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FOCUS REVIEW

Synthesis of poly(diphenylacetylene)s bearing various polar groups and their gas permeability

Toshikazu Sakaguchi and Tamotsu Hashimoto

Diphenylacetylenes having a diisopropylphenoxysilyl, 2-bromoethoxy, trimethylsilyl and *t*-butyl groups (*p*-PhOS*i*(*i*-Pr)$_2$C$_6$H$_4$C≡CC$_6$H$_4$-*p*-SiMe$_3$ (1a), *p*-(BrCH$_2$CH$_2$O)C$_6$H$_4$C≡CC$_6$H$_4$-*p*-SiMe$_3$ (1b), PhC≡CC$_6$H$_4$-*p*-SiMe$_3$ (1c), PhC≡CC$_6$H$_4$-*p*-*t*-Bu (1d)) were polymerized to provide the corresponding poly(diphenylacetylene)s (2a–d). Treatment of the membrane of 2a with *n*-Bu$_4$N$^+$F$^-$ gave silanol-functionalized poly(diphenylacetylene) (3a). Fourier transform-infrared spectroscopy spectrum of 3a revealed that some silanol groups were consumed and the polymer was crosslinked via siloxane bond. The membrane of 3a exhibited very high gas permeability irrespective of the presence of polar silanol groups. Substitution of 1-methylimidazole to the membrane of 2b afforded an imidazolium salt-containing poly(diphenylacetylene) (3b (Br$^-$)). Counteranions of 3b (Br$^-$) could be exchanged by the treatment of the membrane with CF$_3$COOK and (CF$_3$SO$_2$)$_2$NLi, and membranes of 3b (TFAc$^-$) and 3b (Tf$_2$N$^-$) were obtained. Introduction of 1-methylimidazole remarkably increased the selectivity ($P_{CO2}/P_{N2}=31$–44). The P_{CO2} values of 3b (Br$^-$), 3b (TFAc$^-$) and 3b (Tf$_2$N$^-$) were 11, 23 and 53 barrers, respectively, indicating that the CO$_2$ permeability increased as the counteranion became bulkier. Polymers 2c and 2d were sulfonated using acetyl sulfate to give sulfonated poly(diphenylacetylene)s (3c and 3d). Polymer 3c exhibited high CO$_2$ permselectivity, and the P_{CO2}/P_{N2} was as large as 54. Polymer 3d with *t*-butyl groups showed relatively large P_{CO2} of 180 barrers and P_{CO2}/P_{N2} of 30.
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INTRODUCTION

Polymeric gas separation membranes gather much attention as they have the possibility of providing solutions to the energy and environmental problems.[1–5] In general, polyacetylenes with bulky spherical substituents exhibit high gas permeability, for example, the P_{O2} values of poly(1-trimethylsilyl-1-propyne) and poly(1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene) reach up to 9000 and 1500 barrers, respectively.[6–9] This is attributable to the combination of the stiff main chain composed of alternating double bonds and the steric repulsion of the bulky substituents leading to the sparse structure of the membranes on the molecular level.[10] Further, poly(1-trimethylsilyl-1-propyne) and poly(1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene) exhibit good solubility in organic solvents, film-forming ability and high thermal stability (the onset temperature of weight loss in air is 450 °C).[8] Thus, poly(1-trimethylsilyl-1-propyne) and poly(1-(*p*-trimethylsilyl)phenyl-2-phenylacetylene) are promising materials for gas separation membranes, and a large number of poly(diphenylacetylene)s have been synthesized so far.[10–13] On the other hand, the incorporation of polar groups into a polymer is of interest as membranes that separate carbon dioxide from light gases (e.g., N$_2$, H$_2$ and CH$_4$), because the polymers containing polar groups tend to show high CO$_2$ permselectivity. This is because polar groups

in the polymer membranes interact with CO$_2$ molecules, and the membranes preferentially dissolve CO$_2$ molecules.[14] This fact suggests that poly(diphenylacetylene)s having polar groups possibly become high-performance membranes, which achieve both high permeability and high permselectivity. Therefore, our aim is to synthesize novel poly(diphenylacetylene)s bearing polar groups. However, poly(diphenylacetylene)s having polar groups cannot be obtained directly by the polymerization of the corresponding acetylene monomers because the Ta catalyst is deactivated by polar groups in the monomer. Based on this fact, we have synthesized poly(diphenylacetylene)s bearing various polar groups by the polymer reaction.

The incorporation of polar functional groups such as hydroxy groups into the poly(diphenylacetylene)s leads to significant decrease of gas permeability on the polymer membranes.[15–17] In contrast, poly(substituted acetylene)s bearing silyl groups (−SiR$_3$) generally exhibit high gas permeability because high local mobility of silyl groups promotes gas diffusion in the polymer matrix.[18,19] 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 the polymer reaction.

Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui, Fukui, Japan
Correspondence: Dr T Sakaguchi, Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui, Bunkyo 3-9-1, Fukui 910-8507, Japan.
E-mail: sakaguchi@matse.u-fukui.ac.jp

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.[20–23]

Room temperature ionic liquids have attracted great interest because of their unique properties, such as nonvolatility, high ionic conductivity, good thermal stability and tunable solvation properties.[24–26] Recently, room temperature ionic liquids are promising as new CO_2 separation media because ionic liquids generally show preferential solubility for CO_2 over other light gases.[27–29] Further, the nonvolatile nature of ionic liquids prevents solvent loss because of evaporation during separation process compared with conventional liquid membranes. To incorporate excellent features of ionic liquids into polymer membranes, some imidazolium salt-containing polymers have been studied.[30–34] However, their CO_2 permeability is relatively low. The low permeability is expected to be overcome through the introduction of imidazolium salts into high-gas-permeable poly(diphenylacetylene).

Sulfonated polymers have been synthesized to develop proton exchange membrane materials.[35–41] They have such strong polar groups, sulfonic acid groups, that they are also expected to show high CO_2 permselectivity. However, most of the sulfonated polymers were designed for fuel cell, and thus they were not gas-permeable polymers. Some sulfonated polyimides containing hexafluoroisopropylidene linkage were synthesized to develop high CO_2-permeable separation membranes, and they are reported to show high CO_2 permselectivity and relatively high CO_2 permeability.[41]

In the present study, we synthesized novel poly(diphenylacetylene)s having silanol groups, imidazolium salts and sulfonic acid groups in the side chains (Scheme 1). First, we synthesized diphenylacetylene monomer having a phenoxysilyl group and performed metathesis polymerization of the monomer. Silanol-containing polymer was obtained by the decomposition of phenoxysilyl groups in the polymer.[42] Second, poly(diphenylacetylene) having bromoethoxy groups was synthesized, and the membranes of poly(diphenylacetylene) having imidazolium salts was obtained by substitution reaction to the polymer membranes.[43] Finally, sulfonated poly(diphenylacetylene)s was synthesized by sulfonation of poly(diphenylacetylene)s bearing trimethylsilyl and *t*-butyl groups.[44,45]

EXPERIMENTAL PROCEDURE

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 (Shimadzu Co., Kyoto, Japan) equipped with three polystyrene gel columns (Shodex KF-802.5 × 1 and A-80M × 2) and a Shimadzu RID-6A refractive index detector (Shimadzu Co.). IR spectra were recorded on a Nicolet MAGNA 560 spectrometer (Hitachi High-Technologies Co., Tokyo, Japan). Thermogravimetric analyses were conducted with Rigaku TG-DTA 8078G1 (Rigaku Co., Tokyo, Japan) under N_2 at a 10 °C min^{-1} heating rate. Gas permeability coefficients of polymer membranes were measured with a Tsukubarikaseiki K-315-N gas permeability apparatus (Tsukubarikaseiki Co., Ibaraki, Japan) at 25 °C under 1 atm upstream pressure. The permeability coefficient P expressed in the unit of barrer (1 barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm 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:

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

where 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. TaCl$_5$ (Aldrich, Tokyo, Japan; 99.999%), as a main catalyst, was used without further purification, whereas *n*-Bu$_4$Sn as a cocatalyst was purified by distillation. The procedures of synthesis of acetylene monomers and polymer reactions were referring to the previous reports.[42–45]

Polymerization

Polymerization was carried out in a glass tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen. A polymerization procedure is as follows: the monomer solution was prepared in a glass tube. Another glass tube was charged with TaCl$_5$, *n*-Bu$_4$Sn and toluene; this catalyst solution was aged at 80 °C for 10 min, and then the 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 obtained polymer was isolated by precipitation into a large excess of methanol, and its yield was determined gravimetrically.

Membrane fabrication

Membranes (thickness 50–60 µm) of polymers **2a** and **2b** were prepared by casting their toluene solutions (conc. 0.1–0.2 wt%) into glass plates. Membranes (thickness 80–120 µm) of polymers **3c** and **3d** were prepared by casting their methanol solutions (conc. 0.2–0.3 wt%) into polytetrafluoroethylene plates. The plate was covered with a glass vessel to slow solvent evaporation (3–5 days). After a membrane was formed, the membrane was peeled off and dried to constant weight under atmospheric pressure at room temperature.

Decomposition of phenoxysilyl group

The decomposition of siloxy groups in polymer membrane was carried out using a solution of *n*-Bu$_4$N$^+$F$^-$ in dimethylformamide. A detailed procedure is as follows: the membrane of **2a** (0.097 g, 0.21 mmol repeating unit) was put into a flask, and then flushed with nitrogen. Another flask was charged with *n*-Bu$_4$N$^+$F$^-$ (0.55 g, 2.1 mmol), and then it was dried under reduced pressure at 45 °C for 48 h. A dried dimethylformamide (20 ml) was added into the flask under nitrogen, and then the *n*-Bu$_4$N$^+$F$^-$ solution was added to the flask in which the membrane was placed. The decomposition reaction was carried out at room temperature for 72 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.

Substitution of 1-methylimidazole

The reaction was carried out at 60 °C using an excess of 1-methylimidazole. A detailed procedure is as follows: a polymer membrane (*ca.* 0.10 g) was put into a flask. A mixture of 1-methylimidazole (7.0 ml) and CH$_3$CN (43 ml) was poured into the flask, and the flask was heated at 60 °C. After 24 h, the membrane was washed by methanol, and then immersed in methanol for 24 h.

