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Desilylation of copolymer membranes composed of poly[1-(*p*-trimethylsilyl)phenyl-2-(*p*-trimethylsilyl)phenylacetylene] for improved gas permeability

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Efficient gas-separation systems comprising gas-permeable membranes are important for energy conservation in various industrial applications. Herein, high-molecular-weight copolymers (**2ab** and **2ac**) were synthesized in good yields by the copolymerization of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**1a**) with 1-phenyl-2-(*p*-*tert*-butyl)phenylacetylene (**1b**) and 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**1c**) in various monomer feed ratios using TaCl$_5$–*n*-Bu$_4$Sn. Tough membranes were obtained by solution casting. The copolymers exhibited very high gas permeabilities (P_{O_2}: 1700–3400 barrers). Desilylation of **2ac** membranes decreased the gas permeability, but desilylation of **2ab** membranes resulted in a significant increase in the gas permeability. The highest oxygen permeability coefficient obtained was 9300 barrers, which was comparable to that of poly(1-trimethylsilyl-1-propyne), a polymer known to have the highest gas permeability.

Introduction

Efficient gas-separation systems have been extensively investigated for various industrial applications. Gas-permeable polymer membranes have attracted significant attention as they can simplify the systems and allow energy conservation.[1,2] In recent decades, substituted polyacetylenes have been intensively examined for their practical application as gas-permeable materials.[3–6] Polyacetylenes with bulky spherical substituents show large excess free volume and high gas permeabilities because of the presence of rigid main chains comprising alternating double bonds and the steric repulsion of the bulky substituents that inhibits an effective polymer chain packing.[7,8] For instance, poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits the highest gas permeability, where the oxygen permeability coefficient (P_{O_2}) is greater than 9000 barrers.[3] However, aliphatic polyacetylenes such as PTMSP are degraded by heat and oxidation.

In contrast, diarylacetylene polymers are tolerant toward pyrolysis and oxidation. Poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] (PTMSDPA) and poly[1-phenyl-2-(*p*-*tert*-butyl)phenylacetylene] (PTBDPA) are the examples of diarylacetylene polymers, and show high P_{O_2} values of up to 1000 barrers.[9–12] Therefore, these polymers are promising materials for gas separation membranes. Hu *et al.* synthesized polymethylated indan-containing poly(diphenylacetylene), which is the most gas-permeable polymer ever

recorded to date.[13,14] Fukui *et al.* incorporated fluorenyl groups into poly(diarylacetylene) to improve gas permeability,[15] and the highest P_{O_2} value among fluorenyl-containing poly(diarylacetylene)s is 9800 barrers.[16] The incorporation of naphthyl,[17] SiMe$_3$,[5,6,18] *tert*-butyl,[18,19] halogen[20–22] into diarylacetylene is also often considered as a way to obtain high gas-permeable materials, but their gas permeability still lower than PTMSP.

In this study, the copolymerization of **1a** with a *tert*-butyl-containing monomer (**1b**) and trimethylsilyl-containing monomer (**1c**) in various feed ratios was accomplished (Scheme 1). Free-standing membranes were fabricated from the resultant copolymers, and the desilylation of the membranes was performed using a mixture of trifluoroacetic acid/hexane. Gas permeabilities of the copolymer membranes were studied.

