

# Synthesis and properties of poly(diphenylacetylenes) containing siloxy and halogen/methyl groups and their desilylated membranes

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Received 14 September 2006; received in revised form 30 October 2006; accepted 4 November 2006  
Available online 22 November 2006

## Abstract

Diphenylacetylenes containing both siloxy groups and halogen or methyl substituents (*p*-*tert*-BuMe<sub>2</sub>SiOC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>3</sub>R<sub>2</sub>, R = *m,p*-Cl,Cl; *m,m*-Cl,Cl; *m,p*-Br,Br; *m,m*-Br,Br; *m,p*-Me,Me; *m,m*-Me,Me, **1a–f**, respectively) were polymerized with TaCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn catalyst to give high molecular weight polymers (**2a–f**) in good yields. Free-standing membranes were fabricated by casting from toluene solution. Desilylation of these siloxy group-containing polymer membranes with trifluoroacetic acid (TFA) afforded poly(diphenylacetylene) membranes having hydroxy groups (**3a–f**). Polymers **2a–f** were soluble in low polar solvents such as toluene and CHCl<sub>3</sub>, while **3a–f** were insoluble in these solvents. According to thermogravimetric analysis (TGA), **2a–f** and **3a–f** exhibited high thermal stability (*T*<sub>0</sub> ~340 and ~390 °C, respectively). The gas permeability of the halogen-containing polymer membranes was higher than that of methyl group-containing ones. The PCO<sub>2</sub>/PN<sub>2</sub> permselectivity ratios of polymer membranes **3a–f** were in the range of 14–49. The points of **3a–f** in the PCO<sub>2</sub> vs PCO<sub>2</sub>/PN<sub>2</sub> plot were located obviously above Robeson's upper bound.

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**Keywords:** Poly(diphenylacetylene); Gas permeability; Desilylation

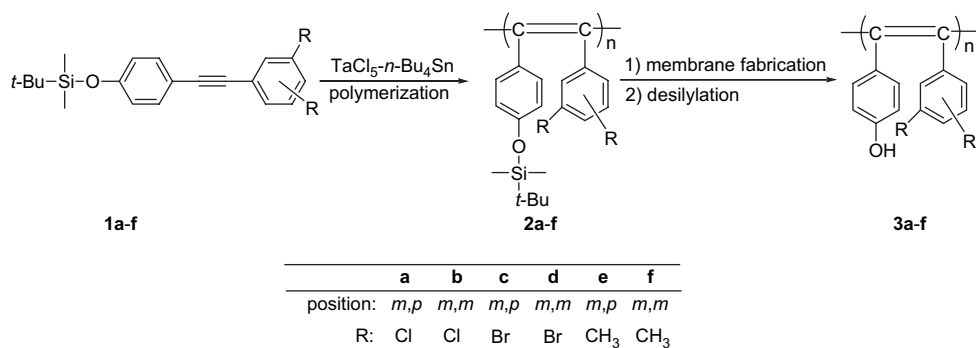
## 1. Introduction

Polyacetylenes exhibit interesting features such as chromism, semiconductivity, paramagnetism, gas permeability, etc. [1–5]. Among them, some substituted polyacetylenes, especially polymers from disubstituted acetylenes, have attracted much attention as gas separation membranes applicable to practical use due to their high thermal stability and high gas permeability [6–10]. For instance, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] is by far the most permeable to every gas among all the existing polymers [11,12]; poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] exhibits both high gas permeability and thermal stability; the oxygen permeability coefficient (*P*O<sub>2</sub>) is as large as 1100 barrers, and the onset temperature of weight loss is 420 °C [13,14].

We have previously reported that solvent-insoluble membranes of poly(diphenylacetylene) can be obtained through the desilylation of silylated poly(diphenylacetylenes) [15,16]. In a similar way, poly[1-phenyl-2-(*p*-hydroxy)phenylacetylene] [poly(**1**)] membrane is prepared using the protection/deprotection methodology, which cannot be obtained directly by the polymerization of the corresponding monomers with Ta catalyst owing to its intolerance to polar groups such as hydroxy group [17,18]. This polymer membrane shows outstanding separation performance for CO<sub>2</sub> against methane and nitrogen, which is of interest in some areas, such as oil recovery, the treatment of landfill gases, sweetening natural gas, and reducing the green house effect. However, the gas permeability of poly(**1**) is rather low compared to other poly(diphenylacetylene) derivatives.

