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Highly Gas-Permeable Silanol-Functionalized Poly(diphenylacetylene)s: Synthesis, Characterization, and Gas Permeation Property

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ABSTRACT: Diphenylacetylenes having a diisopropylphenoxysilyl group [PhOSi(*i*-Pr)₂C₆H₄C \equiv CC₆H₄R; R =H (1a), SiMe₃ (1b)] were synthesized and then polymerized with TaCl₅/*n*-Bu₄Sn to provide the corresponding poly(diphenylacetylene)s (2a and 2b). These siloxy group-containing polymers afforded tough free-standing membranes by casting from toluene solutions. Treatment of the membranes (2a and 2b) with *n*-Bu₄N⁺F⁻ gave the silanol-functionalized poly(diphenylacetylene)s (3a and 3b). FT-IR spectra of the silanol-functionalized polymers revealed that some their silanol groups were consumed and the polymers were cross-linked via siloxane bond. The oxygen



permeability coefficients of membranes of 2a and 2b were 12 and 26 barrers, respectively. The deprotection of these membranes in DMF lowered membrane densities, and consequently their gas permeability significantly increased. The oxygen permeability coefficients of silanol group-containing membranes (3a and 3b) were 210 and 1300 barrers, respectively. These silanolfunctionalized poly(diphenylacetylene) membranes were found to exhibit very high gas permeability irrespective of the presence of the polar silanol groups in the polymers. Membrane of 3a showed relatively high CO₂ permselectivity as well as high CO₂ permeability.

■ INTRODUCTION

Polyacetylenes with bulky spherical substituents show extremely high gas permeability. This is because the combination of their stiff main chain composed of alternating double bonds and the steric repulsion of the bulky substituents make their membranes sparse.¹ Therefore, poly(substituted acetylene)s are promising materials for gas separation membranes. A large number of poly(substituted acetylene)s have been synthesized so far, and the gas permeability of their membranes has been investigated.¹⁻⁴ The incorporation of functional groups into poly(substituted acetylene)s is of great interest in the various fields due to their potential applications as polymer light-emitting devices, sensors, enantioselective materials, and separation membranes for specific gases. With regard to gas permeability, however, the incorporation of polar functional groups such as hydroxy groups, sulfonic acid groups, and amino groups into the poly(diphenylacetylene)s lead to significant decrease of gas permeability on the polymer membranes.^{5–9} In contrast, poly(substituted acetylene)s bearing silyl groups [-SiR₃] generally exhibit high gas permeability because high local mobility of silyl groups promote gas diffusion in polymer matrix.^{10–13} Therefore, poly(diphenylacetylene) having silanol groups $[-Si(OH)R_2]$ as a functional group is expected to become an interesting polar material with high gas permeability. In addition, polymers carrying silanol groups can be used as a reactive polymer for polymer reaction. Silanol groups are highly reactive, and they can undergo hydrolysis and condensation reaction with other reagents. For instance, they are promising polymers as organic components to prepare organic-inorganic hybrid materials through sol-gel method using tetraethoxysilane.¹

In the present study, we synthesized novel silanol-functionalized poly(diphenylacetylene)s by treating tetrabutyl ammonium fluoride (TBAF) on the membranes of precursor polymers. It is known that poly(diphenylacetylene) having polar groups cannot be obtained by metathesis polymerization with $TaCl_5$ catalysts because the polar groups deactivate active species for metathesis polymerization. Therefore, we synthesized diphenylacetylene possessing protected silanol groups and performed metathesis polymerization of the monomers (Scheme 1). Deprotection of the polymers afforded silanol-containing poly(diphenylacetylene) membranes. The membranes of the silanol-functionalized poly-(diphenylacetylene)s exhibited high gas permeability.

EXPERIMENTAL SECTION

Measurements. The molecular weights and polydispersity ratios of polymers were estimated by gel permeation chromatography (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.

Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 $^\circ C$ under

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Scheme 2. Synthesis of Monomers



1 atm upstream pressure. The permeability coefficient *P* expressed in barrer unit (1 barrer $=10^{-10}$ cm³(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.

