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Development of highly gas-permeable polymers by metathesis copolymerization of 1-(p-trimethylsilyl)phenyl-1-propyne with tert-butyl and silyl group-containing diphenylacetylenes†

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The development of highly gas-permeable membranes is required for gas separation applications. In this study, 1-(p-trimethylsilyl)phenyl-1-propyne (**SPP**) was copolymerized with diphenylacetylenes bearing *tert*-butyl (**BDPA**) and SiMe$_3$ (**SDPA**) groups at various feed ratios to obtain **poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)** copolymers, respectively. Free-standing membranes were fabricated from toluene solutions of the copolymers, the gas permeability of which increased as the **SPP** ratio decreased (P_{O_2}: 550–2100 barrers). Interestingly, **poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)** at a 1 : 4 ratio of **SPP**:**BDPA** and **SPP**:**SDPA**, respectively, showed higher permeabilities than the respective homopolymers. Desilylation of the **poly(SPP-co-BDPA)** membrane increased the gas permeability, whereas desilylation of the **poly(SPP-co-SDPA)** membrane had the opposite result.

Introduction

The development of highly gas-permeable membranes is critical for the industrial application of gas-separation membranes.[1] Polymeric membranes have been extensively developed owing to their accessibility and low cost.[2–4] As an important category of polymeric membranes, disubstituted acetylene polymers have been studied extensively because of their extremely high gas permeabilities.[5–9] As typical examples, poly[4-(*tert*-butyl)diphenylacetylene] [**poly(BDPA)**] and poly[4-(trimethylsilyl)diphenylacetylene] [**poly(SDPA)**] have high oxygen permeability coefficients (P_{O_2}) of 1100 and 1500 barrers, respectively (1 barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}).[10–13]

Recently, we reported that the copolymerization of diphenylacetylenes improved their gas permeability.[14–19] For example, the copolymer of 4-(*tert*-butyl)diphenylacetylene (**BDPA**) and 4-(trimethylsilyl)diphenylacetylene (**SDPA**) exhibited a higher P_{O_2} of 2700 barrers than those of the homopolymers [**poly(BDPA)**: 1100 barrers; **poly(SDPA)**: 1500 barrers].[14] The side groups in the copolymers are more diverse than those in the homopolymers, resulting in more irregular arrangement of the polymer chains and thus a higher gas permeability. In this regard, a copolymer composed of disubstituted acetylenes with different degrees of bulkiness is expected to show a high gas permeability. Herein,

we describe the design of copolymers of 1-(p-trimethylsilyl)phenyl-1-propyne (**SPP**) with **BDPA** and **SDPA** (Scheme 1).

The technique of desilylation is commonly applied to substituted polyacetylenes to allow for polymers with low polymerizability or poor solubility to be fabricated into membranes. This reaction can remove the silyl groups in the membrane state to generate molecular-scale voids, thereby changing the gas permeability.[13,20] For example, while poly(diphenylacetylene) membranes [**DSpoly(SDPA)**] cannot be obtained by solution casting, they can be fabricated by the desilylation of **poly(SDPA)**; however, desilylation decreases P_{O_2} from 1500 to 900 barrers.[13,20] On the contrary, it has been reported that the gas permeability of copolymer membranes containing *tert*-butyl groups can be improved by desilylation because the bulky side groups hinder chain packing.[14,15,17]