Our research group previously reported that the copolymers of TMSDPA and TBDPA showed higher gas permeabilities than those of the homopolymers, PTMSDPA and PTBDPA.[18] Furthermore, the desilylation of the copolymer membranes enhanced the gas permeability. This suggested that some micro-scale voids were generated by the elimination of silyl groups. Therefore, the desilylation of the copolymers of 1-(*p*-trimethylsilyl)phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**1a**), with two trimethylsilyl groups, is expected to further improve the gas permeability.
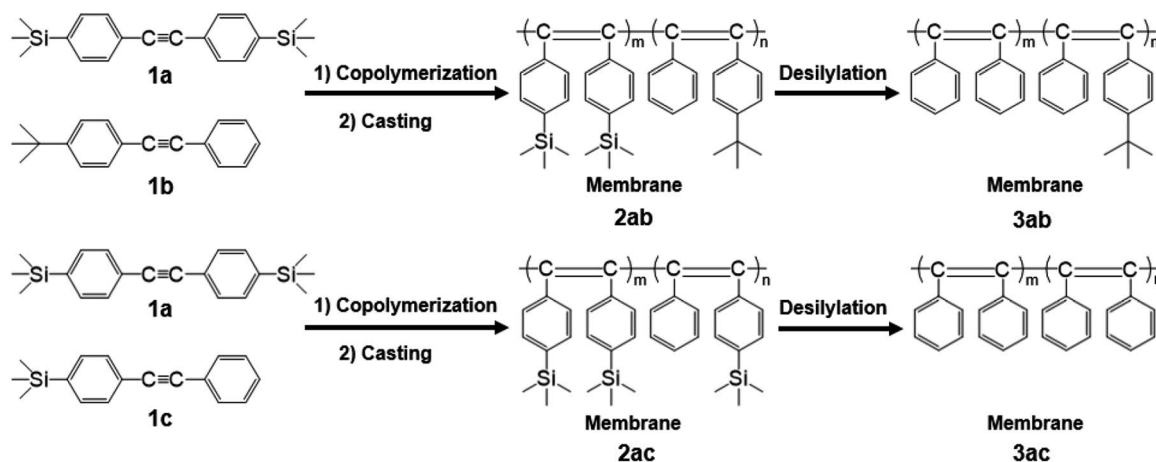
Experimental

Materials

The polymerization solvent, toluene (Fujifilm Wako Pure Chemical Co., Ltd., Osaka, Japan), was purified twice by

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Scheme 1 Synthetic schemes for copolymers and desilylated copolymers.

distillation in the presence of CaH_2 (Fujifilm Wako Pure Chemical Co., Ltd.). The main catalyst, $TaCl_5$ (99.999%, Sigma-Aldrich, St. Louis, Missouri, USA), was used without further purification, while the cocatalyst, n-Bu_4Sn (Fujifilm Wako Pure Chemical Co., Ltd.), was used after distillation in the presence of CaH_2. Phenylacetylene (Sigma-Aldrich), 1,4-dibromobenzene, 1-bromo-4-*tert*-butylbenzene, triethylamine, triphenylphosphine, copper(I) iodide, dichlorobis(triphenylphosphine)palladium(II), n-butyllithium, trifluoroacetic acid (TFA), chlorotrimethylsilane, 2-methyl-3-butyn-2-ol, sodium hydride, aqueous sodium nitrate, and other common solvents (Fujifilm Wako Pure Chemical Co., Ltd.) were used without further purification. 1-(p-Trimethylsilyl)phenyl-2-(p-trimethylsilyl)phenylacetylene (**1a**),[23] 1-phenyl-2-(p-*tert*-butyl)phenylacetylene (**1b**),[11] and 1-phenyl-2-(p-trimethylsilyl)phenylacetylene (**1c**)[10] were synthesized according to the methods reported in literature.

Measurements

The molecular weight distribution (MWD) of the copolymers was measured by gel permeation chromatography (GPC) in $CHCl_3$ (at a 1.0 mL min^{-1} flow rate) at 40 °C on a Shimadzu LC-10AD chromatography system (Shimadzu Corp., Kyoto, Japan) equipped with three polystyrene gel columns (Shodex K-804L, K-805L, and K-807L; Shodex, Tokyo, Japan) and a Shimadzu RID-6A refractive index detector (Shimadzu Corp.). The weight-average molecular weight (M_w) and polydispersity ratio were calculated from the chromatograms based on the polystyrene calibration. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on the Jeol ECX-500 instrument (JEOL Ltd., Tokyo, Japan) in $CDCl_3$ at room temperature. IR spectra were recorded on a Nicolet IS 5 spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). The thickness of membrane was measured using a micrometer, and an average of ten points on each membrane was considered.

Gas permeability was measured using a Rikaseiki K-315-N gas permeability apparatus equipped with an MKS Baratron detector (MKS Instruments, Inc., Andover, Massachusetts, USA)

at 25 °C. The downstream side of the membrane was evacuated at 0.2–1.0 Pa, while the upstream side was filled with a gas at approximately 1 atm (10^5 Pa). The increase in pressure in a downstream receiving vessel was measured. The permeability coefficient P expressed in barrers [1 barrer = 1×10^{-10} cm^3 (STP) $\times$ cm/(cm^2 $\times$ sec $\times$ cmHg)] was calculated from the slopes of the time–pressure curves in the steady state where Fick's law was obeyed. The diffusion coefficient (D) 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 the time–pressure curve to the time axis. The solubility coefficient (S) was calculated using the equation, $S = P/D$.

