetic acid [4]. A detailed procedure is as follows: The polymer membrane was immersed in trifluoroacetic acid at room temperature for 24 h. To remove residual impurities in polymer matrix, the membrane was immersed in acetone followed by methanol at room temperature for 24 h. The membrane was dried at room temperature under atmospheric pressure for 24 h. The completion of desilylation was confirmed by the comparison between IR spectra of 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 ( $\rho_0$ ) is needed, and the membrane density ( $\rho$ ) 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:

$$\text{FFV} = (\nu_{\text{sp}} - \nu_0) / \nu_{\text{sp}} \approx (\nu_{\text{sp}} - 1.3\nu_w) / \nu_{\text{sp}}$$

where  $\nu_{\text{sp}}$  is the polymer specific volume, and  $\nu_0$  is the occupied volume of the polymer. The occupied volume is typically estimated as 1.3 times the van der Waals volume ( $\nu_w$ ), which is calculated using the group contribution method [14].

### 3. Results and discussion

#### 3.1. Polymerization

The polymerizations of monomers (**1a–d** and **1B–D**) were carried out by using  $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$  catalyst in toluene at 80 °C. It is well known that  $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$  catalyst achieves good yields of disubstituted acetylene polymers with high molecular weights [15–17], which is essential for fabrication of tough free-standing membranes. The results of polymerizations are summarized in Table 1.

The polymerization of **1a** having dimethyloctylsilyl group produced a polymer **2a** with high molecular weight in good yield ( $M_w$   $2.68 \times 10^6$ , yield 84%) (Run 1). Monomer **1b** having both dimethyloctylsilyl and *i*-propyl groups polymerized under the same condition to give a polymer **2b** with pretty high molecular weight. The formed polymer **2b** contained insoluble parts in any solvents, and the  $M_w$  of THF-soluble product exceeded three million (Run 2). The high polymerizability of **1b** may be explained by the high electron density of triple bond. Monomer **1b** have both a silyl group and an alkyl groups at *para* position of benzene rings as electron-donating groups. When the initial monomer concentration was lowered to 0.10 M, the polymerization of **1b** gave a high molecular weight polymer **2b** totally soluble in common solvents (Run 3). Membrane preparation and properties of **2b** were examined using the sample obtained by the polymerization with the lower initial monomer concentration (Run 3). The polymerizations of **1c** and **1d** produced polymers **2c** and **2d**, respectively, in good yields. The weight-average molecular weights of **2c** and **2d** were  $1.40 \times 10^6$  and  $1.91 \times 10^6$ , respectively. Although **1c** and **1d** also have both silyl group and an alkyl group, the bulkier alkyl groups may decrease their polymerizability. The polymerizations of **1B** and **1C** without dimethyloctylsilyl groups were carried out in the same method as **1a** to give polymers **2B** and **2C**, respectively. The polymers **2B** and

**2C** have enough high molecular weights to fabricate free-standing membranes.

#### 3.2. Solvent solubility, preparation, and desilylation of membranes

The solubility of the polymers is summarized in Table 2. All the Si-containing polymers **2a–d** completely dissolved in common organic solvents such as hexane,  $\text{CCl}_4$ , toluene, diethyl ether, chloroform, and THF. The polymers without silyl groups (**2B–D**) also exhibited good solubility. Tough free-standing membranes could be fabricated by casting polymers from their toluene solutions. The desilylation of membranes of **2a–d** was carried out in trifluoroacetic acid at room temperature for 24 h to give the corresponding desilylated membranes (**3a–d**). 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  $1250\text{ cm}^{-1}$  derived from stretching of Si–C–H bonds and at  $1120\text{ cm}^{-1}$  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 dimethyloctylsilyl group. After desilylation, weights of the polymer membranes decreased to the values anticipated for desilylation, indicating the completion of the reaction.