As described above, the copolymerization of **SPP** with diphenylacetylene and desilylation are promising for obtaining highly gas-permeable membranes. Herein, we report the copolymerization of **SPP** with **BDPA** and **SDPA** at varying feed ratios, the fabrication of **poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)** membranes, and their conversion to **DSpoly(SPP-co-BDPA)** and **DSpoly(SPP-co-SDPA)** membranes by desilylation. The gas permeability and general properties of these membranes are also described.
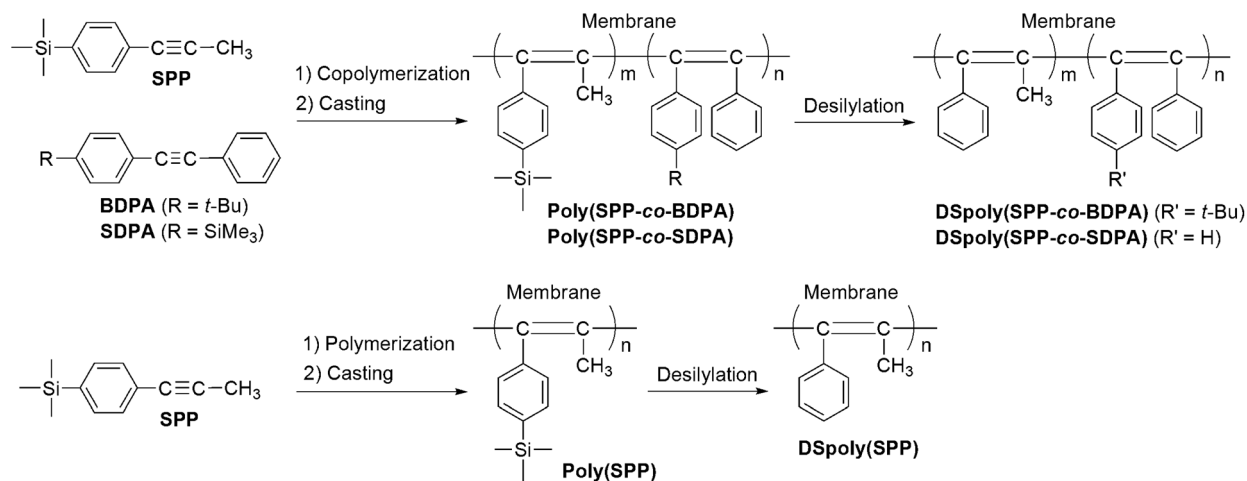
Experimental

Materials

Bis(triphenylphosphine)palladium(II) dichloride, triphenylphosphine, copper(I) iodide, 1-bromo-4-*tert*-butylbenzene, 1,4-dibromobenzene, sodium hydride, iodomethane, 2-methyl-3-butyn-2-ol, tetrahydrofuran (THF), triethylamine, *N,N*-

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† Electronic supplementary information (ESI) available: ¹H-NMR spectra of **poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)**; FT-IR spectra, SEM images, photographs and TGA curves of the membranes. See DOI: 10.1039/d1ra06363d

Scheme 1 Preparation of disubstituted polyacetylenes.

dimethylformamide (DMF), chloroform ($CHCl_3$), methanol (MeOH), trifluoroacetic acid (TFA), dimethyl sulfoxide (DMSO) (Fujifilm Wako Pure Chemical (Wako)), chlorotrimethylsilane (Tokyo Chemical Industry), n-butyllithium (Kanto Chemical), tantalum(v) chloride, and phenylacetylene (Sigma-Aldrich) were used without additional purification. n-Bu_4Sn (cocatalyst for polymerization, Wako) and toluene (solvent for polymerization, Wako) were distilled over CaH_2 (Wako) prior to use. 1-(p-Trimethylsilyl)phenyl-1-propyne (**SPP**),[21] 4-($tert$-butyl)diphenylacetylene (**BDPA**),[10] and 4-(trimethylsilyl)diphenylacetylene (**SDPA**)[11] were prepared according to the literature.

