Enhancement of oxygen permeability by copolymerization of silyl group-containing diphenylacetylenes with tert-buty1 group-containing diphenylacetylene and desilylation of copolymer membranes

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Diphenylacetylenes having various silyl groups [PhC≡CC₆H₄-R; R = p-SiMe₃ (TMSDPA), p-SiEt₃ (TESDPA), p-SiMe₂-n-C₆H₄ (DMOSDPA), and p-SiPh₃ (TPSDPA)] were copolymerized with diphenylacetylene having a tert-buty1 group (PhC≡CC₆H₄-tertBu; TBDPA) using a TaCl₅-n-Bu₄Sn catalyst in various monomer feed ratios to provide high-molecular-weight copolymers in high yields. The free-standing membranes were fabricated by solution-casting, except poly(TPSDPA-co-TBDA). Interestingly, the gas permeability of poly(TMOSDPA-co-TBDA) was higher than those of the homopolymers, poly(TMOSDPA) and poly(TBDA). The permeability of the copolymers became lower as the silyl groups became bulkier. The desilylation of membranes was carried out using a mixture of trifluoroacetic acid/hexane. When bulkier silyl groups were removed, the oxygen permeability increased to larger extents. The oxygen permeability coefficients of the copolymers and desilylated copolymers increased with increasing composition ratio of TBDPA. The gas diffusivity and gas solubility were also increased upon desilylation.

Introduction

Membrane separation for mixed gases has become important because of the low costs and energy consumption compared with traditional separation techniques such as adsorption and absorption, and a variety of polymers with high permeability or high selectivity have been studied. Membranes of disubstituted acetylenic polymers with bulky spherical substituents have a large free volume and exhibit pretty high gas permeability. This feature originates from their stiff main chain composed of alternating double bonds and the steric repulsion of the substituents. For instance, the oxygen permeability coefficient (Pₒₒ) of poly[1-phenyl-2-(p-trimethylsilyl)phenylacetylene], poly(TMSDPA), was as large as 1100–1500 barrer. Poly[1-phenyl-2-(p-tert-buty1)phenylacetylene], poly(TBDA), also shows high gas permeability, and its Pₒₒ value was 1100 barrer. These poly(substituted acetylene)s are promising materials for gas separation membranes, and further high gas-permeable polymer membranes are desired as oxygen-enriched membranes. Teraguchi et al. reported that the desilylation of a membrane of poly(TMOSDPA) afforded a membrane of poly(diphenylacetylene), which cannot be obtained by solution-casting and hot-press methods because it is insoluble and insusceptible. In the desilylation reaction of polymer membrane, it has been predicted that the spaces occupied by silyl groups are maintained in some level as micro-scale voids since the mobility of polymer chain is restrained in a solid state. Contrary to prediction, the desilylation of membrane of poly(TMOSDPA), however, decreased the gas permeability. This is because the chain packing is induced by the elimination of bulky spherical trimethylsilyl groups. If the chain packing during the desilylation is prevented, the gas permeability of the membrane should increase.

In the present study, we synthesized copolymers of diphenylacetylenes having silyl and tert-buty1 groups at para position of phenyl groups (Scheme 1), and examined the desilylation of the membranes. The desilylated copolymers have still bulky tert-buty1 groups, and therefore the spaces occupied by silyl groups are possibly maintained after desilylation by the steric repulsion of tert-buty1 groups.

Experimental

Materials

Toluene which is polymerization solvent was purified by two times of distillation in the presence of CaH₂. Tantalum(v) chloride (TaCl₅, 99.999%, Aldrich) as main catalyst was used without further purification, and tetra-n-buty1tin (n-Bu₄Sn, Wako) as cocatalyst was used after distillation under reduced pressure. Phenylacetylene (Aldrich), triethylamine, triphenyl-phosphine, copper(i) iodide, dichlorobis(triphenylphosphine)
palladium(n), p-bromo-tert-butylbenzene, 1,4-dibromobenzene, trifluoroacetic acid (TFA), n-butyllithium hexane solution (1.6 M), chlorotrimethylsilane, chlorotriethoxysilane, chlorodimethyl-n-octylsilane, chlorotriphenylsilane, and common solvents (Wako Pure Chemical) were used without further purification. 1-Phenyl-2-(p-trimethylsilyl)phenylacetylene (TMSDPA), 1-phenyl-2-(p-triethylsilyl)phenylacetylene (TESDPA), 1-phenyl-2-(p-dimethyl-n-octylsilyl)phenylacetylene (DMOSDPA), 1-phenyl-2-(p-triphenylsilyl)phenylacetylene (TPSDPA), and 1-phenyl-2-(p-tert-butyl)phenylacetylene (TBDPA) were synthesized according to the literatures.