Many efforts have been made to improve the permeation properties of polymer membranes by modifying the chemical structure. Incorporation of halogen atoms into poly(diphenylacetylene) derivatives is effective to enhance gas permeability

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Scheme 1. Synthesis of the poly(diphenylacetylenes) in the present study.

because of their potential to inhibit the polymer chain from packing [19–21]. Therefore, it is expected that introducing halogen atoms into hydroxy-containing poly(diphenylacetylene) membranes will lead to higher gas permeability. Another aim is to have a good understanding of the relationship between the polymer structures and their gas permeation properties. Such rules, when available, would simplify the task of synthesis of novel membrane materials with improved properties.

The present study deals with the polymerization of diphenylacetylene monomers containing both siloxy groups and halogen atoms (**1a–d**), and fabrication of free-standing membranes from the resultant polymers (**2a–d**) (Scheme 1). Analogous poly(diphenylacetylenes) having methyl groups (**2e** and **2f**) are also discussed for comparison. General properties and gas permeability of their free-standing membranes along with the desilylated ones are further elucidated.

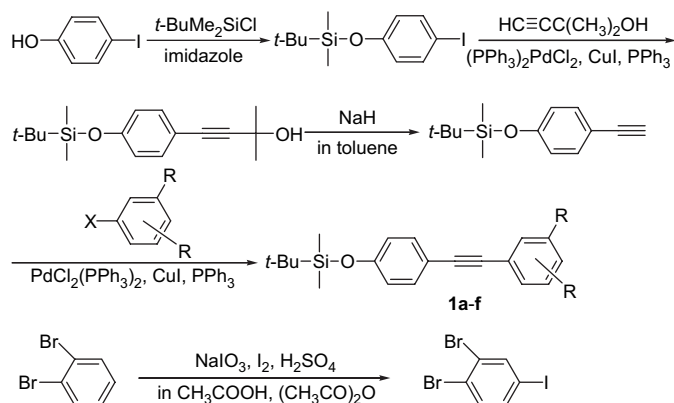
## 2. Experimental section

### 2.1. Materials and methods

TaCl<sub>5</sub> (Strem) was purchased and used without further purification. *n*-Bu<sub>4</sub>Sn (Wako, Japan) was used after distillation. *p*-Iodophenol, trifluoroacetic acid (TFA), and common solvents (Wako, Japan) were used without further purification except toluene as polymerization solvent. *tert*-Butyldimethylsilyl chloride, 1,2-dichloro-4-iodobenzene, 1,3-dichloro-5-iodobenzene, 1,3,5-tribromobenzene (Aldrich), and 1-iodo-3,4-dimethylbenzene, 1-iodo-3,5-dimethylbenzene (Wako) were used as received. *p*-(*tert*-Butyldimethylsilyloxy)phenylacetylene and 1,2-dibromo-4-iodobenzene were prepared according to the literature procedure [22–24]. Monomers **1a–f** were synthesized according to Scheme 2, referring to the literature concerning ethynylation [25] and silylation [26].

### 2.2. Instrumentation

Molecular weights of polymers were estimated by gel permeation chromatography (CHCl<sub>3</sub> as eluent, polystyrene calibration). IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. NMR spectra were observed on a JEOL EX-400 spectrometer. Elemental analysis of monomers was



Scheme 2. Synthesis of diphenylacetylene monomers containing a siloxy and two halogen/methyl groups.

carried out at the Microanalytical Center of Kyoto University. TGA was conducted in air with a Perkin–Elmer TGA7 thermal analyzer. Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

### 2.3. Synthesis of monomers

#### 2.3.1. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,4-dichlorophenyl) acetylene (**1a**)

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, 1,2-dichloro-4-iodobenzene (6.8 g, 25 mmol), dichlorobis(triphenylphosphine)palladium (0.06 g, 0.09 mmol), cuprous iodide (0.10 g, 0.54 mmol) and triphenylphosphine (0.09 g, 0.36 mmol) were placed in the flask and dissolved in triethylamine (100 mL) at room temperature. Then, a solution of *p*-(*tert*-butyldimethylsilyloxy)phenylacetylene (5.0 g, 22 mmol) in triethylamine (20 mL) was added, and stirring was continued at room temperature for 5 h. After that, triethylamine in the reaction mixture was evaporated off, and then ether (200 mL) was added to the residual mass. Solvent-insoluble solid was filtered off, and the filtrate was washed with 1 N 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 **1a** (7.0 g, 85%) as a white solid; mp 33.5–34.5 °C. IR (KBr,  $\text{cm}^{-1}$ ): 2930, 1603, 1509, 1472, 1263, 1167, 911, 825, 781, 695.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.58 (s, 1H, Ar), 7.39 (m, 7.37–7.41, 3H, Ar), 7.31 (s, 1H, Ar), 6.81 (d,  $J = 8.38$  Hz, 2H, Ar), 0.98 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.21 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.4, 133.1, 133.0, 132.5, 132.1, 130.5, 130.3, 123.6, 120.3, 115.2, 91.5, 86.0, 25.6, 18.2, –4.4. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{OSi}$ : C, 63.65; H, 5.88. Found: C, 63.61; H, 5.85.

