Synthesis and gas permeability of poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dialkylsiloxane) block copolymers containing fluoroalkyl substituents

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Poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dialkylsiloxane) (PTMPS/PDAS) block copolymers containing various kinds of fluoroalkyl substituents were synthesized. The gas permeability of the copolymer membranes was evaluated. The PTMPS contents of the copolymers could be controlled in the range 20–80 mol %, and the weight average molecular weights were more than 10^5. Very tough and thin membranes could be prepared from these copolymers by a solvent casting method. The oxygen permeability coefficient P_{O_2} of the copolymer membranes increased as PTMPS content decreased, and was independent of the kinds of substitution. When PTMPS content was below 40 mol %, the P_{O_2} of every copolymer membrane was more than 1×10^{-8} cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1}. The fluoroalkyl substituents affected the selectivity P_{O_2}/P_{N_2}. The values of P_{O_2}/P_{N_2} for PTMPS/PDAS block copolymers were higher than those of PTMPS/poly(dimethylsiloxane) block copolymers, which did not contain the fluoroalkyl group. Some of these copolymers showed excellent oxygen permselectivity, with values of P_{O_2} and P_{O_2}/P_{N_2} in the range 10^{-8}–3×10^{-8} cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1} and 2.30–2.50, respectively.

(Keywords: poly(tetramethyl-*p*-silphenylenesiloxane); poly(dialkylsiloxane); block copolymer; fluoroalkyl substituent; gas permeability; oxygen-enriching membrane)

INTRODUCTION

Recently, the production of oxygen-enriched air by membrane separation has been widely investigated owing to its wide applicability in industry and medicine. In this process, the ability of the polymer membrane plays an important role. For a practical oxygen-enriching membrane, oxygen permeability P_{O_2}, selectivity P_{O_2}/P_{N_2} and mechanical strength are all required to be sufficiently high. Poly(dimethylsiloxane) (PDMS) membrane shows the greatest gas permeability coefficients among polymer membranes because of the high mobility of the polymer main chain. But its selectivity of oxygen toward nitrogen is relatively low, and its mechanical strength is not satisfactory for practical applications. Although its mechanical strength has been increased by putting PDMS chain into block or crosslinked copolymers, selectivity remains low. For instance, a copolymer with polycarbonate has been synthesized by Ward *et al.*[1], and one based on poly(vinyl phenol) by Asakawa *et al.*[2]. The gas permeability of these copolymers was examined to find an oxygen permeability coefficient range 10^{-8}–4×10^{-8} cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1} and selectivity around 2.0–2.2. Kawakami *et al.* studied the gas permeation of silicone-containing graft copolymers which improved the permselectivity of oxygen[3,4].

To improve both the selectivity and the mechanical strength of PDMS membrane, we have attempted to prepare poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dialkylsiloxane) block copolymers containing fluoroalkyl substituents. Poly(tetramethyl-*p*-silphenylenesiloxane) (PTMPS) is known to be a tough, crystalline, fibre-forming polymer[5]. Thus, PTMPS/PDMS block copolymer is expected to be a good membrane-forming material with much higher mechanical strength than PDMS membrane. Furthermore, an increase in the oxygen permeability and selectivity of the copolymer membrane is expected by the introduction of fluorine-containing substituents into the copolymer.

This paper reports on the synthesis of PTMPS/poly(dialkylsiloxane) block copolymers containing fluoroalkyl substituents and evaluation of the copolymer membranes as oxygen-enriching membranes.