Materials. Toluene as a polymerization solvent was purified by distillation over calcium hydride. TaCl₅ (Aldrich, 99.999%) as a main catalyst was used without further purification, while *n*-Bu₄Sn as a cocatalyst was purified by distillation. Phenylacetylene, *p*-bromoiodobenzene, diisopropyldichlorosilane, phenol, tetrabutylammonium fluoride (*n*-Bu₄N⁺F⁻) and common organic solvents were commercially obtained and used without further purification. *p*-Trimethylsilylphenylacetylene was kindly donated by NOF Corporation (Tokyo, Japan). 1-phenyl-2-*p*-bromophenylacetylene¹⁸ and 1-(*p*-trimethylsilyl)phenyl-2-*p*-bromophenylacetylene¹⁹ were synthesized referring to the literatures. Monomers were synthesized according to Scheme 2. The synthesis procedures and analytical data of monomers are as follows.

Synthesis of 1-Phenyl-2-(*p*-diisopropylphenoxysilyl)phenylacetylene (1a). A 500 mL three-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar, and then flushed with nitrogen. A solution of 1-phenyl-2-*p*-bromophenylacetylene (20.4 g, 79.3 mmol) in ether (250 mL) was placed in the flask. Then 1.6 mol/L *n*-Butyllithium hexane solution (49.6 mL, 79.3 mmol) was added dropwise at 0 °C. After addition, the reaction mixture was stirred for 30 min at the same temperature, and then allowed to warm to room temperature. The solution of the produced diphenylacetylene lithium salt was added to a mixture of diisopropyldichlorosilane (14.7 g, 79.3 mmol) and ether (50 mL) dropwise at 0 °C. The reaction mixture was stirred for 3 days at room temperature. After the ether was evaporated, the crude product was dissolved in hexane, and insoluble salt was filtered off. The hexane solution of 1-phenyl-2-(*p*chlorodiisopropylsilyl)phenylacetylene was concentrated at reduced pressure. This product was used in the following reaction without further purification.

Phenol (14.9 g, 157 mmol), imidazole (27.0 g, 397 mmol), and DMF (100 mL) was placed in a three-necked flask equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. A solution of 1-phenyl-2-(*p*-chlorodiisopropylsilyl)phenylacetylene in DMF (100 mL) was added dropwise at 0 °C under nitrogen. The reaction mixture was stirred overnight at room temperature. After ether addition, the solution was washed with water. The ethereal solution was dried over anhydrous sodium sulfate, and then concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent: hexane followed

Scheme 3. Synthesis of Diisopropyl(phenylethynylphenyl)silyl Ether



by a mixture of hexane/chloroform (9/1)) to provide the desired product (15.9 g, overall yield; 46.8%) as white solid. ¹H NMR (CDCl₃, ppm): 7.61 (d, J = 8.0 Hz, 2H, Ar), 7.55–7.53 (m, 4H, Ar), 7.36–7.33 (m, 3H, Ar), 7.20 (t, J = 7.9 Hz, 2H, Ar), 6.94 (t, J = 7.4 Hz, 1H, Ar), 6.90 (d, J = 7.8 Hz, 2H, Ar), 1.43 (sept, J = 7.4 Hz, 2H, SiCH), 1.09 (d, J = 7.5 Hz, 6H, CH₃), 1.04 (d, J = 7.6 Hz, 6H, CH₃). ¹³C NMR (CDCl₃, ppm): 155.6, 134.6, 134.5, 131.6, 130.7, 129.4, 128.3, 124.3, 123.2, 121.3, 119.8, 90.3, 89.4, 17.4, 17.2, 12.7. Anal. Calcd for C₂₆H₂₈OSi: C, 81.2; H, 7.3; O, 4.2; Si, 7.3. Found: C, 81.0; H, 7.5.