**Measurements**

The molecular weight distribution (MWD) of polymers were measured by gel permeation chromatography (GPC) in CHCl3 (at a 1.0 mL min⁻¹ flow rate) at 40 °C on a Shimadzu LC-10AD chromatograph equipped with three polystyrene gel columns (Shodex K-804L, K-805L, and K-807L) and a Shimadzu RID-6A refractive index detector. The weight-average molecular weight (Mw) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (Mw/Mn)] were calculated from chromatograms based on a polystyrene calibration. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded on Jeol ECX-500 instrument in CDCl₃ at room temperature. IR spectra were recorded on a Nicolet iS5 560 spectrometer. A membrane thickness was measured using a micrometer, and it was estimated as an average amount of ten points on each membrane.

Gas permeability coefficients of polymer membranes were measured with a Tsukubarakaseki K-315-N gas permeability apparatus equipped with an MKS Baratron detector at 25 °C. The downstream side of the membrane was evacuated at ca. 0.3 Pa, while the upstream side was filled with a gas at ca. 1 atm (10⁵ Pa), and the increase of pressure in a downstream receiving vessel was measured. The permeability coefficient (P) expressed in barrer unit [1 barrer = 1 × 10⁻¹⁰ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹] was calculated from the slopes of time–pressure curves in the steady state where Fick’s law held. The diffusion coefficient (D) expressed in cm² s⁻¹ units was determined by the time lag method using the following equation:

\[ D = \frac{P}{6\theta} \]

here, \( l \) is the membrane thickness and \( \theta \) is the time lag, which is given by the intercept of the asymptotic line of time–pressure curve to the time axis. The solubility coefficient (S) expressed in cm³ (STP) cm⁻³ cmHg⁻¹ units was calculated by using the following equation:

\[ S = \frac{P}{D}. \]

**Copolymerization**

Copolymerizations were performed in a glass tube equipped with a three-way stopcock at 80 °C for 24 h under dry nitrogen at the following reagent concentrations: \([\text{M}]₀ + [\text{TBDPA}]₀ = 0.20 \text{ M}, [\text{TaCl}_5] = 20 \text{ mM}, [\text{n-Bu}_4\text{Sn}] = 80 \text{ mM}.\) A detailed procedure of polymerization is as follows: the monomer solution was prepared in a glass tube by mixing TMSDPA (0.25 g), TBDPA (0.23 g) and dry toluene (5.0 mL). Another glass tube was charged with TaCl₅ (71 mg), 0.8 M of n-Bu₄Sn in toluene (1.0 mL), and dry toluene (4.0 mL); this catalyst solution was aged at 80 °C for 10 min. Then the monomer solution was added to the catalyst solution. Polymerization was carried out 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 methanol and its yield was determined by gravimetry. Poly(TPSDPA-co-TBDPA) was isolated by precipitation into a large excess of acetone.

**Membrane fabrication and desilylation**

The membranes (thickness ca. 140–200 μm) of copolymers were fabricated by casting from toluene solution of the copolymers (concentration ca. 0.20–0.60 wt%) into Petri dishes at room temperature. The dish was covered with a glass vessel to slow solvent evaporation (3–5 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. With reference to the method described in the literature, the desilylation of membranes was carried out using a mixture of trifluoroacetic acid and hexane. A detailed procedure is as follows: the copolymer membrane was immersed in a mixture of trifluoroacetic acid and hexane (volume ratio 1 : 1) at room temperature for 24 h. To remove residual impurities in the membrane, the membranes were washed with a mixture of trifluoroacetic acid and hexane (1:1) for 24 h. The resulting polymer was isolated by precipitation into a large excess of acetone.

\[ \text{SiDPA} = \begin{array}{c} \text{TMSDPA} \\ \text{TESDPA} \\ \text{DMOSDPA} \\ \text{TPSAPA} \\ \text{DMOSDPA} \end{array}, \quad \text{R} = \begin{array}{c} \text{SiMe₃} \\ \text{SiEt₃} \\ \text{SiMe₂C₆H₁₇} \\ \text{SiPh₃} \end{array} \]
polymer matrix, the membrane was immersed in acetone followed by methanol at room temperature for 24 h. It was dried at room temperature under atmospheric pressure for 24 h. The completion of desilylation was confirmed by the comparison between IR spectra of the polymer membranes before and after the reaction.