Measurements

Gel permeation chromatography (Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex A-80M $\times$ 2 and KF-802.5) and a Shimadzu RID-6A refractive index detector) was used to determine the molecular weight (eluent: THF, flow rate: 1.0 mL min^{-1}, 40 °C, polystyrene calibration). An NMR spectrometer (JEOL ECX-500, Japan) was used to determine the composition ratio of the copolymers and characterize the monomers (solvent: $CDCl_3$). An FT-IR spectrometer (Thermo Fisher Scientific Nicolet iS5) was used to determine the completion of the desilylation reaction. Field-emission scanning electron microscopy (Seiko Instruments Co. Ltd., Chiba, Japan; Zeiss Co. Ltd., Oberkochen, Germany) was used to record images of the membranes. Thermogravimetric analysis (Rigaku TG-DTA 8078G1 analyzer, Japan) was used to determine the thermal stability (heating rate: 10 °C min^{-1}, nitrogen atmosphere). A gas permeation instrument (Tsukuba Rikaseiki K-315-N) was used to measure the gas

Table 1 Copolymerization of **SPP** with **BDPA** and **SDPA**[a]

Copolymer[b]	Feed ratio	Composition ratio[c]	Yield (%)	M_w[d]	M_w/M_n[d]
	SPP : BDPA	**SPP : BDPA**			
Poly(SPP-co-BDPA)	1 : 4	1 : 3.93	81	1 670 000	6.78
	1 : 2	1 : 2.07	71	387 000	5.77
	1 : 1	1 : 1.08	67	774 000	5.62
	2 : 1	2.08 : 1	53	371 000	4.49
	4 : 1	4.09 : 1	55	253 000	2.46

Copolymer[b]	Feed ratio	Composition ratio[c]	Yield (%)	M_w[d]	M_w/M_n[d]
	SPP : SDPA	**SPP : SDPA**			
Poly(SPP-co-SDPA)	1 : 4	1 : 4.15	83	1 890 000	7.71
	1 : 2	1 : 1.91	77	938 000	7.15
	1 : 1	1 : 0.95	63	813 000	6.39
	2 : 1	2.00 : 1	64	250 000	3.38
	4 : 1	3.98 : 1	56	573 000	5.29

[a] Copolymerization at 80 °C for 24 h; [**SPP** + **BDPA/SDPA**]$_0$ = 0.20 M, [$TaCl_5$] = 20 mM, [n-Bu_4Sn] = 40 mM. [b] MeOH-insoluble product. [c] Estimated from 1H-NMR spectra (Fig. S1–S10). [d] Determined by GPC eluted with THF.
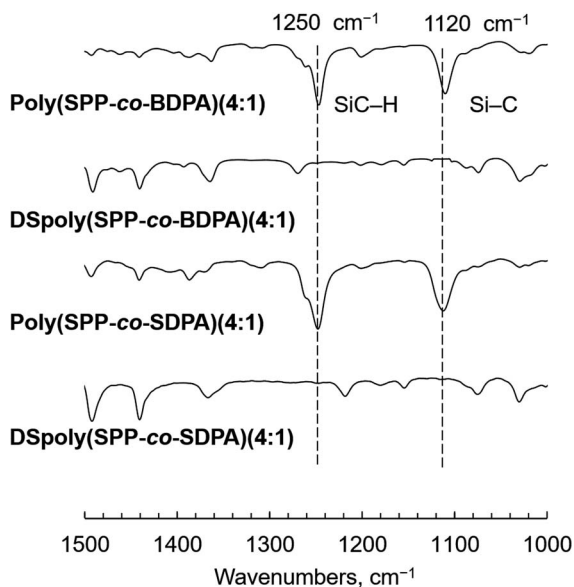
Fig. 1 FT-IR spectra of poly(SPP-*co*-BDPA)(4:1), poly(SPP-*co*-SDPA)(4:1), DSpoly(SPP-*co*-BDPA)(4:1), and DSpoly(SPP-*co*-SDPA)(4:1).