### 2.3.2. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,5-dichlorophenyl) acetylene (**1b**)

This monomer was prepared by the same method as for **1a** using 1,3-dichloro-5-iodobenzene instead of 1,2-dichloro-4-iodobenzene to give a white solid; yield 78%, mp 30–31 °C. IR (KBr,  $\text{cm}^{-1}$ ): 2930, 1580, 1555, 1508, 1267, 1169, 1095, 913, 838, 670.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.38 (m, 7.37–7.40, 4H, Ar), 7.28 (s, 1H, Ar), 6.81 (d,  $J = 8.38$  Hz, 2H, Ar), 0.98 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.21 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.6, 134.8, 133.2, 129.5, 128.1, 126.5, 120.3, 114.9, 91.9, 85.7, 25.6, 18.2, –4.4. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{OSi}$ : C, 63.65; H, 5.88. Found: C, 63.86; H, 5.87.

### 2.3.3. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,4-dibromophenyl) acetylene (**1c**)

This monomer was prepared by the same method as for **1a** using 1,2-dibromo-4-iodobenzene instead of 1,2-dichloro-4-iodobenzene to give a white solid; yield 74%, mp 58–59 °C. IR (KBr,  $\text{cm}^{-1}$ ): 2929, 1603, 1509, 1280, 1167, 1011, 914, 823, 782, 688.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.75 (s, 1H, Ar), 7.55 (d,  $J = 8.38$  Hz, 1H, Ar), 7.39 (d,  $J = 8.38$  Hz, 2H, Ar), 7.25 (d,  $J = 8.38$  Hz, 1H, Ar), 6.81 (d,  $J = 8.38$  Hz, 2H, Ar), 0.98 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.21 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.4, 136.0, 133.4, 133.1, 131.1, 124.6, 124.4, 120.3, 115.2, 91.7, 85.9, 25.6, 18.2, –4.4. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{Br}_2\text{OSi}$ : C, 51.52; H, 4.76. Found: C, 51.30; H, 4.73.

### 2.3.4. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,5-dibromophenyl) acetylene (**1d**)

This monomer was prepared by the same method as for **1a** using 1,3,5-tribromobenzene instead of 1,2-dichloro-4-iodobenzene to give a colorless liquid; yield 61%. IR (KBr,  $\text{cm}^{-1}$ ): 2929, 1578, 1539, 1508, 1267, 1168, 912, 840, 781, 747, 669.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.58 (m, 7.57–7.60, 3H, Ar), 7.39 (d,  $J = 8.38$  Hz, 2H, Ar), 6.82 (d,  $J = 8.38$  Hz, 2H, Ar), 0.99 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.22 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  156.6, 133.5, 133.2, 132.8, 127.1, 122.6, 120.3, 114.9, 92.2, 85.4, 25.6, 18.2, –4.4. Anal. Calcd for  $\text{C}_{20}\text{H}_{22}\text{Br}_2\text{OSi}$ : C, 51.52; H, 4.76. Found: C, 51.75; H, 4.87.

### 2.3.5. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,4-dimethylphenyl) acetylene (**1e**)

This monomer was prepared by the same method as for **1a** using 1-iodo-3,4-dimethylbenzene instead of 1,2-dichloro-4-iodobenzene to give a colorless liquid; yield 81%. IR (KBr,  $\text{cm}^{-1}$ ): 2930, 2858, 1600, 1509, 1471, 1263, 1166, 912, 839,

782, 707.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.38$  Hz, 2H, Ar), 7.26 (m, 7.24–7.29, 2H, Ar), 7.08 (d,  $J = 8.38$  Hz, 1H, Ar), 6.80 (d,  $J = 8.38$  Hz, 2H, Ar), 2.25 (d,  $J = 5.59$  Hz, 6H,  $\text{CH}_3\text{Ar}$ ), 0.98 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.21 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.7, 136.8, 136.5, 132.9, 132.5, 129.6, 128.9, 120.8, 120.2, 116.3, 88.5, 88.4, 25.6, 19.7, 19.6, 18.2, –4.4. Anal. Calcd for  $\text{C}_{22}\text{H}_{28}\text{OSi}$ : C, 78.51; H, 8.39. Found: C, 78.23; H, 8.67.