Exchange of counteranions

The reaction was carried out at room temperature using an excess of CF$_3$COOK and (CF$_3$SO$_2$)$_2$NLi. A detailed procedure is as follows: a polymer membrane (*ca.* 0.10 g) was put into a flask. A mixture of CF$_3$COOK (1.0 g) and methanol (50 ml) was poured into the flask at room temperature. After 24 h, the membrane was washed by methanol, and then immersed in methanol for 24 h.

Sulfonation

Before the polymer sulfonation, acetyl sulfate was prepared by the reaction of acetic anhydride and sulfuric acid in CHCl$_3$. In a typical sulfonation, polymer **2c** (0.12 g) was dissolved in 20 ml of CHCl$_3$ and purged with nitrogen. The polymer solution was stirred at 40 °C, and acetyl sulfate solution prepared as described above was then slowly added to it. The reaction was terminated after 1 h by precipitating in a large amount of THF. The precipitation was washed several times with THF. The obtained polymer was dried in a vacuum at room
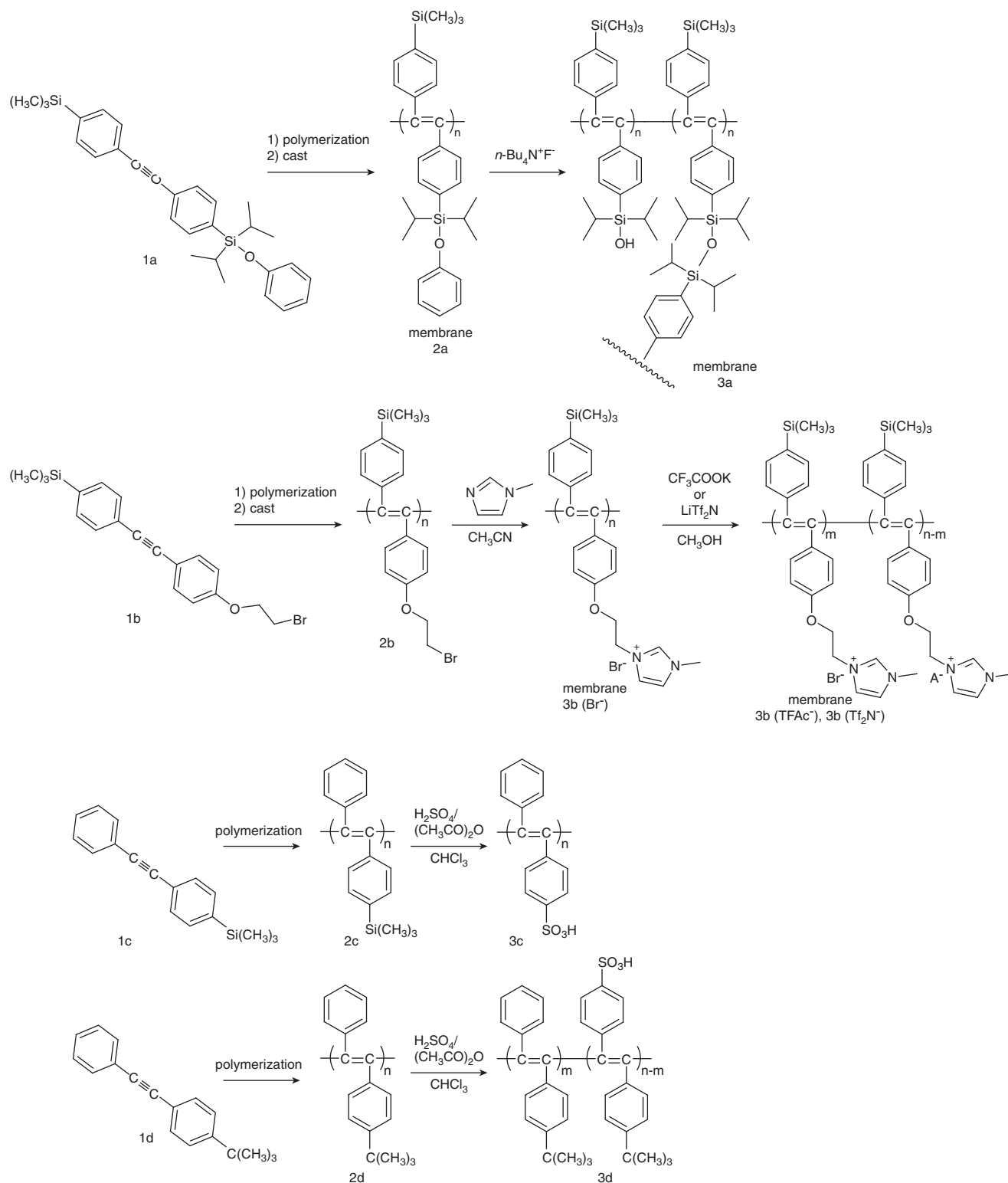
Scheme 1 Synthesis of poly(diphenylacetylene) having various polar groups.

temperature for 24 h. The product was characterized by Fourier transform-infrared spectroscopy, and the degree of sulfonation was calculated by chemical titration: a polymer sample (0.10 g) was dissolved in 100 ml of methanol and the solution was titrated with 0.05 mol l^{-1} ethanolic potassium hydroxide or 0.05 mol l^{-1} aqueous potassium hydroxide using pH instrument.