Table 2 Solvent solubility of copolymers^a

Toluene	CHCl$_3$	THF	MeOH	DMF	DMSO
Poly(SPP-*co*-BDPA), Poly(SPP-*co*-SDPA), DSpoly(SPP-*co*-BDPA)					
+	+	+	−	−	−
DSpoly(SPP-*co*-SDPA)					
−	−	−	−	−	−

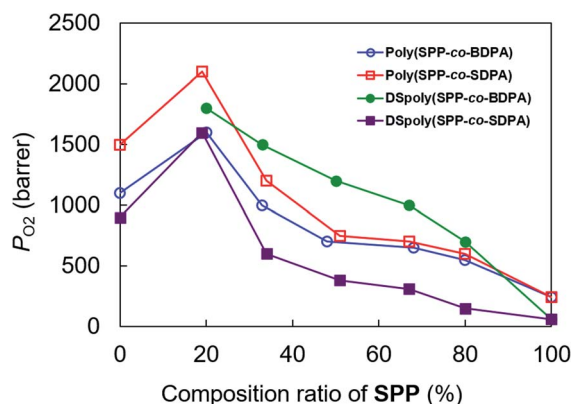^{a} Symbols: +, soluble; −, insoluble.

Fig. 2 Relationship between P_{O_2} and SPP ratio of copolymers.

permeability coefficients (P) of the membranes, which were calculated based on the slope of the steady-state region of the time–pressure curves. The gas diffusion coefficients (D) were calculated from the equation $D = l2/(6\theta)$, where l is the membrane thickness and θ is the time lag. The gas solubility coefficients (S) were calculated using the equation $S = P/D$.

Copolymerization

Two copolymers, **poly(SPP-*co*-BDPA)** and **poly(SPP-*co*-SDPA)**, were synthesized by copolymerization of the corresponding monomers at a variety of feed ratios. Copolymerization was performed at the following reagent concentrations: [**SPP** + **BDPA/SDPA**]$_0$ = 0.20 M, [TaCl$_5$] = 20 mM, [n-Bu$_4$Sn] = 40 mM. The detailed procedure for the copolymerization of **SPP** with **BDPA** at a 1 : 4 ratio was as follows. **SPP** (0.080 g), **BDPA** (0.38 g), and toluene (5.0 mL) were placed in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. TaCl$_5$ (71 mg), n-Bu$_4$Sn (0.13 mL), and toluene (4.9 mL) were placed in another tube under a nitrogen atmosphere. The catalyst solution was heated for 10 min at 80 °C. The catalyst solution was then added to the monomer solution, and the mixed solution was heated to 80 °C for 24 h. After copolymerization, MeOH (∼1.0 mL) was added to the solution to deactivate the catalyst, after which the solution was diluted in toluene and poured in MeOH (∼1.0 L). The desired copolymer was obtained as a precipitate, and the yield was determined using the gravimetric method.

Membrane fabrication and desilylation

Poly(SPP-*co*-BDPA), **poly(SPP-*co*-SDPA)**, and **poly(SPP)** membranes were prepared by casting the corresponding copolymer solutions (solvent: toluene, concentration: ∼1.0 wt%) on Petri dishes. After the evaporation of toluene, the membranes were peeled off, immersed in MeOH for 24 h, and dried to a constant weight under atmospheric pressure.

Desilylated copolymer membranes, **DSpoly(SPP-*co*-BDPA)** and **DSpoly(SPP-*co*-SDPA)**, were prepared by desilylation of the **poly(SPP-*co*-BDPA)** and **poly(SPP-*co*-SDPA)** membranes, respectively. The membranes were immersed in a TFA/hexane solution (1 : 1 v/v) for 24 h. Then, the membranes were washed with MeOH, immersed in MeOH for 24 h, and finally dried to a constant weight under atmospheric pressure.

A desilylated homopolymer membrane, **DSpoly(SPP)**, was prepared by the desilylation of **poly(SPP)** using the same procedure as for the desilylated copolymer membranes using TFA instead of a TFA/hexane mixture (Scheme 1).