**Results and discussion**

**Copolymerization**

The copolymerizations were carried out using TaCl₅/n-Bu₄Sn catalyst at 80 °C in toluene for 24 h under nitrogen, whose conditions are known to produce high-molecular-weight poly(diphenylacetylene) derivatives in high yields. The results of copolymerizations are summarized in Table 1.

The copolymerization of TMSDPA having trimethylsilyl group with TBDPA in feed ratio of 4 : 1 produced poly(TMSDPA-co-TBDPA) with $M_w$ of 3 320 000 in 84% yield. The copolymerizations in feed ratios of 2 : 1, 1 : 1, 1 : 2, and 1 : 4 also proceeded in the same manner and copolymers were obtained with $M_w$ of 3 230 000, 3 160 000, 3 300 000, and 2 080 000, respectively. The copolymerizations of TESDPA having triethylsilyl group with TBDPA under the same conditions gave poly(TESDPA-co-TBDPA) with $M_w$ of 1 120 000–2 170 000. DMOSDPA having dimethyl-n-octysilyl group also copolymerized with TBDPA to afford poly(DMOSDPA-co-TBDPA) with high molecular weight ($M_w$ = 4 080 000–5 010 000). The copolymerizations of TPSDPA having triphenylsilyl group with TBDPA provided poly(TPSDPA-co-TBDPA) in high yields, but the obtained poly(TPSDPA-co-TBDPA)s showed poor solubility. Poly(TPSDPA-co-TBDPA)s were partially soluble in chloroform, and the $M_w$'s of CHCl₃-soluble parts were one order of magnitude lower than those of the other copolymers.

**Fabrication and desilylation of membranes**

The solubility of copolymers is summarized in Table 2. Regardless of the feed ratios, poly(TMSDPA-co-TBDPA), poly(TESDPA-co-TBDPA), and poly(DMOSDPA-co-TBDPA) showed good solubility in relatively low polarity solvents including toluene, chloroform, and tetrahydrofuran, while poly(TPSDPA-co-TBDPA) showed poor solubility. Poly(TPSDPA-co-TBDPA) was slightly soluble in toluene, chloroform and tetrahydrofuran. All the present copolymers were insoluble in polar solvents such as $N,N$-dimethylformamide, dimethyl sulfoxide, and methanol.

Tough free-standing membranes could be fabricated by casting polymers from their toluene solutions for poly(TMSDPA-

### Table 1 Copolymerization of M with TBDPA by TaCl₅/n-Bu₄Sn

| Feed ratio (M : TBDPA) | Polymer | Yield, % | $M_w$ | $M_w/M_n$ |
|------------------------|---------|----------|-------|-----------|
| **TMSDPA**             |         |          |       |           |
| 4 : 1                  | 84      | 3 320 000| 5.05  |           |
| 2 : 1                  | 83      | 3 230 000| 4.61  |           |
| 1 : 1                  | 83      | 3 160 000| 4.86  |           |
| 1 : 2                  | 86      | 3 300 000| 4.88  |           |
| 1 : 4                  | 93      | 2 080 000| 5.43  |           |
| **TESDPA**             |         |          |       |           |
| 4 : 1                  | 64      | 1 120 000| 2.69  |           |
| 2 : 1                  | 66      | 1 440 000| 4.21  |           |
| 1 : 1                  | 73      | 1 800 000| 5.17  |           |
| 1 : 2                  | 74      | 2 170 000| 4.27  |           |
| 1 : 4                  | 91      | 1 630 000| 5.29  |           |
| **DMOSDPA**            |         |          |       |           |
| 4 : 1                  | 67      | 4 080 000| 4.24  |           |
| 2 : 1                  | 80      | 4 560 000| 3.90  |           |
| 1 : 1                  | 81      | 5 010 000| 4.06  |           |
| 1 : 2                  | 88      | 4 360 000| 5.01  |           |
| 1 : 4                  | 87      | 4 500 000| 3.57  |           |
| **TPSDPA**             |         |          |       |           |
| 4 : 1                  | 70$^a$  | 378 000$^c$| 2.79  |           |
| 2 : 1                  | 76$^a$  | 376 000$^c$| 2.51  |           |
| 1 : 1                  | 80$^a$  | 333 000$^c$| 2.27  |           |
| 1 : 2                  | 74$^d$  | 378 000$^c$| 2.79  |           |
| 1 : 4                  | 79$^d$  | 397 000$^c$| 1.79  |           |