RESULTS AND DISCUSSION
Polymerization
The polymerizations of acetylene monomers **1a–d** were carried out using TaCl$_5$/*n*-Bu$_4$Sn catalyst in toluene at 80 °C. The results of polymerizations are summarized in Table 1. Monomers **1a** and **1b**

Table 1 Polymerizations of 1a–d with TaCl$_5$/n-Bu$_4$Sn^a

Monomer	[M]$_O$ (M)	Yield (%)	M$_w$^{c}	M$_w$/M$_n$^{c}
		Polymer^b		
1a	0.20	62	931 000	2.47
1b	0.20	66	1 110 000	2.62
1c	0.50	93	7 370 000	3.30
1d	0.50	90	2 220 000	3.42

Abbreviation: GPC, gel permeation chromatography.
^{a}In toluene at 80 °C for 24 h; [TaCl$_5$] = 20 mm, [n-Bu$_4$Sn] = 40 mm.
^{b}Toluene- and methanol-insoluble product.
^{c}Measured by GPC.

polymerized to afford the corresponding polymers **2a** and **2b** in good yields, whose weight-average molecular weights reached up to 931 000 and 1 110 000, respectively. A variety of poly(diphenylacetylene) derivatives have been synthesized by metathesis polymerization using TaCl$_5$ catalyst so far, and most polymers have high molecular weights ($>$300 000), except ones having very bulky substituents.[11,12] Novel acetylene monomers containing a phenoxysilyl group and a bromoethoxy group (**1a** and **1b**) polymerized similarly to other common diphenylacetylenes, suggesting that metathesis polymerizability of diphenylacetylene is hardly influenced by the functional groups of phenoxysilyl and bromoethoxy groups. The polymerizations of **1c** and **1d** provided the corresponding polymers (**2c** and **2d**) with very high molecular weights in high yields, which is the same as the results reported previously.[8,46] All the polymers (**2a–d**) were totally soluble in toluene, CHCl$_3$ and THF, whereas insoluble in hexane, dimethylformamide, dimethyl sulfoxide and methanol.

Decomposition of phenoxysilyl groups
Free-standing membrane of polymer **2a** was prepared by casting polymer from the toluene solution. The decomposition of phenoxysilyl groups of membrane **2a** was carried out using n-Bu$_4$N$^+$F$^-$ in dimethylformamide at room temperature for 72 h, which afforded membrane **3a** bearing silanol groups. Figure 1 shows the IR spectra of **2a**, **3a** and diisopropyl(phenylethynylphenyl)silyl ether (model compound). The IR spectrum of **2a** showed the absorption at 1150 cm^{-1} assigned to the asymmetric stretching of Si$-$O$-$C in the phenoxysilyl groups, whereas no absorption at 1150 cm^{-1} was observed in the spectrum of **3a**. The characteristic broad peak at 3400 cm^{-1} in the membrane after the phenoxysilyl decomposition is attributed to the O$-$H stretching of the silanol groups. These results represent the completion of the decomposition of phenoxysilyl groups and the generation of silanol. The absorption at 1050 cm^{-1} derived from Si$-$O$-$Si bond appeared after the phenoxysilyl decomposition, which indicates that some silanol groups would form Si$-$O$-$Si bonds through hydrolysis.

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 Si$-$C$-$H bending. Figure 1 shows the spectrum of diisopropyl(phenylethynylphenyl)silyl ether, which was used as a model compound containing 100% of Si$-$O$-$Si bonds. It was found that membrane **3a** included 20% of Si$-$O$-$Si bonds.

Substitution of 1-methylimidazole and exchange of counteranions
First, the substitution reaction of 1-methylimidazole to polymer **2b** was carried out in CHCl$_3$ solution. The polymer precipitated as the reaction proceeded, and the obtained polymer did not completely dissolve in any solvents. The insolubility of the polymer is a problem for the
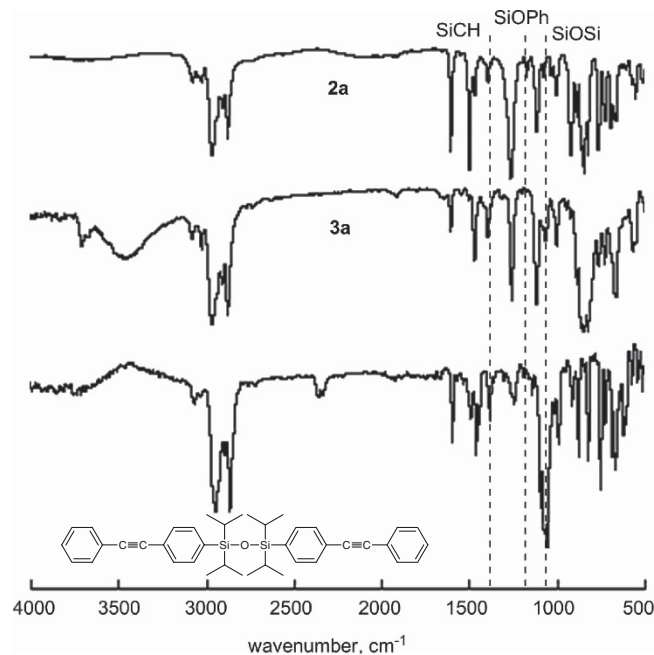