Results and discussion

Copolymerization

Poly(SPP-*co*-BDPA) and **poly(SPP-*co*-SDPA)** were synthesized by copolymerization of the corresponding monomers at various feed ratios. The results are shown in Table 1. The composition ratios of the obtained copolymers were estimated from the ^{1}H-NMR spectra (Fig. S1–S10†) as approximately equal to the feed ratios. **Poly(SPP-*co*-BDPA)(1:4)** with a **SPP : BDPA** feed ratio of 1 : 4 exhibited a high molecular weight (M_w = 1 670 000) and high yield (81%). With increasing **SPP** content, the molecular weight and yield of the obtained copolymers decreased (M_w = 253 000–774 000, yields = 53–71%). Similarly, **poly(SPP-*co*-SDPA)(1:4)** exhibited a high molecular weight (M_w = 1 890 000) and high yield (83%), whereas **poly(SPP-*co*-SDPA)** with higher **SPP** contents exhibited lower molecular weights and yields (M_w = 250 000–938 000, yields = 56–77%). It has been reported that

Table 3   Gas permeability of copolymer and homopolymer membranes[a]

Membrane	Feed ratio	P_{O_2}	P_{CO_2}	P_{N_2}	P_{O_2}/P_{N_2}	Ref.
SPP : BDPA						
Poly(SPP-co-BDPA)	1 : 4	1600	6000	750	2.1	This work
	1 : 2	1000	4000	400	2.5	
	1 : 1	700	3200	250	2.8	
	2 : 1	650	3000	230	2.8	
	4 : 1	550	2400	180	3.1	
DSpoly(SPP-co-BDPA)	1 : 4	1800	6500	770	2.3	
	1 : 2	1500	5500	650	2.3	
	1 : 1	1200	4800	500	2.4	
	2 : 1	1000	4200	350	2.9	
	4 : 1	700	3500	200	3.5	
SPP : SDPA						
Poly(SPP-co-SDPA)	1 : 4	2100	8400	950	2.2	This work
	1 : 2	1200	4300	480	2.5	
	1 : 1	750	3300	280	2.7	
	2 : 1	700	3000	220	3.2	
	4 : 1	600	2500	180	3.3	
DSpoly(SPP-co-SDPA)	1 : 4	1600	5500	700	2.3	
	1 : 2	600	2300	170	3.5	
	1 : 1	380	1600	100	3.8	
	2 : 1	310	1500	80	3.9	
	4 : 1	150	1000	38	3.9	
Poly(SPP)		240	1300	100	2.4	21 and 22
DSpoly(SPP)		60	310	15	4.0	This work
Poly(BDPA)		1100	4800	500	2.2	10
Poly(SDPA)		1500	4900	680	2.2	11 and 13
DSpoly(SDPA)		900		410	2.2	11 and 13
Matrimid5218		2.12		0.32	6.6	23
Polysulfone		1.4		0.24	5.8	23
6FDA-DAM		55		17	3.3	24

[a] Measured at 25 °C, P (barrer), 1 barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

the homopolymerization of **SPP** using TaCl₅/n-Bu₄Sn afforded a polymer with an M_w of 156 000,[21] which is much lower than those of the homopolymers of **BDPA** (M_w = 3 600 000)[10] and **SDPA** (M_w = 2 200 000)[11] obtained under the same conditions. This suggests that the active species derived from **SPP** induce termination reactions more frequently than **BDPA** and **SDPA**. Therefore, copolymerization at a high feed ratio of **SPP** provides a low-molecular-weight polymer.

Membrane fabrication and desilylation

Poly(SPP-co-BDPA) and **poly(SPP-co-SDPA)** membranes were fabricated using the casting method. Desilylation of the membranes was carried out using a TFA/hexane mixture to obtain **DSpoly(SPP-co-BDPA)** and **DSpoly(SPP-co-SDPA)** membranes, respectively. The FT-IR spectra of the membranes were measured to verify the desilylation conversion; the spectra of the polymer membranes prepared at a feed ratio of 4 : 1 are shown in Fig. 1. Absorption bands at 1120 and 1250 cm⁻¹ were clearly observed in the FT-IR spectra of both **poly(SPP-co-BDPA)(4:1)** and **poly(SPP-co-SDPA)(4:1)**, which originate from the stretching of Si–C bonds and vibration of SiC–H bonds, respectively. However, these two absorptions were not observed in the spectra of **DSpoly(SPP-co-BDPA)(4:1)** and **DSpoly(SPP-co-SDPA)(4:1)**, indicating complete desilylation. The same results