### 2.3.6. 1-(4-*tert*-Butyldimethylsilyloxyphenyl)-2-(3,5-dimethylphenyl) acetylene (**1f**)

This monomer was prepared by the same method as for **1a** using 1-iodo-3,5-dimethylbenzene instead of 1,2-dichloro-4-iodobenzene to give a colorless liquid; yield 75%. IR (KBr,  $\text{cm}^{-1}$ ): 2929, 1595, 1508, 1471, 1265, 1167, 913, 844, 782, 688, 534.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.38$  Hz, 2H, Ar), 7.14 (s, 2H, Ar), 6.94 (s, 1H, Ar), 6.80 (d,  $J = 8.38$  Hz, 2H, Ar), 2.30 (s, 6H,  $\text{CH}_3\text{Ar}$ ), 0.98 (s, 9H,  $\text{SiC}(\text{CH}_3)_3$ ), 0.20 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.8, 137.8, 133.0, 129.9, 129.1, 123.2, 120.2, 116.2, 88.7, 88.5, 25.6, 21.1, 18.2, –4.4. Anal. Calcd for  $\text{C}_{22}\text{H}_{28}\text{OSi}$ : C, 78.51; H, 8.39. Found: C, 78.30; H, 8.32.

## 2.4. Polymerization

Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations:  $[\text{TaCl}_5] = 20$  mM,  $[\textit{n}\text{-Bu}_4\text{Sn}] = 40$  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. 40–80  $\mu\text{m}$ ) of polymers **2a–f** 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. 4–7 days). After membranes were prepared, they were 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 [17,18], the desilylation reaction of polymer membranes **2a–f** was carried out using TFA. A typical procedure of the desilylation reaction is as follows; a polymer membrane was immersed in a mixture of TFA and water (volume ratio 4:1) at room temperature for 24 h. The membrane was immersed in water for 24 h and then washed with water to remove residual impurities and dried to constant weight at room temperature for 24 h and in vacuo for 5 h.

## 2.6. Density and fractional free volume (FFV) of polymer membranes

The membrane density was determined by hydrostatic weighing using a Mettler Toledo balance (model AG204,

Switzerland) and a density determination kit [27]. In this method, a liquid with known density ( $\rho_0$ ) is needed, and the membrane density ( $\rho$ ) is given by the following equations:

$$\rho = \rho_0 M_A / (M_A - M_L) \quad (1)$$

where  $M_A$  is the membrane weight in air and  $M_L$  is the membrane weight in the auxiliary liquid. Aqueous  $\text{NaNO}_3$  solution was used as the auxiliary liquid.

FFV ( $\text{cm}^3$  of free volume/ $\text{cm}^3$  of polymer) is commonly used to estimate the efficiency of chain packing and the amount of space (free volume) available for gas permeation in a polymer matrix. It is defined as [28,29]

$$\text{FFV} = (v_{\text{sp}} - v_0) / v_{\text{sp}} \approx (v_{\text{sp}} - 1.3v_w) / v_{\text{sp}} \quad (2)$$

where  $v_{\text{sp}}$  and  $v_0$  are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. Typically,  $v_0$  is 1.3 times larger than the van der Waals volume ( $v_w$ ), which is calculated by the group contribution methods [30].

### 2.7. Measurement of gas permeabilities

Gas permeability coefficients 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 at 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.

## 3. Results and discussion

### 3.1. Polymerization

The polymerization of monomers **1a–f** was carried out using  $\text{TaCl}_5$ – $n\text{-Bu}_4\text{Sn}$  catalyst in toluene, whose results are summarized in Table 1. In general, group 5 transition metals Ta(V) and Nb(V) are effective for the polymerization of disubstituted acetylenes. Especially, the formation of high molecular weight

Table 1  
Polymerization of monomers **1a–f** by  $\text{TaCl}_5$ – $n\text{-Bu}_4\text{Sn}$  catalyst<sup>a</sup>

| Run | Monomer   | Polymer <sup>b</sup> |                                   |                        |
|-----|-----------|----------------------|-----------------------------------|------------------------|
|     |           | Yield (%)            | $M_w \times 10^{-6}$ <sup>c</sup> | $M_w/M_n$ <sup>c</sup> |
| 1   | <b>1a</b> | 74                   | 5.3                               | 3.3                    |
| 2   | <b>1b</b> | 79                   | >6.0                              | —                      |
| 3   | <b>1c</b> | 73                   | 1.7                               | 3.8                    |
| 4   | <b>1d</b> | 75                   | 3.2                               | 2.6                    |
| 5   | <b>1e</b> | 51                   | 2.1                               | 2.4                    |
| 6   | <b>1f</b> | 42                   | 0.9                               | 4.8                    |

<sup>a</sup> In toluene at 80 °C for 24 h;  $[\text{M}]_0 = 0.10$  M,  $[\text{TaCl}_5] = 20$  mM,  $[n\text{-Bu}_4\text{Sn}] = 40$  mM.