Synthesis of 1-(Trimethylsilyl)phenyl-2-(*p***-diisopropylphenoxysilyl)phenylacetylene (1b). The monomer 1b was prepared by the same method as for 1a using** *p***-trimethylsilylphenylacetylene instead of phenylacetylene. Overall yield 54.9%, colorless liquid. ¹H NMR (CDCl₃, ppm):7.61 (d,** *J* **= 7.7 Hz, 6H, Ar), 7.55–7.47 (m, 2H, Ar), 7.20 (t,** *J* **= 7.7 Hz, 2H, Ar), 6.93 (t,** *J* **= 7.3 Hz, 1H, Ar), 6.90 (d,** *J* **= 7.7 Hz, 2H, Ar), 1.43 (sept,** *J* **= 7.5 Hz, 2H, SiCH), 1.08 (d,** *J* **= 7.4 Hz, 6H, CCH₃), 1.04 (d,** *J* **= 7.6 Hz, 6H, CCH₃), 0.28 (s, 9H, Si(CH₃)₃). ¹³C NMR (CDCl₃, ppm): 155.6, 141.2, 134.6, 134.5, 133.2, 130.7, 129.4, 124.4, 123.5, 121.3, 119.8, 90.5, 89.8, 17.4, 17.2, 12.7, -1.2. Anal. Calcd for C₂₉H₃₆OSi₂: C, 76.3; H, 7.9; O, 3.5; Si, 12.3. Found: C, 76.3; H, 8.1.**

Synthesis of Diisopropyl(phenylethynylphenyl)silyl Ether (Model Compound). Diisopropyl(phenylethynylphenyl)silyl ether was synthesized according to Scheme 3. The synthesis procedure and analytical data are as follows.

NaOH (1.0 g, 25 mmol) was put in a flask equipped with a three-way stopcock. After the flask was flushed with nitrogen, NaOH was dissolved in methanol (10 mL). 1-Phenyl-2-(p-diisopropylphenoxysilyl)phenylacetylene (1a) (2.6 g, 6.8 mmol) was placed in another flask equipped with a three-way stopcock and magnetic stirring bar. THF (10 mL) and the NaOH solution were added to it. The mixture was stirred for 18 h at room temperature. After ether addition, the solution was washed with water 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/chloroform (1/1)) to give 1-phenyl-2-(p-diisopropylhydroxysilyl)phenylacetylene (1.6 g, 77%) as white solid.

A solution of 1-phenyl-2-(p-diisopropylhydroxysilyl)phenylacetylene (1.5 g, 4.9 mmol) in THF (50 mL) was placed in a flask equipped with a three-way stopcock and a magnetic stirring bar, and then 1.6 mol/L n-butyllithium hexane solution (3.1 mL, 4.9 mmol) was added at 0 °C. After stirring for 10 min, a solution of 1-phenyl-2-(p-chlorodiisopropylsilyl)phenylacetylene (1.6 g, 4.9 mmol) in THF (2.5 mL) was introduced into the flask at 0 °C. The reaction mixture was stirred for 42 h at room temperature. The mixture was washed with water three times, dried, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent: hexane followed by a mixture of hexane/chloroform (9/1)) to give diisopropyl(phenylethynylphenyl)silyl

ether (0.2 g, 6.8%) as white solid. ¹H NMR (CDCl₃, ppm): 7.65–7.46 (m, 12H, Ar), 7.40–7.35 (m, 6H, Ar), 1.37 (sept, J = 7.4 Hz, 4H, SiCH), 1.08 (d, J = 7.5 Hz, 12H, CH₃), 1.01 (d, J = 7.6 Hz, 12H, CH₃). ¹³C NMR (CDCl₃, ppm): 136.7, 134.2, 131.6, 130.5, 128.3, 128.2, 123.8, 123.3, 90.0, 89.5, 17.7, 17.5, 13.7. Anal. Calcd for C₄₀H₄₆OSi₂: C, 80.2; H, 7.7; O, 2.7; Si, 9.4. Found: C, 79.6; H, 7.7.

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: [monomer] = 0.20 M, $[TaCl_5] = 20$ mM, and $[n-Bu_4Sn] = 40$ mM. A detailed procedure of polymerization is as follows: The monomer solution was prepared in a glass tube. Another glass tube was charged with TaCl₅, *n*-Bu₄Sn, 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 acetone, and its yield was determined gravimetrically.