$^a$ In toluene at 80 °C for 24 h; $[M]_0 + [TBDPA]_0 = 0.20$ M; $[TaCl₅] = 20$ mM, $[n-Bu₄Sn] = 80$ mM$^b$. $^b$ Acetone-insoluble product. $^c$ CHCl₃-soluble part. $^d$ Methanol-insoluble product.

### Table 2 Solubility of poly(TMSDPA-co-TBDPA), poly(TESDPA-co-TBDPA), poly(DMOSDPA-co-TBDPA), and the desilylated analogues

| Feed ratio (RDPA : TBDPA) | Toluene | CHCl₃ | THF | DMF | DMSO | Methanol |
|---------------------------|---------|-------|-----|-----|------|----------|
| **Poly(TMSDPA-co-TBDPA)** |         |       |     |     |      |          |
| 4 : 1                     | ±       | ±     | ±   | −   | −    | −        |
| 2 : 1                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 1                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 2                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 4                     | ±       | ±     | ±   | −   | −    | −        |
| **D Poly(TMOSDPA-co-TBDPA)** |       |       |     |     |      |          |
| 4 : 1                     | −       | −     | −   | −   | −    | −        |
| 2 : 1                     | −       | −     | −   | −   | −    | −        |
| 1 : 1                     | −       | −     | −   | −   | −    | −        |
| 1 : 2                     | −       | −     | −   | −   | −    | −        |
| 1 : 4                     | ±       | ±     | ±   | −   | −    | −        |
| **D Poly(TESDPA-co-TBDPA)** |       |       |     |     |      |          |
| 4 : 1                     | −       | −     | −   | −   | −    | −        |
| 2 : 1                     | −       | −     | −   | −   | −    | −        |
| 1 : 1                     | −       | −     | −   | −   | −    | −        |
| 1 : 2                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 4                     | ±       | ±     | ±   | −   | −    | −        |
| **D Poly(DMOSDPA-co-TBDPA)** |       |       |     |     |      |          |
| 4 : 1                     | −       | −     | −   | −   | −    | −        |
| 2 : 1                     | −       | −     | −   | −   | −    | −        |
| 1 : 1                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 2                     | ±       | ±     | ±   | −   | −    | −        |
| 1 : 4                     | ±       | ±     | ±   | −   | −    | −        |

$^a$ Symbols: (+) soluble, (±) partly soluble, (−) insoluble.
co-TBDPA)s, poly(TESDPA-co-TBDPA)s, and poly(DMOSDPA-co-
TBDPA)s. However, it was difficult to prepare a membrane of
poly(TPSDPA-co-TBDPA) by solution-casting because of too poor
solubility. The desilylation was carried out in a mixture of
hexane/trifluoroacetic acid (1:1 volume ratio) at room
temperature for 24 h to afford the desilylated membranes. It is
known that the aryl–Si bond is easily cleaved by proton acids.\textsuperscript{18,19}

Fig. 1 shows the IR spectra of membranes of poly(DMOSDPA-co-
TBDPA) and desilylated analogue [DSpoly(DMOSDPA-co-
TBDPA)] in the feed ratio of 1:4. The absorptions at 1250 cm\(^{-1}\)
derived from the stretching of Si–C bonds and at 1120 cm\(^{-1}\)
derived from the vibration of Si–C completely disappeared in
the spectrum after desilylation reaction. This indicates that the
silyl groups were completely eliminated from the polymer
membrane even the silyl groups were bulky dimethyl-silyl
groups. For poly(TMSDPA-co-TBDPA)s and poly(TESDPA-co-
TBDPA)s, the completion of desilylation was confirmed by IR
spectra of the polymer membranes. The color of polymer
membranes changed from yellow to orange through desilyla-
tion, which would suggest that the conjugated main chains
were maintained during the reaction. The results of desilyla-
tion are the same as the previous studies.\textsuperscript{18,19}