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

<sup>c</sup> Measured by GPC in  $\text{CHCl}_3$  calibrated with polystyrenes as standards.

poly(diphenylacetylenes) is possible by using mixed catalysts composed of  $\text{TaCl}_5$  and suitable organometallic cocatalysts [31,32]. Chlorine-containing monomer **1a** afforded polymer with a high molecular weight ( $M_w = 5.3 \times 10^6$ ) in good yield. The polymer from **1b** possessed a very high molecular weight ( $M_w > 6.0 \times 10^6$ ). Bromine-containing monomers **1c** and **1d** also gave polymers in high yields ( $\sim 75\%$ ), and the  $M_w$ 's were as high as  $1.7 \times 10^6$  and  $3.2 \times 10^6$ , respectively. The polymerization of the monomers with two methyl groups, **1e** and **1f**, under the same conditions produced polymers in moderate yields (51% and 42%, respectively) with similar or slightly lower  $M_w$  values ( $2.1 \times 10^6$  and  $0.9 \times 10^6$ , respectively). Thus, all of polymers **2a–f** had sufficiently high molecular weights for the fabrication of free-standing membranes.

### 3.2. Fabrication and desilylation of polymer membranes

Tough free-standing membranes could be prepared by casting from toluene solution of the polymers. The formed membranes were sufficiently tough, uniform, and transparent. The desilylation of polymer membranes **2a–f** was carried out in a mixture of TFA and water (4:1 volume ratio) at room temperature for 24 h. The reaction proceeded to completion, which successfully gave the hydroxy-containing polymer membranes **3a–f**. The completion of desilylation was confirmed by IR spectroscopy. Fig. 1 shows the IR spectra of membranes **2a** and **3a** which are polymers before and after desilylation, respectively. In the IR spectrum of **3a**, a very broad and strong absorption characteristic of hydroxy group was observed at  $3396 \text{ cm}^{-1}$ , and the peaks at  $916$  and  $780 \text{ cm}^{-1}$  indicative of the presence of siloxy group in **2a** disappeared.

### 3.3. Solubility and thermal stability of the polymers

The solubility of a polymer greatly affects its processability for fabricating membrane. Table 2 summarizes the solubility of polymers **2a–f** and **3a–f**. The siloxy-containing polymers **2a–f** completely dissolved in relatively nonpolar solvents such as hexane, cyclohexane, toluene,  $\text{CHCl}_3$ , and THF, while

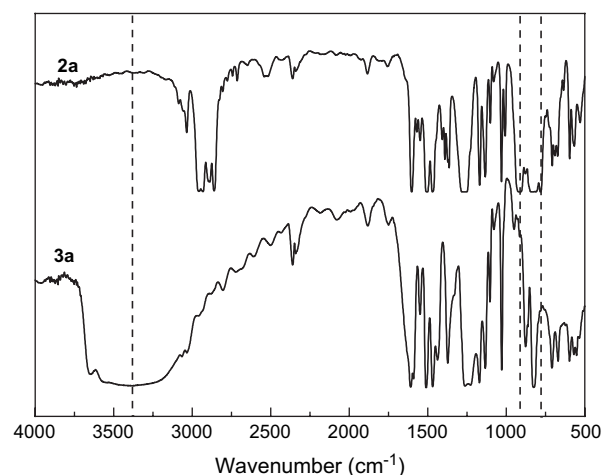


Fig. 1. IR spectra of polymer **2a** and its desilylated product **3a** (films).

Table 2  
Solubility of the polymers<sup>a</sup>

| Polymer           | 2a | 2b | 2c | 2d | 2e | 2f | 3a | 3b | 3c | 3d | 3e | 3f |
|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|
| Hexane            | +  | +  | +  | +  | ±  | +  | –  | –  | –  | –  | –  | –  |
| Cyclohexane       | +  | +  | +  | +  | ±  | +  | –  | –  | –  | –  | –  | –  |
| Toluene           | +  | +  | +  | +  | +  | +  | –  | –  | –  | –  | –  | –  |
| CHCl <sub>3</sub> | +  | +  | +  | +  | +  | +  | –  | –  | –  | –  | –  | –  |
| THF               | +  | +  | +  | +  | +  | +  | –  | –  | ±  | ±  | –  | –  |
| Methanol          | –  | –  | –  | –  | –  | –  | ±  | ±  | ±  | ±  | ±  | ±  |
| DMF               | –  | –  | –  | –  | –  | –  | ±  | ±  | ±  | ±  | ±  | ±  |
| DMSO              | –  | –  | –  | –  | –  | –  | –  | –  | ±  | ±  | –  | ±  |

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

they were insoluble in highly polar solvents such as methanol, DMF, and DMSO. In contrast, hydroxy-containing polymers **3a–f** were insoluble in nonpolar solvents, while partly soluble in methanol, DMF, and DMSO. This variation in solubility should be due to the very different natures of siloxy and hydroxy groups.