The density of membrane was determined by hydrostatic weighing using a Mettler Toledo balance (Mettler Toledo, Columbus, Ohio, USA) and a density determination kit. In this method, a liquid with a known density (ρ_0) is required, and the membrane density (ρ) is obtained by the following equation:

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

where, M_A is the weight of the membrane in air and M_L is the weight of the membrane in an auxiliary liquid. Aqueous sodium nitrate was used as the auxiliary liquid.

Copolymerization

Copolymerization was carried out in a Schlenk tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen with the following reagent concentrations: [**1a**] + [**1b** or **1c**] = 0.20 M, [$TaCl_5$] = 20 mM, and [n-Bu_4Sn] = 80 mM. A detailed procedure for copolymerization is described as follows. The monomer solution was prepared in a Schlenk tube by mixing the monomers and dry toluene. An additional Schlenk tube was charged with $TaCl_5$, n-Bu_4Sn, and dry toluene; this catalyst solution was aged at 80 °C for 10 min. Then, the monomer solution was added to the catalyst solution. After 24 h,

copolymerization was quenched with a small amount of methanol. The resulting copolymer was isolated by precipitation into excess methanol. The polymer yield was determined gravimetrically.

Membrane fabrication and desilylation

The membranes (thickness: *ca.* 30–130 μm) of the copolymers were prepared by casting from toluene solution of the copolymers (0.15–0.50 wt%) into the Petri dishes. The dish was covered with a glass vessel to decrease the evaporation rate of the solvent (3–5 d). After the formation of the membrane, it was immersed in methanol for 24 h, followed by drying for 24 h at 25 °C. The desilylation of membranes was performed using the method described in literature.[24] The detailed procedure is described as follows. The membrane was immersed in a mixture of trifluoroacetic acid and hexane (volume ratio 1 : 1) at room temperature for 24 h. To remove the residual impurities in the polymer matrix, the membrane was immersed in acetone followed by methanol at room temperature for 24 h. Thereafter, it was dried under atmospheric pressure at room temperature for 24 h. The completion of the reaction was confirmed by comparing the IR spectra of the copolymers before and after desilylation.

Results and discussion

Copolymerization

It is well known that $TaCl_5/n$-Bu_4Sn is the best catalyst for the metathesis polymerization of diphenylacetylene derivatives to afford high-molecular-weight polymers.[25–27] Therefore, in this study, the copolymerization of **1a** with **1b** and **1c** was performed using $TaCl_5/n$-Bu_4Sn catalyst at 80 °C in toluene for 24 h under nitrogen. The results of copolymerization were summarized in Table 1.

The copolymerization of **1a** with **1b** in the feed ratio of 1 : 4 afforded the copolymer, **2ab(1:4)**, whose M_w was up to 902 000.

The copolymerizations of **1a** with **1b** in the feed ratios of 1 : 2, 1 : 1, 2 : 1, and 4 : 1 resulted in the production of copolymers, **2ab(1:2)**, **2ab(1:1)**, **2ab(2:1)**, and **2ab(4:1)**, respectively, in good yields. The molecular weights of **2ab(1:2)**, **2ab(1:1)**, and **2ab(2:1)** were very high, but that of **2ab(4:1)** could not be measured by GPC because **2ab(4:1)** was insoluble in all solvents. The copolymerizations of **1a** with **1c** in the feed ratios of 1 : 4, 1 : 2, 1 : 1, and 2 : 1 under the same conditions afforded the copolymers [**2ac(1:4)**, **2ac(1:2)**, **2ac(1:1)**, and **2ac(2:1)**, respectively] in high yields with high molecular weights ($M_w = 872\,000$–$2\,540\,000$). Similar to **2ab(4:1)**, the copolymer **2ac(4:1)** was obtained in good yield, but the solubility was poor.