EXPERIMENTAL

Materials

p-Bis(dimethylhydroxysilyl)benzene (TMPS monomer) and silanol-terminated polydimethyl siloxane ($\bar{M} = 30\,000$) were purchased from Chisso Corporation. *p*-Bis(dimethylhydroxysilyl)benzene was purified twice by recrystallization from THF/n-hexane (1/9 by volume) solution before use. Dimethyldichlorosilane, methyldichlorosilane, 3,3,3-trifluoropropylmethyldichlorosilane, 1H,1H,2H,2H-heptadecafluorodecylmethyl-

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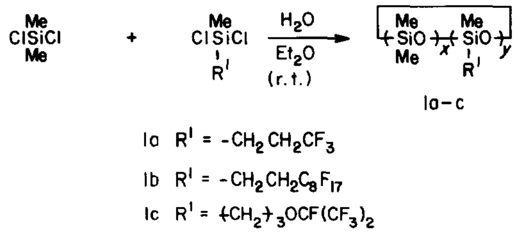
dichlorosilane and 3-(heptafluoroisopropoxy)propylmethyldichlorosilane, which were used for the preparation of cyclosiloxanes containing fluoroalkyl substituents, were all freshly distilled before use.

Preparation of cyclosiloxanes containing fluoroalkyl substituents

The preparation of cyclosiloxanes containing fluoroalkyl substituents was conducted by two methods.



Scheme 1 Preparation of cyclosiloxanes

Scheme 1 shows the first method. A typical procedure for the preparation of cyclosiloxane **1a** was as follows: A mixture of 50.4 g of dimethyldichlorosilane (23.9 mmol) and 30.8 g of 3,3,3-trifluoropropylmethyldichlorosilane (23.9 mmol) in 50 ml of dry diethyl ether was added dropwise to a mixture of 250 ml of water and 50 ml of diethyl ether under an argon atmosphere at room temperature (r.t.) over 4 h. The product was extracted with diethyl ether, and purified by fractional distillation. The fraction of b.p. = 70–120°C (15 mmHg) was collected – its weight was 24.8 g. The structure and composition (x/y) of the product (**1a**) were confirmed by ^{1}H nuclear magnetic resonance (n.m.r.) spectrometry: shifts relative to TMS: δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.75 (2H, *t*), 1.98 (2H, *t*); $x/y = 40/60$ (mol%).

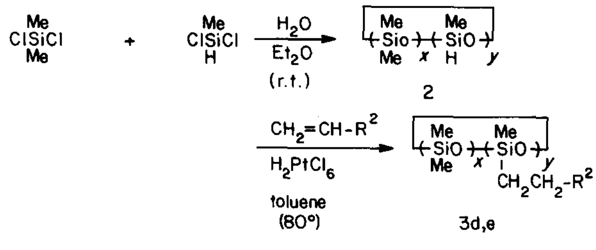
Cyclosiloxanes **1b**, **1c** and **2** were prepared by the same procedure as for **1a**, using 1H,1H,2H,2H-heptadecafluorodecylmethyldichlorosilane, 3-(heptafluoroisopropoxy)propylmethyldichlorosilane and methyldichlorosilane, respectively, instead of 3,3,3-trifluoropropylmethyldichlorosilane. Boiling points, ^{1}H n.m.r. shifts relative to TMS and compositions of cyclosiloxanes **1b**, **1c** and **2** were as follows:

1b: b.p. = 103–105°C (0.35 mmHg), δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.85 (2H, *t*), 2.01 (2H, *t*); $x/y = 70/30$ (mol%).

1c: b.p. = 102–185°C (13 mmHg), δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.70 (2H, *t*), 1.85 (2H, *m*), 4.03 (2H, *m*); $x/y = 72/28$ (mol%).

2: b.p. = 30–55°C (65 mmHg), δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.15 (3H, *d*), 4.68 (1H, *m*); $x/y = 73/27$ (mol%).

Cyclosiloxanes **3d** and **3e** were synthesized by the second method, i.e. the hydrosilylation of pentafluorostyrene and 4-pentafluorophenoxybutene with **2**, as shown in *Scheme 2*. A typical procedure was as follows.