were observed in the FT-IR spectra of the other membranes (Fig. S11–S15†). Further, SEM images of membranes were shown in Fig. S16 and S17.† The morphologies of membranes did not change through desilylation, and the mapping data of silicon atom for membrane cross-section supported to completion of desilylation. On the other hand, the color of membranes changed to orange from yellow though desilylation (Fig. S18†).

The solvent solubilities of the copolymers are shown in Table 2. **Poly(SPP-co-BDPA)**, **poly(SPP-co-SDPA)**, and **DSpoly(SPP-co-BDPA)** exhibited the same solubility and were soluble in toluene, CHCl₃, and THF but insoluble in MeOH, DMF, and DMSO. In contrast, **DSpoly(SPP-co-SDPA)** was insoluble in all the tested solvents. **Poly(SPP-co-SDPA)**s exhibited high thermal stability, and the onset temperatures were around 400 °C (Fig. S19†). The temperatures increased as the feed ratio of **SDPA** increased.

Gas permeability

Fig. 2 plots P_{O_2} of the copolymers as a function of the ratio of **SPP**, and Table 3 summarizes the detailed gas permeability data. The P_{O_2} values of the **poly(SPP-co-BDPA)** membranes were in the range of 550–1600 barrers, which increased with decreasing **SPP** ratio and were much higher than that of

Table 4 Gas diffusivity and solubility of copolymer membranes

Membrane	Feed ratio	D^a			S^b		
		O_2	CO_2	N_2	O_2	CO_2	N_2
SPP : BDPA							
Poly(SPP-co-BDPA)	1 : 4	41	35	38	39	170	20
	1 : 2	38	33	37	26	120	11
	1 : 1	26	28	24	26	114	10
	2 : 1	25	27	23	26	110	10
	4 : 1	23	24	19	24	100	9.5
DSpoly(SPP-co-BDPA)	1 : 4	45	37	39	40	176	20
	1 : 2	42	35	38	36	157	17
	1 : 1	40	33	33	30	145	15
	2 : 1	37	30	25	27	140	14
	4 : 1	27	27	20	26	130	10
SPP : SDPA							
Poly(SPP-co-SDPA)	1 : 4	100	80	70	21	105	14
	1 : 2	70	60	50	17	72	9.6
	1 : 1	50	50	32	15	66	8.8
	2 : 1	48	47	30	14	64	7.3
	4 : 1	44	40	28	13	62	6.4
DSpoly(SPP-co-SDPA)	1 : 4	80	60	65	20	83	10
	1 : 2	40	33	30	15	70	5.7
	1 : 1	35	30	20	11	54	5.0
	2 : 1	30	28	17	10	53	4.7
	4 : 1	20	23	10	7.5	43	3.8

^{a} Diffusion coefficient (10^{-7} cm^2 s^{-1}). ^{b} Solubility coefficient [10^{-3} cm^3 (STP) cm^{-3} cmHg^{-1}].

poly(SPP) (240 barrers). **Poly(SPP-co-BDPA)(1:4)** showed the highest P_{O_2} (1600 barrers) among the **poly(SPP-co-BDPA)** samples, which was also higher than that of **poly(BDPA)** (1100 barrers). Similarly, the gas permeabilities of the **poly(SPP-co-SDPA)** samples were higher than that of **poly(SPP)** (P_{O_2}: 600–2100 vs. 240 barrers, respectively), and the gas permeability of **poly(SPP-co-SDPA)(1:4)** was higher than that of **poly(SDPA)** (P_{O_2}: 2100 vs. 1500 barrers, respectively). These results are consistent with our previous studies, which showed that copolymerization enhances the gas permeability of the materials.[14–19] This can be explained by the fact that the copolymers have more abundant substituents than the homopolymers, resulting in more irregular chain packing. Comparing **poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)** at the same **SPP** ratio, **poly(SPP-co-SDPA)** showed a somewhat higher gas permeability, which is consistent with the higher gas permeability of **poly(SDPA)** than **poly(BDPA)**.