Fabrication of copolymer membranes and their solubility

Tough free-standing membranes of **2ab** and **2ac** were fabricated by casting the copolymers from their toluene solutions, except **2ab(4:1)** and **2ac(4:1)**, because of their insolubility. The desilylation was carried out using trifluoroacetic acid and hexane (volume ratio 1 : 1) to afford the desilylated membranes (**3ab** and **3ac**).

To verify the completion of the desilylation of copolymer membranes, IR measurements were carried out. The IR spectra of the membranes of **2ab(1:2)**, **2ac(1:2)**, and the desilylated analogues, **3ab(1:2)** and **3ac(1:2)**, were shown in Fig. 1. The spectra of **2ab(1:2)** and **2ac(1:2)** showed the peaks at 1250 cm^{-1}, assigned to the stretching of SiC–H bond, and 1120 cm^{-1} corresponding to the vibration of Si–C bond. No absorptions at 1250 cm^{-1} and 1120 cm^{-1} were observed in the spectra after desilylation (Fig. 1, **3ab** and **3ac**). The results suggest the completion of the desilylation reaction.

The solubilities of the copolymers were summarized in Table 2. Copolymers **2ab** and **2ac** showed the same solubility, and completely dissolved in relatively low polarity solvents such

Table 1 Copolymerization of **1a** with **1b** and **1c** by $TaCl_5$–n-Bu_4Sn^a

	Feed ratio	Copolymer[b]		
	(**1a** : **1b** or **1c**)	Yield (%)	$M_w{}^c$ (g mol^{-1})	$M_w/M_n{}^c$
1b	1 : 4	91	902 000	4.40
	1 : 2	84	1 260 000	4.05
	1 : 1	81	546 000	4.55
	2 : 1	73	820 000	4.03
	4 : 1	71	Insoluble	
1c	1 : 4	87	1 770 000	3.57
	1 : 2	81	2 540 000	2.13
	1 : 1	88	1 350 000	2.11
	2 : 1	90	872 000	2.62
	4 : 1	80	Insoluble	

[a] In toluene at 80 °C for 24 h; [**1a**] + [**1b** or **1c**] = 0.20 M, [$TaCl_5$] = 20 mM, [n-Bu_4Sn] = 40 mM. [b] Methanol-insoluble product. [c] Measured by GPC ($CHCl_3$).
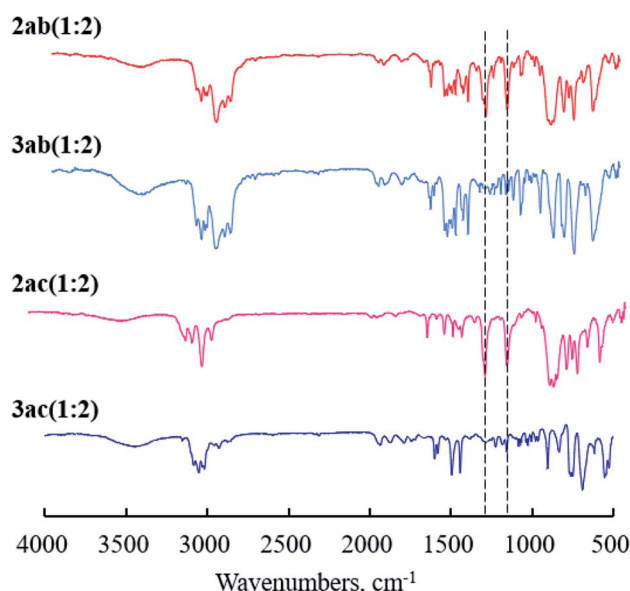

Fig. 1 IR spectra of the copolymers of **2ab(1:2)**, **3ab(1:2)**, **2ac(1:2)**, and **3ac(1:2)**.

as toluene, chloroform, and tetrahydrofuran. However, **2ab(4:1)** and **2ac(4:1)** were insoluble in all solvents. Homopolymer of **1a** is known to be insoluble in all solvents.[23] Copolymers **2ab(4:1)** and **2ac(4:1)** mainly consist of the **1a** component and therefore showed a similar solubility behavior as that of the homopolymer of **1a**. Similar to **2ab**, the desilylated polymer **3ab** was soluble in low polarity solvents. However, **3ac** was not soluble in any solvent. This variation in solubility before and after desilylation should come from the substituent of *tert*-butyl groups. Table 2 showed the substitution ratios for the phenyl groups. When the ratio was zero or more than 90%, copolymers were insoluble. Therefore, an appropriate ratio of substituents is necessary for the solubility of poly(diphenylacetylene).