The solubility of the desilylated polymers **3a–d** is shown in Table 2. The desilylated polymers **3a–d** showed less solubility than Si-containing polymers **2a–d**. The polymer **3a**, which has no alkyl substituent on phenyl groups, was insoluble in any solvents, while **2a** was soluble in various organic solvents. The desilylated polymers **3b–d** have the identical chemical structures to **2B–D**, respectively. However, the desilylated polymers **3b** and **3c** exhibited somewhat poor solubility than **2B** and **2C**, respectively. The desilylated polymer **3b** was partly soluble in  $\text{CCl}_4$ , toluene,  $\text{CHCl}_3$ , and THF, although **2B** was completely dissolved in these solvents. The desilylated polymer **3c** partially dissolved in  $\text{Et}_2\text{O}$ , which was a good solvent to **2C**. This may be accounted for by the idea that the geometric structures of **3b** and **3c** are somewhat different from those of **2B** and **2C**, respectively. The main chains of **3b** and **3c** are generated by the polymerization of **1b** and **1c** which have bulky silyl group, so the structures of **3b** and **3c** would have high stereoregularity compared to the polymers **2B** and **2C**. The metathesis polymerization of substituted acetylene produces the polyacetylene main chain composed of a mixture of *cis*-form and *trans*-form [17]. Khotimsky et al. reported that the geometric structure of the substituted acetylene polymer is defined by a combination of the size of substituent, kind of transition metal, polymerization solvent, and temperature [18]. They determined the ratios of *cis* and *trans* structures of poly[1-(trimethylsilyl)-1-propyne] and poly[1-(trimethylgermyl)-1-propyne] by using  $^{13}\text{C}$  NMR. In order to examine the structures of main chains of **2B** and **3b**,  $^{13}\text{C}$  NMR spectra of the polymers were measured. However, no peaks

**Table 1**  
Polymerizations of monomers.<sup>a</sup>

Run	Monomer	[M] <sub>0</sub>	Yield <sup>b</sup> [%]	$M_w \times 10^{-6c}$	$M_w/M_n^c$
1	<b>1a</b>	0.20	84	2.68	8.60
2	<b>1b</b>	0.20	76	3.13	8.39
3	<b>1b</b>	0.10	77	2.08	5.19
4	<b>1c</b>	0.20	59	1.40	5.10
5	<b>1d</b>	0.20	76	1.91	4.90
6	<b>1B</b>	0.20	84 <sup>d</sup>	1.76	10.4
7	<b>1C</b>	0.20	73 <sup>d</sup>	0.836	4.49

<sup>a</sup> Polymerized with  $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$  in toluene at 80 °C for 24 h;  $[\text{TaCl}_5]_0 = 20\text{ mM}$ ,  $[n\text{-Bu}_4\text{Sn}]_0 = 80\text{ mM}$ .

<sup>b</sup> Acetone-insoluble product.

<sup>c</sup> Measured by GPC.

<sup>d</sup> Methanol-insoluble product.

**Table 2**  
Solubility of polymers.<sup>a</sup>

solvent	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>	<b>2B</b>	<b>2C</b>	<b>2D<sup>b</sup></b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>
hexane	+	+	+	+	–	–	–	–	–	–	–
$\text{CCl}_4$	+	+	+	+	+	+	+	–	±	+	+
toluene	+	+	+	+	+	+	+	–	±	+	+
$\text{Et}_2\text{O}$	+	+	+	+	–	+	±	–	–	±	±
$\text{CHCl}_3$	+	+	+	+	+	+	+	–	±	+	+
THF	+	+	+	+	+	+	+	–	±	+	+
acetone	–	–	–	–	–	–	–	–	–	–	–
DMF	–	–	–	–	–	–	–	–	–	–	–
DMSO	–	–	–	–	–	–	–	–	–	–	–

<sup>a</sup> Symbols: +; soluble, ±; partly soluble, –; insoluble.

<sup>b</sup> Data from Ref. [10].