The solubility of the desilylated copolymers, DSpoly(TMSDPA-
co-TBDPA)s, DSpoly(TESDPA-co-TBDPA)s, and DSpoly-
(DMOSDPA-co-TBDPA)s was examined (Table 2). The desilyl-
ated copolymers showed less solubility than silyl group-
containing copolymers. DSpoly(TMSDPA-co-TBDPA)s, DSpoly(-
TESDPA-co-TBDPA)s, and DSpoly(DMOSDPA-co-TBDPA)s in
the feed ratios of 4:1 and 2:1 were practically insoluble copolymers
in any solvents, indicating that the incorporation of the particular
content of tert-butyl groups is essential for the solubility of pol-
y(diphenylacetylene). The desilylated copolymers in the feed
ratios of 1:1, 1:2, 1:4 indeed showed better solubility in
toluene, CHCl\(_3\), and THF in general because they had tert-butyl
groups in relatively high contents.

**Oxygen permeability of the copolymers**

Copolymer membranes were immersed in methanol for 24 h
and dried to constant weight at room temperature, and then
their permeability was measured at 25 °C. The oxygen
and nitrogen permeability coefficients of membranes of poly-
(TMOSDPA-co-TBDPA)s, poly(TESDPA-co-TBDPA)s, poly-
(DMOSDPA-co-TBDPA)s, and the desilylated analogues were
summarized in Tables 3-5.

The \(P_\Omega\) value of poly(TMOSDPA-co-TBDPA) (4:1) obtained by
the polymerization in feed ratio of 4:1 was 2200 barrer. The other
poly(TMOSDPA-co-TBDPA)s also exhibited high gas permeability
and their \(P_\Omega\) values were more than 1900 barrer. Poly(TMOSDPA-co-TBDPA) (1:4) exhibited the highest perme-
ability and its \(P_\Omega\) value was as large as 2700 barrer. Interest-
ingly, all the poly(TMOSDPA-co-TBDPA)s exhibited high oxygen
permeability compared to homopolymers. The \(P_\Omega\) values of
homopolymers of TMSDPA and TBDPA were 1500 and 1100
barrer, respectively. The higher gas permeability of copolymers
may be due to the heterogeneous structure; i.e., the copolymers

| Membrane | Ratio | \(P_\Omega\) | \(P_N\) | \(P_\Omega/P_N\) |
|----------|-------|----------|--------|------------|
| Poly(TMOSDPA-co-TBDPA) | 1:0 | 1500 | 680 | 2.2 |
| 4:1 | 2200 | 1200 | 1.8 |
| 2:1 | 1900 | 1000 | 1.9 |
| 1:1 | 2300 | 1300 | 1.8 |
| 1:2 | 2100 | 1100 | 1.9 |
| 1:4 | 2700 | 1700 | 1.6 |
| 0:1 | 3100 | 690 | 1.6 |
| DSpoly(TMOSDPA-co-TBDPA) | 1:0 | 900 | 410 | 2.2 |
| 4:1 | 1600 | 1000 | 1.6 |
| 2:1 | 1900 | 1000 | 1.9 |
| 1:1 | 2700 | 1600 | 1.7 |
| 1:2 | 2800 | 1800 | 1.6 |
| 1:4 | 3200 | 2100 | 1.5 |
| 0:1 | — | — | — |

\(P_\Omega\) value in the units of \(1\text{cmHg}\/\text{cm}^2\text{cm}^{-2}\text{sec}^{-1}\text{STP}^{-1}\text{cm}\text{cal}^{-1}\) (=1 barrer).

| Membrane | Ratio | \(P_\Omega\) | \(P_N\) | \(P_\Omega/P_N\) |
|----------|-------|----------|--------|------------|
| Poly(TESDPA-co-TBDPA) | 1:0 | 190 | 80 | 2.4 |
| 4:1 | 290 | 120 | 2.4 |
| 2:1 | 480 | 200 | 2.4 |
| 1:1 | 840 | 410 | 2.1 |
| 1:2 | 1500 | 780 | 1.9 |
| 1:4 | 1400 | 690 | 2.0 |
| 0:1 | 1100 | 690 | 1.6 |
| DSpoly(TESDPA-co-TBDPA) | 1:0 | 760 | 440 | 1.7 |
| 4:1 | 1100 | 590 | 1.9 |
| 2:1 | 1900 | 1100 | 1.7 |
| 1:1 | 1900 | 1100 | 1.7 |
| 1:2 | 2700 | 1500 | 1.8 |
| 1:4 | 2100 | 1100 | 1.8 |
| 0:1 | — | — | — |

\(P_\Omega\) value in the units of \(1\text{cmHg}\/\text{cm}^2\text{cm}^{-2}\text{sec}^{-1}\text{cal}^{-1}\) (=1 barrer).