The desilylated **DSpoly(SPP-co-BDPA)** membranes showed higher gas permeabilities (P_{O_2}: 700–1800 barrers) than the corresponding **poly(SPP-co-BDPA)** membranes. This is because the tert-butyl substituents hinder chain packing and maintain the microscale voids generated by the removal of silyl groups during desilylation. Similar to **poly(SPP-co-BDPA)**, the gas permeabilities of **DSpoly(SPP-co-BDPA)** were much higher than those of **DSpoly(SPP)** [formed by the desilylation of **poly(SPP)**], and **DSpoly(SPP-co-BDPA)(1:4)** showed the highest gas permeability. Interestingly, although the desilylation of **poly(SPP)** decreased the gas permeability, the desilylation of **poly(SPP-co-BDPA)** increased the gas permeability, even at high **SPP** ratios.

In contrast, the desilylation of **poly(SPP-co-SDPA)** decreased the gas permeability, similar to the trend observed with **poly(SDPA)** and **poly(SPP)**. Therefore, bulky substituents such as tert-butyl groups play an important role in enhancing the gas permeability of polymer membranes by desilylation. Nevertheless, the gas permeability of **DSpoly(SPP-co-SDPA)** was still high; especially, P_{O_2} of **DSpoly(SPP-co-SDPA)(1:4)** was 1600 barrers, which is higher than that of **DSpoly(SDPA)** (900 barrers).

The gas permeability of copolymer membranes in this study were much higher than that of conventional glassy polymer membranes. For example, the commercially available Matrimid 5218 and polysulfone exhibit the P_{O_2} less than 10 barrers,[23] and relatively high gas permeable polyimide, 6FDA-DAM, shows 55 barrers.[24] The P_{O_2} of **poly(SPP-co-SDPA)(1:4)** was 38 times higher than that of 6FDA-DAM.

Gas diffusivity and solubility

The gas diffusion and solubility coefficients of the membranes are listed in Table 4. The diffusivity and solubility of all the membranes decreased with increasing **SPP** ratio. The D and S values of **DSpoly(SPP-co-BDPA)** were higher than those of **poly(SPP-co-BDPA)**, which is consistent with the gas permeability trend. This increase in D and S may be attributable to desilylation increasing the free volume. In contrast, D and S of **DSpoly(SPP-co-SDPA)** were lower than those of **poly(SPP-co-SDPA)**. As discussed above, the increase in gas permeability for **poly(SPP-co-BDPA)** and decrease in gas permeability for **poly(SPP-co-SDPA)** originated from variations in both the diffusivity and solubility.

Conclusions

Disubstituted polyacetylene membranes with high gas permeabilities were developed in this work by copolymerizing 1-(p-trimethylsilyl)phenyl-1-propyne (**SPP**) with diphenylacetylenes bearing tert-butyl (**BDPA**) and SiMe$_3$ (**SDPA**) groups at various feed ratios. **Poly(SPP-co-BDPA)** and **poly(SPP-co-SDPA)** with a 20% **SPP** content exhibited higher gas permeabilities than the homopolymers, **poly(BDPA)** and **poly(SDPA)**, respectively, despite the much lower permeability of **poly(SPP)**. Desilylation of **poly(SPP-co-BDPA)** increased the gas permeability, whereas desilylation of **poly(SPP-co-SDPA)** reduced the gas permeability. These findings reveal that various disubstituted acetylene monomers can be applied to copolymerization to improve the gas permeability of the resulting membranes even if the corresponding homopolymers exhibit low gas permeabilities. Therefore, copolymerization is a promising method for the development of highly gas-permeable membranes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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