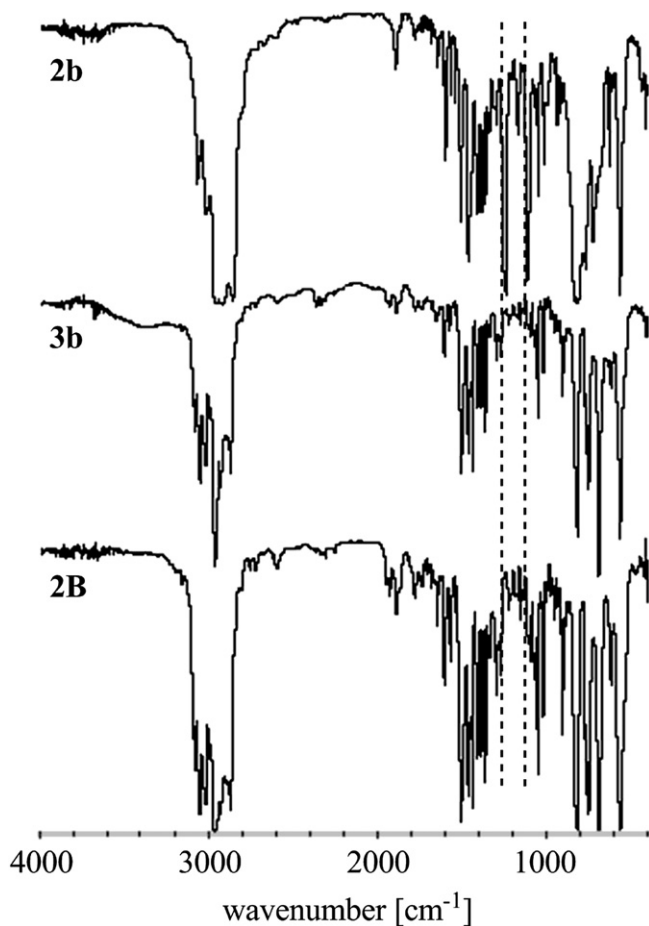


Fig. 1. IR spectra of membranes before and after desilylation (2b, 3b, and 2B).

were observed because of too high molecular weight of the polymers. The desilylated polymer **3d** having *n*-butyl groups showed the same solubility as **2D**, and they were soluble in CCl<sub>4</sub>, toluene, CHCl<sub>3</sub>, and THF, and partly soluble in Et<sub>2</sub>O. Polymers **3d** and **2D** might have different geometric structures, but they have linear alkyl (*n*-butyl) groups, which improve the solubility of polymers. Therefore, a conspicuous difference of solubility between **3d** and **2D** was not observed.

### 3.3. Gas permeability

The permeability of Si-containing polymer membranes (**2a–d**) and desilylated membranes (**3a–d**) to various gases was examined at 25 °C (Table 3). Oxygen permeability coefficients ( $P(O_2)$ ) of **2a–d** were 34, 29, 26, and 25 barrers, respectively. The Si-containing

polymer membranes exhibited almost the same oxygen permeability despite the fact that they each have different kinds of alkyl groups. With regard to nitrogen and carbon dioxide, no obvious difference of permeability was observed between **2a–d**. Gas permeability of Si-containing membranes seems to be controlled mainly by dimethyloctylsilyl groups. The densities and FFV of Si-containing membranes were also nearly the same. Their FFV values ranged from 0.154 to 0.182, which are small compared to poly(diphenylacetylene)s without long alkyl groups. For instance, the FFV values of poly[1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene] and poly[1-(*p*-*t*-butyl)phenyl-2-phenylacetylene] are reported to be 0.26 [19] and 0.27 [20], respectively. The long alkyl chains of dimethyloctylsilyl groups would occupy the free volume in the polymer matrix because of the flexibility of octyl groups.

The desilylated membranes of **3a–c** showed larger oxygen permeability than Si-containing membranes. The  $P(O_2)$  values of **3a–c** were 1200, 300, and 820 barrers, respectively. In addition, the desilylation lead to large increases in the FFV of membranes. The long alkyl chains of dimethyloctylsilyl groups were disadvantageous to gas permeation because linear alkyl chains occupy the free volume in Si-containing membranes. The gas permeability coefficient and FFV of desilylated membrane of **3d** having *n*-butyl groups was 37 barrers and 0.152, respectively, which are similar to those of **2d**. This is because the free volume is still occupied by the flexible *n*-butyl groups even after elimination of dimethyloctylsilyl groups.