Figure 1 Infrared spectroscopy (IR) spectra of the membranes of **2a**, **3a** and diisopropyl(phenylethynylphenyl)silyl ether.

preparation of membrane. Next, the membrane of polymer **2b** was prepared by solution casting, and the substitution reaction was carried out in the membrane state. Figure 2 shows the IR spectra of membranes before and after the substitution reaction, that is, membranes of **2b** and **3b** (Br$^-$). The IR spectrum of **2b** showed two absorptions at *ca.* 1600 and 1500 cm^{-1} assignable to the stretchings of conjugated C$-$C bonds in the aromatic rings. After substitution reaction, the spectrum of polymer **3b** (Br$^-$) showed another absorption around 1600 cm^{-1} besides the two peaks of aromatic rings. The absorption is assigned to heterocyclic ring, which suggests that 1-methylimidazole was substituted to poly(diphenylacetylene).

To determine the degree of substitution, the content of nitrogen atom was measured by elemental analysis. The content of nitrogen for **3b** (Br$^-$) was 5.90%, whereas the content should be 6.12% if the bromoethoxy group was quantitatively converted to the imidazolium salt. From the result of elemental analysis, the degree of substitution for **3b** (Br$^-$) was determined to be as high as 0.96.

Figure 2 shows the spectra of membranes before and after anion exchange reaction. In the spectrum of **3b** (TFAc$^-$), the absorption at 1700 cm^{-1} characteristic of C=O and the absorption at 1200 cm^{-1} because of C–F bond were observed, whereas the spectrum of **3b** (Br$^-$) does not show such absorptions. In the spectrum of **3b** (Tf$_2$N$^-$), the absorption at 1200 cm^{-1} assigned to C–F bond and the absorptions at 1400 and 1050 cm^{-1} assigned to S=O were observed. These results suggest that the anion exchange reactions proceeded and afforded polymer membranes having TFAc$^-$ and Tf$_2$N$^-$ as counteranions. According to elemental analyses, the contents of fluorine atom for **3b** (TFAc$^-$) and **3b** (Tf$_2$N$^-$) were 9.83% and 15.95%, respectively. When the exchange reactions proceed quantitatively, the contents of fluorine atom for **3a** (TFAc$^-$) and **3a** (Tf$_2$N$^-$) should be 11.31% and 16.98%, respectively. Thus, the conversions of Br$^-$ to the desired anions were calculated as 87% and 94%, respectively. There is not much difference between the conversions of TFAc$^-$ and Tf$_2$N$^-$. Anionic species is generally stabilized by electron-withdrawing group, which may affect the anion exchange reaction.
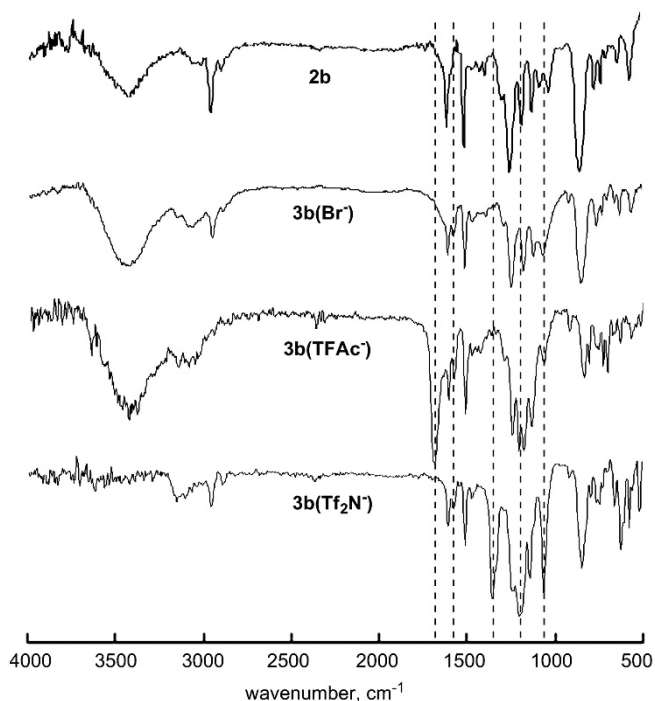
Figure 2 Infrared spectroscopy (IR) spectra of the membranes of 2b, 3b (Br$^-$), 3b (TFAc$^-$) and 3b (Tf$_2$N$^-$).

Figure 3 Infrared spectroscopy (IR) spectra of polymers 2c and 2d and the sulfonated polymers 3c and 3d.