The thermal stability of the polymers was examined by TGA in air (Figs. 2 and 3). The onset temperatures of weight loss ( $T_0$ ) of **2a–f** were all approximately 340 °C, indicating the considerably high thermal stability among substituted polyacetylenes. When siloxy groups-containing **2a–f** were heated above 800 °C in air, the ash composed of silica remained, whose amount agreed with the expected value. The  $T_0$  values of desilylated polymers **3a–f** were almost the same to one another (approximately 390 °C). In the case of **3a–f**, no SiO<sub>2</sub> residue was detected, which confirms that the desilylation of the membranes proceeded quantitatively.

### 3.4. Density and FFV of polymer membranes

The densities and fractional free volumes (FFV) of the polymer membranes are listed in Table 3. The densities of **2a–d** having both siloxy groups and halogen atoms were in the range of 1.05–1.28 g/cm<sup>3</sup>, which were higher than those of methyl-containing counterparts **2e** and **2f** (0.95 and

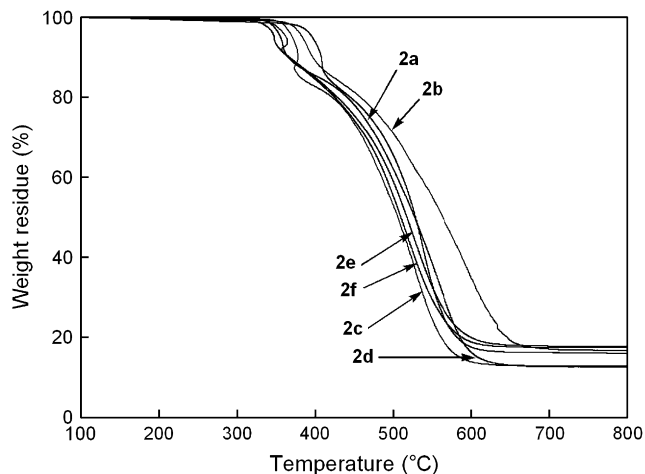


Fig. 2. TGA curves of siloxy group-containing poly(diphenylacetylenes) **2a–f** (in air, heating rate 10 °C/min).

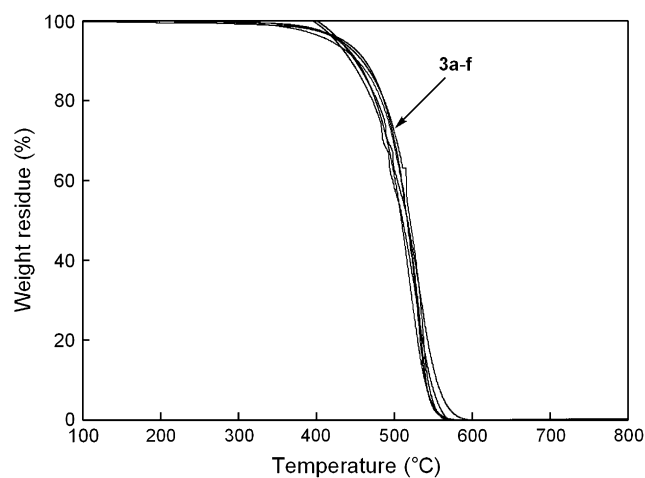


Fig. 3. TGA curves of hydroxy group-containing poly(diphenylacetylenes) **3a–f** (in air, heating rate 10 °C/min).

0.94 g/cm<sup>3</sup>). These results are reasonable because halogen atoms tend to increase the density. The densities of **3a–f** showed a similar tendency to those of **2a–f**.