Membrane Fabrication and Decomposition of Siloxy Groups. Membranes (thickness $30-80 \ \mu m$) of polymers (2a and 2b) were fabricated by casting their toluene solutions (concentration 0.2-0.4 wt %) into Petri dishes. The dish was covered with a glass vessel to slow solvent evaporation (5-6 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. The decomposition of siloxy groups in polymer membrane was carried out using a solution of *n*-Bu₄N⁺F⁻ in CH₃CN or DMF. A detailed procedure is as follows: The membrane of 2a (0.085 g, 0.22 mmol repeating unit) was put into a flask, and then flushed with nitrogen. Another flask was charged with n-Bu₄N⁺F⁻ (0.58 g, 2.2 mmol), and then it was dried under reduced pressure at 45 °C for 48 h. A dried CH₃CN (20 mL) was added into the flask under nitrogen, and then the *n*-Bu₄N⁺F⁻ solution was added to the flask in which the membrane was placed. The decomposition reaction was carried out at room temperature for 24 h under nitrogen. Then, the membrane was immersed in a mixture of methanol/water (9/1) for 6 h followed by in methanol for 24 h. The membrane was dried at room temperature under atmospheric pressure for 24 h. In the case of 2b, the membrane of 2b (0.097 g, 0.21 mmol repeating unit) and n-Bu₄N⁺F⁻ (0.55 g, 2.1 mmol) were used, and the decomposition reaction was carried out at the same condition as for 2a. However, the reaction time was 72 h because 2b showed poor reactivity. The decomposition of siloxy groups was confirmed by the comparison between IR spectra of membranes before and after the reaction.

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

$$ho =
ho_0 imes M_{
m A} / (M_{
m A} - M_{
m L})$$

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:

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

Here 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.²⁰

RESULTS AND DISCUSSION

Polymerization. The polymerizations of monomers (1a and 1b) were carried out using $TaCl_5/n$ -Bu₄Sn catalyst in toluene at 80 °C. The results of polymerizations are summarized in Table 1. Polymerization of 1a was performed at the initial monomer concentrations of 0.20 and 0.030 M to produce the polymers, which contained insoluble products (runs 1 and 2). Toluene-insoluble product was filtered off, and toluene-soluble part was isolated by precipitation into acetone. In the case of the polymerization at $[M]_0 = 0.20$ M, most part of the formed polymer was insoluble, and consequently the soluble polymer

Table	1. Polymeri	zations o	f Monomers	with TaCl ₅ -	- <i>n</i> -Bu ₄ Sn ^a
run	monomer	$[M]_{0}$	yield ^b [%]	$M_{ m w}{}^c$	$M_{\rm w}/M_{\rm n}^{\ c}$
1	1a	0.20	3.9	763 000	3.34
2	1a	0.030	30	1 160 000	3.66
3	1b	0.20	62	931 000	2.47
-					

^{*a*} In toluene at 80 °C for 24 h; [TaCl₅] = 20 mM, [*n*-Bu₄Sn] = 40 mM. ^{*b*} Toluene-soluble and acetone-insoluble product. ^{*c*} Measured by GPC. was obtained in very low yield (3.9%). When the polymerization was operated at $[M]_0 = 0.030$ M, the generation of insoluble polymer was prevented in some degree, and the yield of soluble polymer reached up to 30%. Monomer 1b, which has trimethylsilvl groups, was polymerized at $[M]_0 = 0.20$ M to give a soluble polymer with high molecular weight in good yield (M_w 931 000, yield 62%) (run 3). The significant difference of solubility between 2a and 2b would be attributed to the difference of the geometric structure in the main chain besides the difference of substituent. Monomer 1a has a bulky substituent on a phenyl group adjacent to the triple bond, while monomer 1b has bulky silyl groups on both of the two phenyl groups. The main chain of polymer 2a synthesized by the polymerization of monomer 1a would have high stereoregularity because of the conspicuous difference of the size of substituent compared to that of polymer 2b synthesized by the polymerization of monomer 1b. The metathesis polymerization of substituted acetylene produces the polyacetylene main chain composed of a mixture of cis-form and trans-form.²¹ 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.²² The weight-average molecular weights of all the polymers were very high, and they were in the range of 763 000 to 1 160 000. The property and preparation of membrane of 2a were examined using the polymer sample obtained by the polymerization at lower monomer concentration (run 2).

Decomposition of Phenoxysilyl Groups of Membranes. Free-standing membranes of polymers 2a and 2b were prepared by casting polymers from their toluene solutions. The decomposition of phenoxysilyl groups of membrane 2a was carried out by TBAF in CH₃CN or DMF at room temperature for 24 h, which afforded membrane 3a bearing silanol groups. Figure 1 shows the IR spectra of 2a, membranes after the reaction in CH₃CH and DMF, and diisopropyl(phenylethynylphenyl)silyl



Figure 1. IR spectra of membranes of 2a (a), after decomposition of phenoxysilyl groups in 2a using CH₃CN (b) and DMF (c) as solvent, and model compound 4 (d).