Sulfonation

Figure 3 depicts the IR spectra of polymers (2c and 2d) and their sulfonated polymers (3c and 3d). The spectrum of 3c showed the broad absorption at $1200 \, cm^{-1}$ and the two sharp absorptions at 1060 and $1050 \, cm^{-1}$, which were not observed in the spectrum of 2c. In general, sulfonic acid (SO_3H) shows absorptions at 1350 and $1150 \, cm^{-1}$, and sulfonic acid monohydrate ($[H_3O]^+[SO_3]^-$) shows an absorption at $1200 \, cm^{-1}$.[47] Therefore, it is thought that polymer 3c has the sulfonic acid groups as $[H_3O]^+[SO_3]^-$ rather than SO_3H. The spectrum of 3c, in addition, showed the broad absorption in the range from 3700 to $3200 \, cm^{-1}$ derived from OH groups, which supports that polymer 3c contains sulfonic acid groups. The spectrum of 2c showed the absorptions at 850 and $810 \, cm^{-1}$ derived from the stretching of Si-CH$_3$, and the absorptions completely disappeared after sulfonation. These results indicate that sulfonic acid groups were substituted to trimethylsilyl groups. Same as in 3c, the spectrum of 3d showed the absorptions at ca. 3500, 1200, 1060 and $1050 \, cm^{-1}$ because of SO_3H, indicating that the sulfonated polymer was successfully formed from polymer 2d.

To determine the degree of sulfonation, the chemical titration was operated. The solutions of sulfonated polymers were titrated by $0.05 \, mol \, l^{-1}$ potassium hydroxide solution. From the titration, the degree of sulfonation values of 3c and 3d were estimated to be 1.01 and 0.83, respectively.

Thermal properties

The thermal stability of all the polymers in the present study was examined by thermogravimetric analysis under N_2 (Figure 4). Thermal decomposition temperature (T_d) of 2a was approximately 400 °C, indicating good thermal stability. Polymer 2b also exhibited high thermal stability, but the decomposition started at 220 °C. This would be attributed to the dehydration of silanol groups. The T_d's of 3a, 3b (Br$^-$) and 3b (Tf$_2$N$^-$) were over 300 °C, whereas that of 3b (TFAc$^-$)
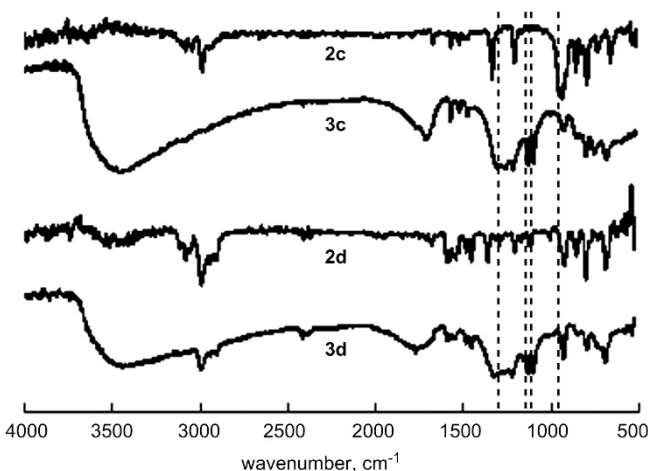
was as low as 180 °C. Polymers 2c and 2d showed high thermal stability, and their T_d's were 430 °C. However, the T_d's of the sulfonated polymers 3c and 3d were 200 °C and 250 °C, respectively. The decomposition of sulfonic acid groups would occur at relatively low temperature.

Gas permeability

The permeability of the membranes of 2a–d and 3a–d to various gases was examined at 25 °C (Table 2). The permeability coefficients (P) of 2a to oxygen, nitrogen and carbon dioxide were 12, 3.9 and 61 barrers, respectively, whose values are comparable with bulky silyl group-containing poly(diphenylacetylene)s reported previously.[48–52] The phenoxysilyl decomposition of the membrane of 2a markedly increased the gas permeability, and the P_{O2}, P_{N2} and P_{CO2} of the membrane of 3a were 1300, 770 and 4300 barrers, respectively. This is supported by the decrease of membrane density ($1.09 \, g \, cm^{-3}$ for 2a and $0.887 \, g \, cm^{-3}$ for 3a). It was expected that the polar silanol groups makes the membrane dense owing to their interaction. The decomposition was carried out at a solid state, and partial crosslinking was formed during the reaction. Therefore, the polymer chain packing was inhibited even though polar silanol groups were generated. It is noteworthy that the permeability of 3a is one of the highest among all the known polymers bearing polar groups.[53]