Gas permeability and density of copolymer membranes

The permeability coefficients (P) of the membranes of **2ab**, **2ac**, **3ab**, and **3ac** toward various gases were measured at 25 °C after conditioning the membranes by immersing in methanol for 24 h and drying to constant weight at room temperature for an additional 24 h (Table 3). The density of the copolymer membranes are shown in Table 3.

High gas permeabilities were observed for the membranes of **2ab** and **2ac**. The P_{O_2} values of **2ab** were in the range of 1700–2900 barrers, which were higher than that of PTBDPA (P_{O_2}: 1100 barrers). Copolymer **2ab(1:2)** exhibited the highest gas permeability and its P_{O_2} value was 2900 barrers, which was 2.6 times as that of PTBDPA. Similarly, **2ac** showed a higher gas permeability than that of PTMSDPA. The P_{O_2} values of **2ac** were in the range of 1800–3400 barrers. The higher gas permeability of copolymers may be due to their asymmetrical structure of the repeating unit that generates micro-scale voids. It is obvious that incorporation of trimethylsilyl group or *tert*-butyl group into poly(diphenylacetylene)s in the way of copolymerization is effective to enhance the gas permeability.

The CO_2 and N_2 permeabilities of **2ab** and **2ac** were higher than those of PTBDPA and PTMSDPA, as well as the corresponding oxygen permeabilities. This suggests that the membranes of **2ab** and **2ac** have large free volumes. Accordingly, the membranes of **2ab** and **2ac** showed low densities of 0.787–0.902 g cm^{-3}.

The desilylated membranes of **3ab** exhibited significantly higher oxygen permeabilities than those of **2ab**. The membrane density reduced upon desilylation. This indicates that the spaces occupied by the silyl groups were retained as micro-scale voids after desilylation due to the steric hindrance of *tert*-butyl groups. It is suggesting that the incorporation of *tert*-butyl groups prevents the chain packing effectively to enhance the gas permeability. Notably, **3ab(1:2)** exhibited extremely high permeability and its P_{O_2} value reached up to 9300 barrers, which was the highest value observed among all synthetic polymers. Contrary to **3ab**, the desilylated membranes of **3ac** showed lower gas permeabilities than those of the membranes of **2ac**. The decrement of gas permeability through desilylation was due to the elimination of spherical bulky trimethylsilyl groups that caused the membrane to become dense. The P_{O_2} values of **3ac** were in the range of 980–1080 barrers. These were similar to the P_{O_2} value of 900 barrers for poly(1-phenyl-2-phenylacetylene), which was formed by the desilylation of PTMSDPA.[18] The densities of the membranes increased after desilylation. These results indicate that *tert*-butyl groups play an important role in the generation of micro-voids through membrane desilylation.

Interestingly, the P_{O_2} values of **3ab** were significantly higher than those of desilylated poly(TMSDPA–TBDPA) reported in our previous work,[18] irrespective of the similarity in chemical structures (Fig. 2). For example, the P_{O_2} of **3ab(1:1)** was 6600 barrers, but the P_{O_2} of desilylated poly(TMSDPA–TBDPA) (1 : 1) was 2700 barrers. The gas permeability increased as the amount of eliminated silyl group increased, when the desilylated polymer had *tert*-butyl groups.

Table 2 Solubility of copolymers and the desilylated analogues[a]

	Toluene	CHCl$_3$	THF	DMF	DMSO	Methanol	Substitution ratio[b] [%]
2ab(1:4)	+	+	+	−	−	−	60
2ab(1:2)	+	+	+	−	−	−	67
2ab(1:1)	+	+	+	−	−	−	75
2ab(2:1)	+	+	+	−	−	−	83
2ab(4:1)	−	−	−	−	−	−	90
2ac(1:4)	+	+	+	−	−	−	60
2ac(1:2)	+	+	+	−	−	−	67
2ac(1:1)	+	+	+	−	−	−	75
2ac(2:1)	+	+	+	−	−	−	83
2ac(4:1)	−	−	−	−	−	−	90
3ab(1:4)	+	+	+	−	−	−	40
3ab(1:2)	+	+	+	−	−	−	33
3ab(1:1)	±	+	+	−	−	−	25
3ab(2:1)	−	±	±	−	−	−	17
3ac(1:4)	−	−	−	−	−	−	0
3ac(1:2)	−	−	−	−	−	−	0
3ac(1:1)	−	−	−	−	−	−	0
3ac(2:1)	−	−	−	−	−	−	0

[a] Symbols: (+) soluble, (±) partly soluble, (−) insoluble. [b] Ratio of the substituent (*tert*-butyl or SiMe$_3$) for the phenyl groups on polymer side chain.