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Fig. 1 IR spectra of membranes of poly(DMOSDPA-co-TBDPA) and
DSpoly(DMOSDPA-co-TBDPA) in the feed ratio of 1:4.
has both trimethylsilyl and tert-butyl groups as substituents. It is thought that the heterogeneity of substituents generates micro-scale voids when the membrane is formed. Desilylation of homopolymer of TMSDPA decreased the $P_{O_2}$ value from 1500 to 900 barrer. Similarly, the desilylated poly(TMSDPA-co-TBDPA) in the low contents of TBDPA, DSpoly(TMSDPA-co-TBDPA) (4 : 1), showed the lower oxygen permeability than poly(TMSDPA-co-TBDPA) (4 : 1). This is because the membrane became dense by the elimination of bulky spherical trimethylsilyl groups. However, the desilylation of poly(TMSDPA-co-TBDPA)s with high contents of TBDPA increased the gas permeability. DSpoly(TMSDPA-co-TBDPA) (1 : 4) showed the highest oxygen permeability and the $P_{O_2}$ value was as large as 3200 barrer. It is probably because that the spaces occupied by trimethylsilyl groups were maintained as micro-scale voids due to the steric repulsion of tert-butyl groups. These findings indicate that tert-butyl groups play an important role to generate micro-scale voids through desilylation.

The $P_{O_2}$ values of poly(TESDPA-co-TBDPA)s were 290–1500 barrer, which are larger than that of homopolymer, poly(TESDPA). Poly(TESDPA) has flexible ethyl chains, which would occupy the free volume in the membrane. Therefore, poly(TESDPA) exhibits lower gas permeability than poly(TMSDPA) and poly(TBDPA). The $P_{O_2}$ values of poly(TESDPA-co-TBDPA)s in low TBDPA contents were smaller than that of poly(TBDPA), but the $P_{O_2}$ values of poly(TESDPA-co-TBDPA)s in feed ratios of 1 : 2 and 1 : 4 were larger than that of poly(TBDPA) irrespective the copolymers contained relatively low gas-permeable TESDPA component. This result also suggests that the heterogeneity of substituent enhances the gas permeability. In the previous study, the desilylation of triethylsilyl groups increased the gas permeability because the free volume in the membrane were increased due to the elimination of bulkier silyl groups. All the DSpoly(TESDPA-co-TBDPA)s showed higher gas permeability than poly(TESDPA-co-TBDPA).

Poly(DMOSDPA) has more flexible long alkyl chains and shows much lower gas permeability. Therefore, the $P_{O_2}$ values of poly(DMOSDPA-co-TBDPA)s were smaller than that of poly(TBDPA). However, the desilylation drastically enhanced the gas permeability and DSpoly(DMOSDPA-co-TBDPA) in 1 : 4 feed ratio showed the highest permeability. In this way, the presence of tert-butyl groups is important to achieve high gas permeability when the bulkier silyl groups were eliminated.

The oxygen/nitrogen separation factors ($P_{O_2}/P_{N_2}$) of all the copolymer membranes before and after desilylation were in the range 1.3–3.4, and the values tended to decrease as the $P_{O_2}$ increased. These results agree with the general tendency of gas permeation through polymer membranes.

### Diffusivity and solubility of gases in the copolymer membranes

To inspect the gas permeability of the present polymers in detail, gas diffusion coefficients ($D$) were measured by time lag method and gas solubility coefficients ($S$) were calculated from $P$ and $D$ values. Tables 6–8 listed the diffusion and solubility coefficients of poly(TMSDPA-co-TBDPA)s, poly(TESDPA-co-TBDPA)s, and poly(DMOSDPA-co-TBDPA)s. The $S$ values were calculated by the following equation,