Figure 2. IR spectra of membranes of 2b (a), after decomposition of phenoxysilyl groups in 2b using CH_3CN (b) and DMF (c) as solvent, and model compound 4 (d).

ether (model compound). The IR spectrum of of **2a** shows the absorption at 1150 cm⁻¹ assigned to the asymmetric stretching of Si–O–C in the phenoxysilyl groups (Figure 1a), while no absorption at 1150 cm⁻¹ was observed in the spectra after the phenoxysilyl-decomposition (Figure 1, parts b and c). The characteristic broad peak at 3400 cm⁻¹ in the membranes after the phenoxysilyl-decomposition is attributed to the O–H stretching of the silanol groups. These results represent the completion of silanol. The absorption at 1050 cm⁻¹ derived from Si–O–Si bond appeared after the phenoxysilyl-decomposition of **2a** (Figure 1, parts b and c), which indicates that some silanol groups would form Si–O–Si bonds through hydrolysis.

The decomposition of phenoxysilyl groups of membrane 2b having trimethylsilyl groups was carried out for 72 h under the same condition as for 2a except reaction time. Figure 2 shows the IR spectra of **2b**, membranes after the reaction in CH₃CH and DMF, and diisopropyl(phenylethynylphenyl)silyl ether (model compound 4). The phenoxysilyl-decomposition of membrane **2b** did not proceed in CH₃CN (Figure 2b), whereas the reaction of membrane 2a was achieved. The decomposition of phenoxysilyl groups of 2b was accomplished in DMF, which was confirmed by the absence of the absorption at 1150 cm^{-1} derived from Si-O-C and the presence of the absorption at 3400 cm⁻¹ derived from O–H in the spectrum (Figure 2c). The absorption at 1050 cm⁻¹ derived from Si-O-Si appeared after the phenoxysilyl-decomposition similarly to the case of 2a. The results of IR spectra suggest that membranes of 3a and 3b had silanol groups and cross-linking sites via siloxane bonds. The presumable structure after decomposition is shown in Figure 3.

The conversion of phenoxysilyl groups in decomposition and the content of Si–O–Si bonds within the membranes after the reaction (**3a** and **3b**) were summarized in Table 2. The content of Si–O–Si bonds was calculated from the peak strength at 1050 cm⁻¹ on the basis of the peak at 1380 cm⁻¹ attributed to



Figure 3. Schematic structure of membrane containing silanol groups (**3a**, **b**): (i) represents the silanol group; (ii) represents the cross-linking.

Si-C-H bending. Figure 1d and Figure 2d show the spectrum of diisopropyl(phenylethynylphenyl)silyl ether, which were used as model compound containing 100% of Si-O-Si bonds. The membranes of **3a** obtained by the complete phenoxysilyl-decomposition in CH₃CN and DMF included 20% and 30% of Si-O-Si bonds, respectively. The content of Si-O-Si bonds in membrane **3b** was 20%. The conversion of phenoxysilyl groups in the decomposition of **2b** using CH₃CN was 0%, while that in the reaction of **2a** was 100%. The poor reactivity of membrane **2b** in CH₃CN would be ascribed to the presence of electron-donating trimethylsilyl groups, which lower the electrophilicity at Si atoms of phenoxysilyl groups. The decomposition

of phenoxysilyl of **2b** proceeded completely in DMF, while the reaction did not occur in CH_3CN . This would be accounted for by swelling of membranes in the reaction solvents. To examine the membrane-swelling in solvents, the membranes of **2a** and **2b** were immersed in CH_3CN and DMF at room temperature until the weights of membranes were constant. After removing the excess solvent, the weights of swelling membranes were measured. The degrees of swelling are shown in Table 3. The increases in weight of membrane **2b** after immersion in CH_3CN and DMF were 2.5% and 9.9%, respectively. In other words, the membrane of **2b** swells more effectively in DMF than CH_3CN . In the phenoxysilyl-decomposition using DMF as solvent, the reagent diffuses into membrane more smoothly. The reactivity of polymer membrane would be influenced by membrane-swelling besides activity of reactant.