The FFVs of membranes **2a–f** were 0.21–0.23, which are obviously larger than that of unsubstituted counterpart poly[1-phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene] (0.18) [18]. These results indicate small spherical substituents sterically hinder intersegmental packing. In the case of

Table 3  
Density and FFV<sup>a</sup> of the polymer membranes

| Membrane  | Density (g/cm <sup>3</sup> ) | FFV   |
|-----------|------------------------------|-------|
| <b>2a</b> | 1.05                         | 0.231 |
| <b>2b</b> | 1.05                         | 0.231 |
| <b>2c</b> | 1.28                         | 0.224 |
| <b>2d</b> | 1.27                         | 0.230 |
| <b>2e</b> | 0.95                         | 0.207 |
| <b>2f</b> | 0.94                         | 0.216 |
| <b>3a</b> | 1.24                         | 0.212 |
| <b>3b</b> | 1.28                         | 0.187 |
| <b>3c</b> | 1.66                         | 0.182 |
| <b>3d</b> | 1.67                         | 0.177 |
| <b>3e</b> | 1.15                         | 0.112 |
| <b>3f</b> | 1.18                         | 0.089 |

<sup>a</sup> FFV: fractional free volume. Calculated using Eq. (2), where occupied volume  $v_0 \approx 1.3v_w$  was estimated by group contribution method.

halogen-containing polymers, further, the chain packing is inhibited by intermolecular repulsion between halogen atoms that have high electron density. Desilylation led to the decrease of FFVs of the membranes. It is noted that the FFVs of membranes of halogen-containing polymers did not significantly decrease. For instance, chlorine-containing membrane **2a** decreased from 0.231 to 0.212, while the FFVs of methyl-containing membranes **2e** and **2f** decreased from 0.207 and 0.216 to 0.112 and 0.089, respectively.

### 3.5. Gas permeability of the polymer membranes

The gas permeability of membranes **2a–f** and **3a–f** to various gases was examined at 25 °C (Table 4). The oxygen permeability coefficient ( $PO_2$ ) of **2a** having two chlorine atoms at the *para* and *meta* positions of the phenyl ring was 550 barrers, which was relatively high among those of poly(diphenylacetylenes) containing siloxy groups; e.g. poly[1-phenyl-2-(4-*tert*-butyldimethylsiloxy)phenylacetylene]:  $PO_2 = 160$  barrers,  $PO_2/PN_2 = 3.2$  [17]; poly[1-(3,4-difluoro)phenyl-2-(*p*-*tert*-butyldimethylsiloxy)phenylacetylene]:  $PO_2 = 370$  barrers,  $PO_2/PN_2 = 2.2$  [20]. Membrane **2b** possessing two chlorine atoms at the *meta* positions of the phenyl ring exhibited the highest gas permeability among the present membranes, whose  $PO_2$  value was 610 barrers. The  $PO_2$  values of **2c** and **2d** with two bromine atoms in the repeating unit were 370 and 410 barrers, respectively, which were also relatively high among poly(diphenylacetylene) derivatives containing siloxy groups. In contrast, membranes **2e** and **2f** displayed somewhat lower  $PO_2$  values (240 and 290 barrers, respectively) than those of **2a–d** having halogen atoms. These results indicate that incorporation of halogen atoms into the polymers is effective to enhance the gas permeability, which is attributable to the loosening of interchain packing by the incorporation of halogen atoms into the polymer, as demonstrated by the increase of FFV.

The  $PO_2$  values of the desilylated membranes **3a–f** were in the range of 5.2–410 barrers. It is considered that this decrease of gas permeability compared to those of the precursors is due to the decrease of FFVs upon desilylation. The  $PO_2$

Table 4  
Gas permeability coefficients ( $P$ )<sup>a</sup> of polymer membranes

| Membrane  | $P$ (barrer) |                |                |                |                 |                 | $PO_2/PN_2$ | $PCO_2/PN_2$ | $PCO_2/PCH_4$  |
|-----------|--------------|----------------|----------------|----------------|-----------------|-----------------|-------------|--------------|----------------|
|           | He           | H <sub>2</sub> | O <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub> | CH <sub>4</sub> |             |              |                |
| <b>2a</b> | 550          | 1100           | 550            | 250            | 2700            | 670             | 2.2         | 11           | 4.0            |
| <b>2b</b> | 580          | 1200           | 610            | 270            | 2900            | 750             | 2.3         | 11           | 3.9            |
| <b>2c</b> | 370          | 780            | 370            | 150            | 1900            | 430             | 2.5         | 13           | 4.4            |
| <b>2d</b> | 420          | 860            | 410            | 180            | 2100            | 500             | 2.3         | 12           | 4.1            |
| <b>2e</b> | 310          | 580            | 240            | 92             | 1200            | 240             | 2.6         | 13           | 5.0            |
| <b>2f</b> | 350          | 650            | 290            | 110            | 1400            | 310             | 2.6         | 13           | 4.5            |
| <b>3a</b> | 640          | 1400           | 410            | 160            | 2200            | 220             | 2.6         | 14           | 10             |
| <b>3b</b> | 370          | 830            | 260            | 98             | 1500            | 170             | 2.7         | 15           | 8.8            |
| <b>3c</b> | 290          | 720            | 200            | 64             | 1300            | 110             | 3.1         | 20           | 12             |
| <b>3d</b> | 250          | 610            | 160            | 50             | 1100            | 86              | 3.2         | 22           | 13             |
| <b>3e</b> | 100          | 160            | 23             | 6.5            | 140             | 9.1             | 3.5         | 22           | 15             |
| <b>3f</b> | 58           | 79             | 5.2            | 1.0            | 49              | – <sup>b</sup>  | 5.2         | 49           | – <sup>b</sup> |