$$S = P/D$$

### Table 5 Gas permeability coefficient ($P_{O_2}$) of poly(DMOSDPA-co-TBDPA) and DSpoly(DMOSDPA-co-TBDPA)

| Membrane                  | Ratio | $P_{O_2}$ | $P_{N_2}$ | $P_{O_2}/P_{N_2}$ |
|---------------------------|-------|-----------|-----------|-------------------|
| Poly(DMOSDPA-co-TBDPA)    | 1 : 0 | 27        | 8.2       | 3.3               |
|                           | 4 : 1 | 28        | 8.5       | 3.3               |
|                           | 2 : 1 | 31        | 9.1       | 3.4               |
|                           | 1 : 1 | 52        | 24        | 2.2               |
|                           | 1 : 2 | 230       | 150       | 1.5               |
|                           | 1 : 4 | 300       | 120       | 2.5               |
|                           | 0 : 1 | 1100      | 690       | 1.6               |
| DSpoly(DMOSDPA-co-TBDPA)  | 1 : 0 | 650       | 300       | 2.2               |
|                           | 4 : 1 | 670       | 310       | 2.2               |
|                           | 2 : 1 | 1300      | 670       | 1.9               |
|                           | 1 : 1 | 1800      | 1100      | 1.6               |
|                           | 1 : 2 | 2000      | 1200      | 1.7               |
|                           | 1 : 4 | 3300      | 2100      | 1.6               |
|                           | 0 : 1 | —         | —         | —                 |

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

### Table 6 Gas diffusion coefficient ($D_{O_2}$) and solubility coefficient ($S_{O_2}$) of poly(TESDPA-co-TBDPA) and DSpoly(TESDPA-co-TBDPA)

| Membrane                  | Ratio | $D_{O_2} \times 10^3$ | $D_{N_2} \times 10^3$ | $S_{O_2} \times 10^3$ | $S_{N_2} \times 10^3$ |
|---------------------------|-------|-----------------------|-----------------------|-----------------------|-----------------------|
| Poly(TESDPA-co-TBDPA)     | 4 : 1 | 55                    | 46                    | 40                    | 26                    |
|                           | 2 : 1 | 75                    | 62                    | 25                    | 16                    |
|                           | 1 : 1 | 94                    | 80                    | 38                    | 30                    |
|                           | 2 : 1 | 69                    | 65                    | 50                    | 40                    |
|                           | 1 : 4 | 87                    | 51                    | 12                    | 19                    |
| DSpoly(TESDPA-co-TBDPA)   | 4 : 1 | 34                    | 32                    | 47                    | 31                    |
|                           | 2 : 1 | 78                    | 62                    | 39                    | 19                    |
|                           | 1 : 1 | 110                   | 95                    | 51                    | 25                    |
|                           | 2 : 1 | 110                   | 95                    | 51                    | 25                    |
|                           | 1 : 4 | 120                   | 100                   | 27                    | 21                    |

* Determined by the “time lag” method at 25 °C. In the units of cm$^2$ s$^{-1}$.

### Table 7 Gas diffusion coefficient ($D_{O_2}$) and solubility coefficient ($S_{O_2}$) of poly(TMSDPA-co-TBDPA) and DSpoly(TMSDPA-co-TBDPA)

| Membrane                  | Ratio | $D_{O_2} \times 10^3$ | $D_{N_2} \times 10^3$ | $S_{O_2} \times 10^3$ | $S_{N_2} \times 10^3$ |
|---------------------------|-------|-----------------------|-----------------------|-----------------------|-----------------------|
| Poly(TMSDPA-co-TBDPA)     | 4 : 1 | 41                    | 35                    | 7.1                   | 3.4                   |
|                           | 2 : 1 | 62                    | 53                    | 7.7                   | 3.8                   |
|                           | 1 : 1 | 73                    | 55                    | 12                    | 7.5                   |
|                           | 1 : 2 | 100                   | 65                    | 15                    | 12                    |
|                           | 1 : 4 | 98                    | 51                    | 14                    | 14                    |
| DSpoly(TMSDPA-co-TBDPA)   | 4 : 1 | 83                    | 70                    | 13                    | 8.4                   |
|                           | 2 : 1 | 100                   | 88                    | 19                    | 13                    |
|                           | 1 : 1 | 110                   | 95                    | 17                    | 12                    |
|                           | 1 : 2 | 140                   | 120                   | 19                    | 13                    |
|                           | 1 : 4 | 130                   | 94                    | 16                    | 12                    |

* Determined by the “time lag” method at 25 °C. In the units of cm$^2$ s$^{-1}$.
lylation of poly(TESDPA-TBDPA) and DSPoly(DMOSDPA-co-TBDPA). Since both values. Especially in high TESDPA ratios, the large enhance-

desilylation was also quite noticeable, and the enhancement of TMSDPA decreased the gas permeability. In addition, DSPoly(TMOSDPA-co-TBDPA) showed still low gas permeability in 80% feed ratio of TBDPA, indicating that even a small content of long alkyl chain caused a significant decrease in gas permeability.