Solvent Solubility. The solubility of the polymers is summarized in Table 4. The polymers having phenoxysilyl groups (**2a** and **2b**) completely dissolved in common organic solvents such as CCl₄, toluene, CHCl₃, and THF. The phenoxysilyl-decomposition of polymer **2a** produced practically insoluble polymer **3a**

Table 2. Conversion of Si–O–Ph and Content of Si–O–Si Bonds in Membranes After Decomposition of Phenoxysilyl Groups

membrane	reaction solvent	% conversion of Si–O–Ph ^a	% content of Si–O–Si bonds ^a				
3a	CH ₃ CN	100	20				
3a	DMF	100	30				
3b	CH ₃ CN	0	_				
3b	DMF	100	20				
^a Estimated from IR spectra.							

Estimated from IR spectra

Table 3. Swelling of Solvents in Membrane 2a and 2b

	liquid sorption, wt %			
solvent	2a	2b		
CH ₃ CN	4.8	2.5		
DMF	16	9.9		

Table 4. Solubility of Polymers^a

	hexane	CCl_4	toluene	Et_2O	$CHCl_3$	THF	$\rm CH_3OH$	DMF
2a	_	+	+	±	+	+	_	_
2b	_	+	+	\pm	+	+	_	_
3a	_	-	_	_	_	-	_	_
3b	_	-	_	\pm	_	\pm	_	_
^{<i>a</i>} Symbols: +, soluble; \pm , partly soluble; $-$, insoluble.								

in any solvents. Polymer **3b**, which was synthesized by the phenoxysilyl-decomposition of polymer **2b** containing trimethylsilyl groups, did not dissolved completely in any solvents, and it was partly soluble in Et_2O and THF. The poor solubility of membranes of **3a** and **3b** would be ascribed to their cross-linked structures and the combination of hydrophilic silanol groups and hydrophobic diphenylacetylene moiety.

Gas Permeability. The permeability of the membranes of 2a, 2b, 3a, and 3b to various gases was examined at 25 °C, and the CO₂ diffusion coefficients ($D(CO_2)$) and CO₂ solubility coefficients ($S(CO_2)$) were measured by time lag method (Table 5). Unfortunately, the time lags to oxygen and nitrogen permeability measurement were so small that $D(O_2)$ and $D(N_2)$ could not be calculated. The fractional free volume (FFV) of the membranes



Figure 4. Relationship between $P(CO_2)/P(N_2)$ and $P(CO_2)$ for the present polymers and other polyacetylenes bearing polar groups.



Figure 5. Relationship between $P(O_2)/P(N_2)$ and $P(O_2)$ for the present polymers and other polyacetylenes bearing polar groups.

Table 5. Ga	s Permeation Pro	perties and Densities o	of Phenoxysilyl	l Group-Containing	g and Silanol Grou	p-Containing Pol	ymers
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membrane	reaction solvent	$P(O_2)^a$	$P(N_2)^a$	$P(CO_2)^a$	$D(\mathrm{CO}_2)^b imes 10^8$	$S(\rm CO_2)^c \times 10^3$	density [g cm ⁻³]	FFV
2a	_	12	3.9	61	36	17	1.12	0.127
3a	CH ₃ CN	97	32	610	110	58	1.10	d
3a	DMF	210	79	1200	180	66	1.01	d
2b	_	26	7.8	130	100	13	1.09	0.124
3b	DMF	1300	770	4300	1100	40	0.887	d

^{*a*} In the unit of barrer [1 barrer =1 × 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹]. ^{*b*} In the units of cm² s⁻¹. ^{*c*} In the units of cm³(STP) cm⁻³ cmHg. ^{*d*} FFV value could not be calculated because 3a and 3b had cross-linked structures.



Figure 6. Structures of polar-group-containing polyacetylenes (PA1-4).

of 2a and 2b was calculated from the membrane density, and the data are shown in Table 5. However the FFV of 3a and 3b could not be calculated because they have cross-linked structures. The permeability coefficients (P) of 2a to oxygen, nitrogen, and carbon dioxide were 12, 3.9, and 61 barrers, respectively. The P values of 2b were about twice as large as those of 2a. The permeability coefficients of phenoxysilyl group-containing poly-(diphenylacetylene)s are comparable to bulky silyl group-containing poly(diphenylacetylene)s reported previously.²³⁻²⁷ The $D(CO_2)$ value of **2b** was 2.8 times larger than that of **2a**, while the FFVs of 2a and 2b were nearly the same value. FFV value is one of important factors for permeability of membrane, but local mobility of substituents also affects gas permeability. Trimethylsilyl groups in poly(substituted acetylene)s are known to show high local mobility,^{12,13} the high local mobility would enhance gas diffusivity in membrane of 2b.