### 3.4. CO<sub>2</sub> diffusivity and solubility

The CO<sub>2</sub> diffusion coefficients ( $D(CO_2)$ ) were measured by time lag method, and the CO<sub>2</sub> solubility coefficients ( $S(CO_2)$ ) were calculated using  $P$  and  $D$  values (Table 3). Unfortunately, the time lags on oxygen and nitrogen permeability measurement were so small that  $D(O_2)$  and  $D(N_2)$  values could not be determined. The desilylated membranes of **3a–c** showed much higher CO<sub>2</sub> diffusivity than Si-containing counterparts. The CO<sub>2</sub> solubility of these membranes greatly increased through desilylation. The increases of diffusivity and solubility would be due to the increment of FFV. The elimination of dimethyloctylsilyl groups of membranes ought to affect gas solubility more effectively than gas diffusivity. The CO<sub>2</sub> solubility coefficient of **3a**, for instance, was approximately 15 times as large as that of **2a**, while the diffusivity coefficient of **3a** was approximately 1.7 times of that of **2a**.

However, membrane of **3d** exhibited unanticipated behavior of variation in CO<sub>2</sub> diffusivity and solubility. Desilylation of membrane of **2d** caused decrease of diffusivity and increase of solubility even though the FFV scarcely changed by desilylation. Gas diffusivity of polymer membranes is determined by local mobility of substituents as well as free volume of membranes [21]. It is reported that flexible alkyl groups such as an octyl group exhibit relatively large local mobility [22]. Therefore, the decrease of CO<sub>2</sub> diffusivity through desilylation can be explained by a lack of dimethyloctylsilyl

Table 3  
Membranes properties of Si-containing and Desilylated membranes.

Membrane	2							3						
	$P(O_2)^a$	$P(N_2)^a$	$P(CO_2)^a$	$D(CO_2)^b \times 10^8$	$S(CO_2)^c \times 10^3$	Density (g cm <sup>-3</sup> )	FFV	$P(O_2)^a$	$P(N_2)^a$	$P(CO_2)^a$	$D(CO_2)^b \times 10^8$	$S(CO_2)^c \times 10^3$	Density [g cm <sup>-3</sup> ]	FFV
a	34	11	170	490	3.4	0.975	0.182	1200	740	4200	810	52	0.966	0.283
b	29	9.1	120	190	6.1	0.995	0.154	300	150	1100	400	27	1.04	0.191
c	26	7.5	100	430	2.8	0.973	0.169	820	360	3000	770	39	0.890	0.296
d	25	7.9	110	550	2.6	0.979	0.164	37	11	160	100	15	1.07	0.152

<sup>a</sup> Measured at 25 °C. In the unit of barrer [1 barrer =  $1 \times 10^{-10}$  cm<sup>3</sup>(STP) cm cm<sup>-2</sup> s<sup>-1</sup> cm Hg<sup>-1</sup>].

<sup>b</sup> Measured at 25 °C by the 'time lag' method. In the units of cm<sup>2</sup> s<sup>-1</sup>.

<sup>c</sup> Calculated from the equation  $S = P/D$ . In the units of cm<sup>3</sup>(STP) cm<sup>-3</sup> cm Hg.

**Table 4**  
Comparison of membrane properties of polymers without Si-groups.

	$P(\text{O}_2)^a$	$P(\text{O}_2)/P(\text{N}_2)$	$D(\text{CO}_2)^b \times 10^8$	$S(\text{CO}_2)^c \times 10^3$	FFV
<b>3b</b>	300	2.0	400	27	0.191
<b>4b</b>	320	2.1	240	63	0.251
<b>2b</b>	350	2.2	490	31	0.261
<b>3c</b>	820	2.3	770	39	0.296
<b>4c</b>	910	2.1	780	46	0.277
<b>2c</b>	780	2.3	490	65	0.272
<b>3d</b>	37	3.4	100	15	0.152
<b>4d</b>	28	3.5	120	10	0.146
<b>2d</b> <sup>d</sup>	89	3.0	200	22	0.202

<sup>a</sup> Measured at 25 °C. In the unit of barrer [ $1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$ ].