Table 3 Gas permeation properties and density of the membranes of **2ab**, **2ac**, **3ab**, and **3ac**

Membrane	Ratio	$P_{O_2}{}^a$	$P_{CO_2}{}^a$	$P_{N_2}{}^a$	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}	Density^b
2ab	1 : 4	2100	7830	1100	1.92	7.18	0.891
	1 : 2	2900	10 000	1550	1.87	6.44	0.854
	1 : 1	2200	8080	1130	1.94	7.13	0.884
	2 : 1	1700	6900	740	2.30	9.31	0.902
2ac	1 : 4	1800	6940	870	2.07	7.98	0.900
	1 : 2	2700	9280	1470	1.83	6.31	0.866
	1 : 1	3000	10 200	1610	1.86	6.35	0.858
	2 : 1	3400	10 300	2060	1.65	5.00	0.787
3ab	1 : 4	6200	13 000	4000	1.55	3.25	0.837
	1 : 2	9300	18 670	7500	1.24	2.49	0.757
	1 : 1	6600	13 800	4800	1.38	2.88	0.812
	2 : 1	4400	10 940	2990	1.47	3.66	0.848
3ac	1 : 4	980	4000	380	2.54	10.39	0.984
	1 : 2	990	4100	390	2.54	10.51	0.972
	1 : 1	1070	4300	480	2.24	8.98	0.957
	2 : 1	1080	4500	490	2.21	9.20	0.951
Poly(TMSDPA-*co*-TBDPA)[18]	1 : 1	2300	8300	1300	1.8	6.4	
DSpoly(TMSDPA-*co*-TBDPA)[18]	1 : 1	2700	8600	1600	1.7	5.4	
PTMSDPA[12]		1200	4900	560	2.1	8.7	0.91
PTBDPA[11]		1100	4800	500	2.2	9.6	
PTMSP[12]		9700	34 000	6300	1.5	5.4	0.75
Indan-polyacetylenes[13,14]		18 700	44 200	16 600	1.13	2.66	
Naphthyl-polyacetylenes[17]		4300	13 000	2700	1.6	4.8	
Flurenyl-polyacetylenes[15,16]		9800	24 000	8100	1.2	3.0	
Halogen-polyacetylenes[20–22]		5400	19 000	3700	1.5	5.1	1.01
PIM-1 (ref. 28)		2270	13 600	823	2.8	16.5	1.09

^{a} Units: 1×10^{-10} cm^3 (STP) $\times$ cm/(cm^2 $\times$ sec $\times$ cmHg) (=1 barrer). ^{b} Determined by hydrostatic weighing; units: g cm^{-3}.

The oxygen/nitrogen separation factors (P_{O_2}/P_{N_2}) for all the membranes before and after desilylation were in the range of 1.2–2.5, and the values tended to increase with a decrease in the P_{O_2} value. These findings are consistent with the general observation that the highly gas-permeable polymers typically exhibit low gas separation abilities.

Table 3 showed the data of several gas-permeable polyacetylenes and PIM-1 [a typical polymer in polymers of intrinsic microporosity (PIMs)].[28] PTMSP[3] has been known as the most gas-permeable polymer, whose P_{O_2} value is as high as 9700 barrers. Indan-based polyacetylenes[13,14] show the highest gas permeability among all the existing polymers. The other polyacetylenes containing various aromatic rings also show high gas permeability. PIM-1 (ref. 28) is known to show high gas permeability (P_{O_2} = 2270 barrers). Compared to these highly gas-permeable polymers, the desilylated membranes **3ab(1:2)** comparably showed ultrahigh permeability.