<sup>a</sup> In the units of  $1 \times 10^{-10}$  cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup> (=1 barrer).

<sup>b</sup> Could not be measured.

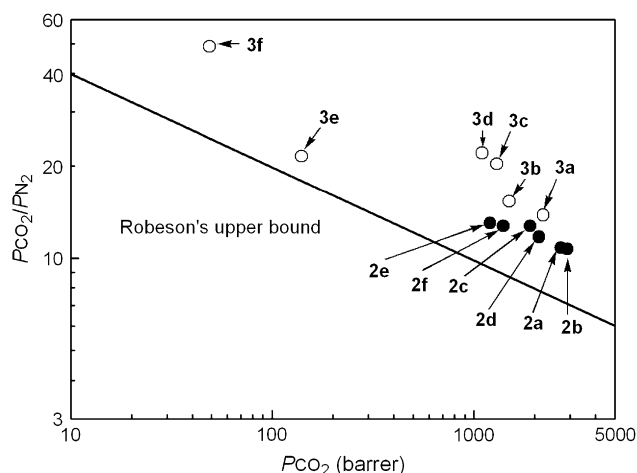


Fig. 4. Relationship between the  $CO_2/N_2$  permselectivity and  $CO_2$  permeability of the membranes before and after desilylation.

values of **3a–e** (23–410 barrers) were higher than that of unsubstituted poly(**1**) ( $PO_2 = 8.0$  barrers), while the  $PO_2$  of **3f** ( $PO_2 = 5.2$  barrers) was somewhat smaller than that of poly(**1**). Further, membranes **3a–d** having halogen atoms showed much higher gas permeability than did **3e** and **3f** with methyl groups. For instance, the  $PO_2$  values of **3a–d** were in the range of 160–410 barrers, while those of **3e** and **3f** were 23 and 5.2 barrers, respectively.

The separation factors of oxygen against nitrogen ( $PO_2/PN_2$ ) of the present polymer membranes were in the range of 2.2–5.2, and they tended to decrease as the  $PO_2$  value increased. These results agree with the general tendency for gas permeation through polymeric membranes. The separation factors of  $CO_2$  against  $N_2$  ( $PCO_2/PN_2$ ) of **3a–f** were 14–49, and more or less increased compared to those of **2a–f** (11–13), which can be explained by the idea that the polar hydroxy groups in the desilylated membranes **3a–3f** have affinity to  $CO_2$ . The  $PCO_2$  values of halogen-containing **3a–d** were in the range of 1100–2200 barrers, which were much higher than those of **3e** and **3f** containing methyl groups ( $PCO_2 = 140$  and 49, respectively). Fig. 4 shows the effects of halogen and methyl substituents on the relationship between  $CO_2/N_2$  selectivity and  $CO_2$  permeability of the membranes. As is clear from this figure, all the present membranes were located above the “upper bound” proposed by Robeson [33].

## 4. Conclusions

In this research, we synthesized a group of poly(diphenylacetylenes) possessing different substituents such as siloxy, halogen, and methyl groups on both phenyl rings. The present polymers had high molecular weights, and exhibited good solubility, high thermal stability, and membrane-forming ability. The polymer membranes with hydroxy groups were obtained by desilylation of the precursor polymer membranes using TFA. The FFV values of halogen-containing polymer membranes were larger, and they showed higher gas permeability than those of the corresponding polymer membranes with

methyl groups irrespective of the presence and absence of the siloxy groups. The present polymer membranes exhibited excellent separation performance for CO<sub>2</sub> against N<sub>2</sub>, and all of them were located above the “upper bound” proposed by Robeson. It is concluded that the incorporation of chlorine and bromine atoms into poly(diphenylacetylenes) enhances the gas permeability of their membranes.

### Acknowledgements

YMH acknowledges Scholarship from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This research was partly supported by a Programmed R&D for CO<sub>2</sub> Sequestration from RITE.

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