The P_{O2}, P_{N2} and P_{CO2} of polymer 2b were 46, 16 and 250 barrers, respectively. Compared with poly(1-trimethylsilyl-1-propyne) and poly(1-(p-trimethylsilyl)phenyl-2-phenylacetylene)), polymer 2b exhibited low gas permeability, which can be attributed to the flexible bromoethoxy group. It is known that high gas permeability of poly(substituted acetylene)s is in many cases based on spherical substituents, whereas the presence of long flexible side chains either hardly affects gas permeability or rather decreases it.[10] The substitution reaction of 1-methylimidazole caused a decrease in gas permeability and a pronounced increase in CO_2 permselectivity. The decrease in gas permeability was originated from the decrease of diffusion and solubility coefficients (Table 3). These decreases are considered because the intermolecular interaction is strengthened by polar imidazolium salts. The CO_2/N_2 separation factor (P_{CO2}/P_{N2}) of 3b (Br$^-$) was 44, which is much larger than that of 2b ($P_{CO2}/P_{N2} = 16$). The diffusivity selectivity (D_{CO2}/D_{N2}) of 3b (Br$^-$) and 2b were 0.70 and 0.92, respectively, indicating that imidazolium salts in poly(diphenylacetylene) do not critically affect diffusivity selectivity.
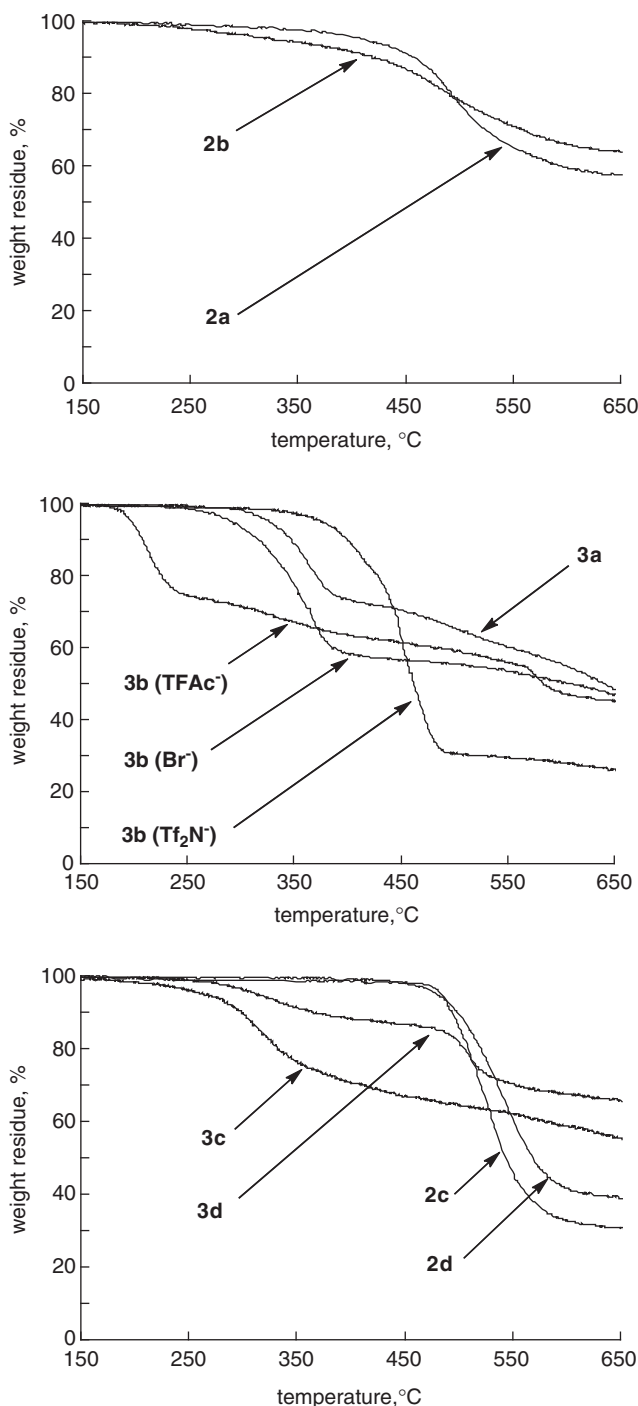
Figure 4 Thermogravimetric analysis (TGA) thermograms of the present polymers under N_2.

Table 2 Gas permeability coefficients and separation factors of membranes

Membrane	P_{O2}[a]	P_{N2}[a]	P_{CO2}[a]	P_{O2}/P_{N2}	P_{CO2}/P_{N2}
2a	26	7.8	130	3.3	17
3a	1300	770	4300	1.7	5.6
2b	46	16	250	2.9	16
3b (Br$^-$)	1.5	0.25	11	6.0	44
3b (TFAc$^-$)	3.2	0.67	23	4.8	34
3b (Tf$_2$N$^-$)	6.3	1.7	53	3.7	31
2c	1800	960	6700	1.9	7.0
3c	0.63	0.072	3.9	8.8	54
2d	2100	890	6500	2.4	7.3
3d	31	6.0	180	5.2	30

Abbreviation: STP, standard temperature and pressure.
[a]In the unit of barrer (1 barrer $= 1 \times 10^{-10}$ cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}).

Table 3 Gas diffusion and solubility coefficients

	D_{N2}[a]	D_{CO2}[a]	D_{CO2}/D_{N2}	S_{N2}[b]	S_{CO2}[b]	S_{CO2}/S_{N2}
2b	78	72	0.92	2.1	35	17
3b (Br$^-$)	6.3	4.4	0.70	0.37	24	65
3b (TFAc$^-$)	6.8	5.1	0.75	0.99	45	45
3b (Tf$_2$N$^-$)	21	18	0.86	0.81	29	36

Abbreviation: STP, standard temperature and pressure.
[a]In the units of 1×10^{-8} cm^2 s^{-1}.
[b]In the units of 1×10^{-3} cm^3 (STP) cm^{-3} cm Hg.

and **3b** (Tf$_2$N$^-$) were 23 and 53 barrers, respectively. For instance, TFAc$^-$ is bulkier than Br$^-$, and the polymer chain packing is thought to be looser with the TFAc$^-$ counteranion owing to steric effect. Tf$_2$N$^-$ is an even bulkier counteranion, and **3b** (Tf$_2$N$^-$) exhibited the highest permeability among the imidazolium salt-containing polymers. The CO_2/N_2 permselectivity and solubility selectivity gradually decreased as the bulkiness of the counteranion increased. This is because the bulkier counteranions weaken the effect of the ionic functionality.