Diffusivity and solubility coefficients

To investigate the changes in gas permeability through desilylation in more detail, gas diffusion coefficients (D) were measured by the time lag method and the gas solubility coefficients (S) were calculated using the P and D values. Table 4 included the D and S values of **2ab**, **2ac**, **3ab**, and **3ac**.

The membranes of **3ab** showed higher gas diffusivity and gas solubility values than those of **2ab**. The increase in diffusivity and solubility was due to the increase in the free volume of the
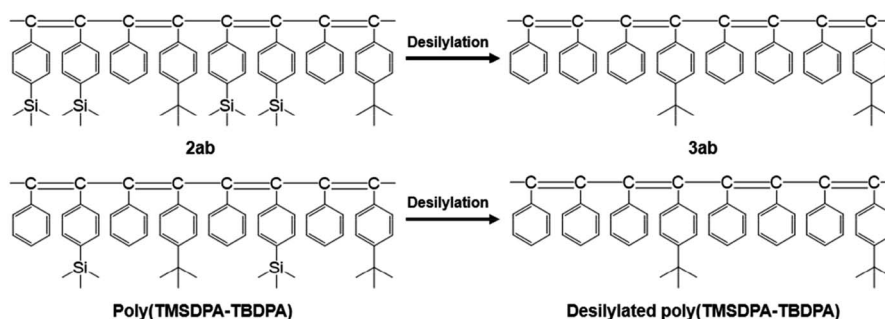

Fig. 2 Chemical structures of **2ab**, poly(TMSDPA–TBDPA), and their desilylated polymers.

Table 4 Gas diffusion coefficients $(D)^a$ and solubility coefficients $(S)^b$ of **2ab**, **2ac**, **3ab**, and **3ac**

Membrane	Ratio	$D_{O_2} \times 10^7$	$D_{CO_2} \times 10^7$	$D_{N_2} \times 10^7$	$S_{O_2} \times 10^3$	$S_{CO_2} \times 10^3$	$S_{N_2} \times 10^3$
2ab	1 : 4	130	160	110	16.3	48	9.9
	1 : 2	160	163	135	18.1	59	11.6
	1 : 1	135	160	118	16.1	48	9.6
	2 : 1	105	120	70	15.7	54	10.0
2ac	1 : 4	83	90	68	20.9	75	12.9
	1 : 2	155	130	105	17.1	67	14.3
	1 : 1	165	140	115	17.9	73	14.3
	2 : 1	180	160	130	19.5	65	16.0
3ab	1 : 4	135	180	120	43.9	80	33.2
	1 : 2	340	355	295	27.3	60	25.2
	1 : 1	170	180	140	35.3	81	33.2
	2 : 1	110	150	91	39.5	77	33.0
3ac	1 : 4	78	68	63	12.5	59	7.0
	1 : 2	80	68	64	12.0	58	7.1
	1 : 1	87	70	65	12.3	60	7.3
	2 : 1	99	76	70	10.9	58	7.0

^{a} Determined by the "time lag" method at 25 °C; units: cm^2 s^{-1}. ^{b} Calculated using equation, $S = P/D$; units: cm^3 (STP)/(cm$^3 \times$ cmHg).

membrane. Contrary to **3ab**, the membranes of **3ac** exhibited lower gas diffusivities and solubilities than those of **2ac**. These behaviors were observed for all gases. If the membrane has an affinity to a specific gas, the variation in diffusivity and solubility for a specific gas is different from those for the other gases. Therefore, the changes in gas permeability through desilylation are probably due to the change in free volume rather than the affinity to a specific gas.

Conclusions

Two types of diphenylacetylene copolymers (**2ab** and **2ac**) were synthesized in various monomer feed ratios by metathesis copolymerization. The copolymers, **2ab** and **2ac**, exhibited high gas permeabilities and the P_{O_2} values were in the range of 1700–3400 barrers. The desilylation of **2ab** led to an extremely high gas permeability. Particularly, **3ab(1:2)** showed the highest gas permeability in comparison to other copolymers, and a P_{O_2} value of 9300 barrers was obtained. In contrast, the desilylation of **2ac** resulted in a decrease in gas permeability. The desilylation generated free volume in the membranes with poly(diphenylacetylene) possessing *tert*-butyl groups.

Conflicts of interest

There are no conflicts to declare.

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