The phenoxysilyl-decomposition of membrane of 2a increased the gas permeability. The $P(O_2)$, $P(N_2)$, and $P(CO_2)$ of membrane of 3a obtained by the phenoxysilyl-decomposition in CH₃CN were 97, 32, and 610 barrers, respectively. It was expected that the polar silanol groups makes the membrane dense owing to their interaction, but the density of membrane of 3a obtained using CH₃CN was comparable to that of 2a. The decomposition was carried out at a solid state, and partially crosslinking was formed during the reaction. Therefore, the polymer chain packing was inhibited even though polar silanol groups were generated. Membrane of 3a synthesized using DMF as solvent exhibited high gas permeability compared to 3a obtained using CH₃CN. As shown in Table 2, membranes 3a obtained using CH₃CN and DMF had 20% and 30% of Si-O-Si bonds, respectively. The higher degree of cross-linking in membrane of 3a obtained using DMF resulted in lower mobility of polymer chain and hindering dense packing. The density of membrane of 3a obtained using DMF was 1.01 g/cm³, which was much lower than that of 3a obtained using CH₃CN. Membrane of 3b after the phenoxysilyl-decomposition of membrane of 2b bearing trimethylsilyl groups exhibited the high gas permeability, which may result from its low density. The $P(O_2)$, $P(N_2)$, $P(CO_2)$, and density of membrane of 3b were 1300, 770, and 4300 barrers and 0.887 g/cm^3 , respectively. It is noteworthy that the permeability of $\mathbf{3b}$ is one of the highest among all the known polymers bearing polar groups.²⁸

Permselectivity for CO₂/N₂ and O₂/N₂. The permeability coefficients and the separation factors of the present polymer membranes are plotted on a log–log scale (Figures 4 and 5). Figures 4 and 5 contain the data of other polyacetylenes bearing polar groups such as hydroxy,⁶ sulfonic acid,⁸ ethylene glycol,²⁹ and esters³⁰ (PA1–4), whose structures are shown in Figure 6. Generally, more

permeable polymer membranes have less selectivity and vice versa. Robeson's upper bound, which was determined in 2008, represents the experimental limit of the separation performance of polymer membranes.²⁸ Most materials lie below the upper bound, and membranes exhibiting good performance for gas separation were located beside or above the bound. The separation factors of CO₂ against N₂ ($P(CO_2)/P(N_2)$) in membranes of 3a obtained using CH₃CN and DMF were 19 and 15, respectively, which were slightly larger than 16 of membrane of 2a. The phenoxysilyl-decomposition of membrane of 2a led to about 10 or 20 times increase in the CO₂ permeability coefficient without decrease in CO₂/N₂ selectivity, indicating improvement in CO₂ separation performance. It would be due to that the interaction of silanol groups with CO₂ molecules enhances CO₂ solubility in the polymer membrane. From Figures 4 and 5, it is obvious that the present polymers exhibit much higher gas permeability than other polyacetylenes with polar groups.

CONCLUSIONS

A novel functional polyacetylenes have been developed to introduce silanol groups into poly(diphenylacetylene)s. Poly-(diphenylacetylene)s having silanol groups were obtained by treatment of the precursor polymers having siloxy groups with *n*-Bu₄N⁺F⁻. Poly(diphenylacetylene) having siloxy groups were prepared by metathesis polymerization of corresponding diphenylacetylene with TaCl₅. Membranes of silanol-functionalized poly(diphenylacetylene)s exhibited low membrane densities and very high gas permeability. The oxygen permeability coefficient of poly(diphenylacetylene) bearing both silanol and trimethylsilyl groups was 1300 barrers, whose value is the largest among all the substituted acetylene polymers with functional groups. Moreover, silanol-functional poly(diphenylacetylene)s could be used as a novel reactive conjugated polymer for organic/inorganic materials, separation membranes, and light-emitting devices.

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