<sup>b</sup> Measured at 25 °C by the 'time lag' method. In the units of  $\text{cm}^2 \text{ s}^{-1}$ .

<sup>c</sup> Calculated from the equation  $S = P/D$ . In the units of  $\text{cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ cm Hg}^{-1}$ .

<sup>d</sup> Data from Ref. [10].

groups with large local mobility. The  $S(\text{CO}_2)$  of **3d** was much larger than that of **2d**, as is the case for **2a–c**. This implies that dimethyloctylsilyl groups lower gas solubility performance of polymer membrane.

### 3.5. Comparison of three types of membranes

Polymer membranes of **4b–d** were fabricated by re-casting using toluene solutions of the desilylated polymers (**3b–d**, respectively). Polymer **3b** did not dissolve completely in toluene, and hence membrane of **4b** was prepared by using toluene-soluble parts of **3b**. The other kind of membranes without dimethyloctylsilyl groups were fabricated from **2b** and **2c**, which were obtained directly by the polymerization of the corresponding monomers **1b** and **1c**. The desilylated membrane of **3b** has an identical chemical structure with **4b** and **2b**, but they were prepared by different methods. The oxygen permeability coefficients, permselectivity,  $\text{CO}_2$  diffusivity,  $\text{CO}_2$  solubility, and FFV of membranes without dimethyloctylsilyl group (**3b–d**, **4b–d**, and **2b–d**) are listed in Table 4.

The  $P(\text{O}_2)$  values of membranes of **3b**, **4b**, and **2b** were 300, 320, and 350 barrers, respectively, which were similar to each other. The  $P(\text{O}_2)$  value of **3c** having *t*-butyl groups was also almost the same as those of **4c** and **2c**. These results suggest that excess free volume was not generated by desilylation in a solid state. The membranes of **3d** and **4d**, which contain *n*-butyl groups, showed nearly the same oxygen permeability, while the  $P(\text{O}_2)$  value of **2d** was obviously larger than those of **3d** and **4d**. The FFV of **2d** was also much larger than those of **3d** and **4d**. High oxygen permeability and FFV of **2d** would be attributed to the difference of geometric structure of polymer main chain. The polymer **2d** was synthesized directly from the monomer without Si-group. Therefore, the polymer **2d** should have different geometric structure from the polymers **3d** and **4d**. The polymer **3b** and **3c** also would have different geometric structures from **2b** and **2c**, respectively, as described in the section of solvent solubility. However, they have large FFV owing to the steric repulsion of the branched alkyl groups. Hence the difference of geometric structure may not affect their FFV and gas permeability significantly.

## 4. Conclusions

Novel poly(diphenylacetylene)s having both dimethyloctylsilyl and various alkyl groups were synthesized, and free-standing membranes of the produced polymers could be fabricated by solution-casting. The desilylation of these membranes proceeded quantitatively. All the polymer membranes with dimethyloctylsilyl groups exhibited almost the same gas permeability. The dimethyloctylsilyl groups would control gas permeability of the polymers. The desilylation of polymer membranes containing no alkyl group (**2a**) and branched alkyl groups (*i*-propyl (**2b**) and *t*-butyl (**2c**)) resulted in increases of gas permeability and FFV. The  $\text{CO}_2$  solubility increased more significantly than the  $\text{CO}_2$  diffusivity through desilylation of these membranes. The desilylated membrane having *n*-butyl groups (**3d**) exhibited nearly the same gas permeability coefficient as Si-containing counterpart (**2d**) did. The desilylation of **2d** increased  $\text{CO}_2$  solubility, and decreased  $\text{CO}_2$  diffusivity. The desilylated membranes showed almost the same gas permeability as the membranes prepared by re-casting of the desilylated polymers. This indicates that microvoid was not generated by the elimination of silyl groups in a solid state on poly[1-(*p*-dimethyloctylsilyl)phenyl-2-phenylacetylene] with linear or branched alkyl groups.

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