The three type’s desilylated copolymer showed similar oxygen permeability. This means that as the alkyl group becomes longer, an extent of increment in $P_{O_2}$ through desilylation became larger. In this reason, DSPoly(TMOSDPA-co-TBDPA) exhibited the highest $P_{O_2}$ enhancement. Similarly to the case of copolymers before desilylation, the permeability of the desilylated copolymers increased as increasing TBDPA ratio. It suggests that tert-butyl groups are important to generate microscale voids after desilylation as well as before desilylation.

### Conclusions

Four types of copolymers having silyl and tert-butyl groups were synthesized by the copolymerization of the corresponding monomers with various feed ratios. Poly(TMOSDPA-co-TBDPA)s exhibited higher gas permeability than homopolymers, poly(TMOSDPA) and poly(TBDPA), because of heterogeneity of substituents. Poly(TMOSDPA-co-TBDPA)s and poly(TMOSDPA-co-TBDPA)s showed lower gas permeability than poly(TMOSDPA-co-TBDPA)s, because the flexible alkyl chains occupy the free volume. The desilylation of poly(TMOSDPA) decreased the gas permeability, but the $P_{O_2}$ values of poly(TMOSDPA-co-TBDPA)s increased through desilylation in high feed ratios of tert-butyl group. This indicates that tert-butyl groups play an important role in increasing gas permeability.

### Comparison of three types of copolymer membranes

The $P_{O_2}$ values of three types of copolymer membranes before and after desilylation were shown in Fig. 2. The copolymer membrane having longer alkyl chains exhibited lower oxygen permeability. This is because the flexible alkyl chains of ethyl and octyl groups would occupy the free volume in the polymer matrix. For poly(TESDPA-co-TBDPA) and poly(TMOSDPA-co-TBDPA), the permeability increased as the feed ratio of TBDPA increased. However, poly(TMOSDPA-co-TBDPA) showed still low gas permeability in 80% feed ratio of TBDPA, indicating that even a small content of long alkyl chain caused a significant decrease in gas permeability.

### Table 8 Gas diffusion coefficient ($D$) and solubility coefficient ($S$) of poly(TMOSDPA-co-TBDPA) and DSPoly(TMOSDPA-co-TBDPA)

| Membrane          | Ratio | $D_{O_2} \times 10^7$ | $D_{N_2} \times 10^7$ | $S_{O_2} \times 10^3$ | $S_{N_2} \times 10^3$ |
|-------------------|-------|----------------------|----------------------|----------------------|----------------------|
| Poly(TMOSDPA-co-TBDPA) | 4:1   | 12                   | 3.8                  | 2.3                  | 2.2                  |
|                   | 2:1   | 14                   | 7.0                  | 2.2                  | 1.3                  |
|                   | 1:1   | 27                   | 12                   | 1.9                  | 2.0                  |
|                   | 1:2   | 30                   | 25                   | 7.7                  | 6.0                  |
|                   | 1:4   | 41                   | 15                   | 9.7                  | 8.0                  |
| DSPoly(TMOSDPA-co-TBDPA) | 4:1   | 48                   | 36                   | 14                   | 8.6                  |
|                   | 2:1   | 55                   | 50                   | 24                   | 13                   |
|                   | 1:1   | 99                   | 80                   | 18                   | 14                   |
|                   | 1:2   | 110                  | 85                   | 18                   | 14                   |
|                   | 1:4   | 180                  | 150                  | 18                   | 14                   |

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

Fig. 2 Relationship between $P_{O_2}$ and TBDPA ratio in copolymers for poly(TMOSDPA-co-TBDPA)s, poly(TESDPA-co-TBDPA)s, poly(TMOSDPA-co-TBDPA)s, and the desilylated analogues.
role to maintain micro-scale voids through desilylation. When bulkier silyl groups were removed, the $P_{O_2}$ increased to larger extents. The gas diffusivity and gas solubility were also increased upon desilylation due to the increase of free volume that eliminated of silyl groups.

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