The gas permeability coefficients of membranes before sulfonation (**2c** and **2d**) were almost the same as the data reported in previous papers;[9,42] poly(diphenylacetylene)s bearing spherical bulky trimethylsilyl or *t*-butyl groups exhibited high gas permeability. Sulfonation of poly(diphenylacetylene)s led to a significant decrease of gas permeability. For instance, the P_{O2}, P_{N2} and P_{CO2} values of **3c** were 0.63, 0.072 and 3.9 barrers, respectively, which are three or four orders of magnitude smaller than those of **2c**. The decrease of gas permeability upon sulfonation can be accounted for by the strong intermolecular interaction between high polar sulfonic acid groups. In contrast, the P_{CO2}/P_{N2} of **3c** was as high as 54, which is the highest among the present polymers. The high CO_2 permselectivity of sulfonated poly(diphenylacetylene)s is thought to be due to the increase in the solubility of CO_2 into polymer matrix, because the CO_2 molecule strongly interacts with sulfonic acid groups. Interestingly, polymer **3d** exhibited relatively high gas permeability and possesses sulfonic acids. Polymer **3d** has spherical bulky *t*-butyl groups even after sulfonation. The bulky substituents would prevent polymer chain packing by the steric repulsion. For the application to batteries and fuel cells, polymer materials that have both proton-conducting and oxygen-permeable properties are desired. Therefore, polymer **3d** is an interesting material as polymer electrolytes for batteries and fuel cells.

On the other hand, the S_{CO2}/S_{N2} of **3b** (Br$^-$) and **2b** were 66 and 17, respectively, which manifests that the solubility selectivity (S_{CO2}/S_{N2}) is largely enhanced by substitution of 1-methylimidazole to poly (diphenylacetylene). Thus, the significant increase in the CO_2 permselectivity is based on solubility selectivity, which is, in turn, attributable to the strong interaction of the imidazolium salt with the CO_2 molecule.

The exchange of counteranions to bulkier ones resulted in increases of gas permeability. Thus, the P_{CO2} values of **3b** (TFAc$^-$)

CONCLUSIONS

A novel polyacetylene has been developed to introduce functional groups into poly(diphenylacetylene)s. Poly(diphenylacetylene)s having silanol groups were obtained by treatment of the precursor polymers having phenoxysilyl groups with n-Bu$_4$N$^+$F$^-$. Membranes of silanol-functionalized poly(diphenylacetylene)s exhibited very high gas permeability. The P_{O2} value of poly(diphenylacetylene) bearing both silanol groups and crosslinked siloxane moieties was 1300 barrers, whose value is the largest among all the substituted acetylene polymers with functional groups. Poly(diphenylacetylene)s having imidazolium salts were synthesized by substitution of 1-methylimidazole to bromoethoxy groups. Exchange of counteranions was achieved quantitatively, and poly(diphenylacetylene)s with Br$^-$, TFAc$^-$ and Tf$_2$N$^-$ as counteranions was obtained. Membranes of imidazolium salt-containing poly(diphenylacetylene)s exhibited high CO_2/N_2 permselectivity ($P_{CO2}/P_{N2} = 31$–44) because of their high CO_2/N_2 solubility selectivity. Bulky counteranions prevented polymer chains from packing together, and thus the permeability coefficients of membranes became larger in the order of Br$^-$ < TFAc$^-$ < Tf$_2$N$^-$. Poly(diphenylacetylene)s having sulfonic acid groups were successfully obtained using acetyl sulfate as a reactant. The sulfonated poly(diphenylacetylene) having t-butyl groups showed high permeability and high permselectivity for CO_2. Sulfonation of poly(diphenylacetylene) having trimethylsilyl groups gave desilylated and sulfonated poly(diphenylacetylene), which displayed pretty high CO_2 permselectivity.

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Dr Toshikazu Sakaguchi was born in Osaka, Japan in 1977. He received his Doctoral degree of Engineering in 2006 from Kyoto University under the supervision of Professor Toshio Masuda. He is currently an Associate Professor at the Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui. His research interests include transition metal-catalyzed polymerization, gas separation membranes, luminescence materials and synthesis of conjugated polymers including substituted polyacetylenes, poly(*p*-phenyleneethynylene)s and poly(*p*-phenylenevinylene)s. He was a recipient of Award for Encouragement of Research in Polymer Science, the Society of Polymer Science, Japan in 2011.

Dr Tamotsu Hashimoto was born in Kyoto, Japan in 1960. He received his B.S. degree in chemistry from Doshisha University in 1983 and his M.S. degree in chemistry from Kyoto Institute of Technology in 1985. He received his Ph.D degree in polymer chemistry from the Kyoto University in 1991 under the direction of Professor Toshinobu Higashimura and Professor Mitsuo Sawamoto. He started his academic carrier at the Shiga Prefectural Junior College in 1987 and moved to the University of Fukui as Associate Professor in 1991. He is currently Professor of Department of Materials Science and Engineering, Graduate School of Engineering, University of Fukui. His research interests include controlled polymerization and the development of degradable polymers for chemical recycling.