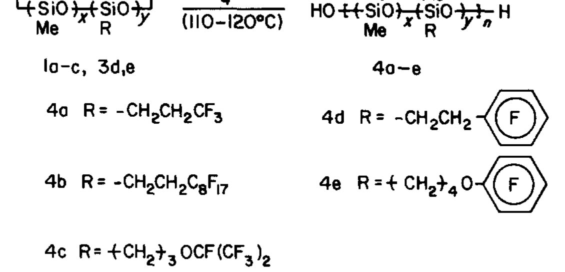
Scheme 2 Preparation of cyclosiloxanes

A mixture of 12.5 g of cyclosiloxane **2**, 11.2 g of pentafluorostyrene and 20 μl of ethanol solution of chloroplatinic acid (0.193 mol l^{-1}) in 40 ml of toluene was stirred at 80°C under an argon atmosphere for 19 h. Infrared (i.r.) spectra of the reaction mixture showed no absorption peak at 2175 cm^{-1}, which is due to Si–H bonding. The reaction mixture was evaporated and distilled under reduced pressure. The fraction of b.p. = 111–115°C (1.5 mmHg) was collected – its weight was 13.4 g. The structure and composition (x/y) of the product (**3d**) were confirmed by ^{1}H n.m.r. spectrometry: δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.75 (2H, *t*), 2.70 (2H, *t*); $x/y = 73/27$ (mol%).

Cyclosiloxane **3e** was prepared by the same procedure as for **3d** using 4-pentafluorophenoxybutene instead of pentafluorostyrene. Boiling point, ^{1}H n.m.r. shifts relative to TMS and composition of cyclosiloxane **3e** were: b.p. = 165–173°C (0.23 mmHg), δ (CCl_4, ppm) = 0.10 (3H, *s*), 0.55 (2H, *t*), 1.75 (4H, *m*), 4.14 (2H, *t*); $x/y = 68/32$ (mol%).

Preparation of poly(dialkylsiloxane)s

Cyclosiloxanes **1a**, **1b**, **1c**, **3d** and **3e** thus obtained were polymerized by heating at 110–120°C in the presence of basic catalyst as shown in *Scheme 3*. A typical procedure is as follows.



Scheme 3 Preparation of poly(dialkylsiloxane)s

A mixture of 6.90 g of cyclosiloxane **1a** and a few drops of 10 wt% methanol solution of tetramethylammonium hydroxide was heated at 110–120°C for 1 h. The reaction mixture was washed with water and heated at 200°C in vacuo for 5 h to remove unreacted cyclosiloxane. 5.83 g of highly viscous silanol-terminated poly(dialkylsiloxane) **4a** was obtained. The structure and composition (x/y) of the product (**4a**) were confirmed by ^{1}H n.m.r. spectrometry, and the number average and weight average molecular weights were determined by gel permeation chromatography (g.p.c.). $x/y = 60/40$ (mol%), $\overline{M}_n = 2.09 \times 10^4$, $\overline{M}_w = 3.48 \times 10^4$.

Other poly(dialkylsiloxane)s **4b**–**4e** were prepared by the same procedure as for **1a** using cyclosiloxanes **1b**, **1c**, **3d** and **3e**, respectively, instead of cyclosiloxane **1a**. The compositions and molecular weights of **4b**–**4e** were:

4b: $x/y = 73/27$ (mol%), $\overline{M}_n = 2.54 \times 10^4$, $\overline{M}_w = 4.55 \times 10^4$

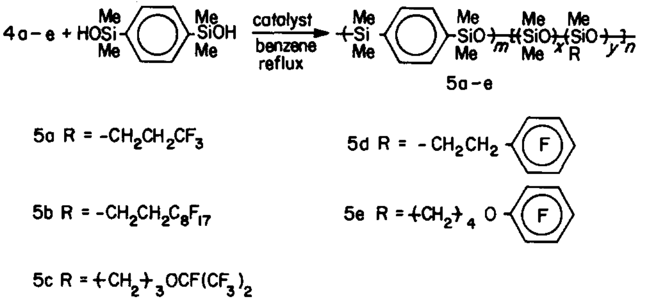
4c: $x/y = 66/34$ (mol%), $\overline{M}_n = 2.08 \times 10^4$, $\overline{M}_w = 4.15 \times 10^4$

4d: $x/y = 66/34$ (mol%), $\overline{M}_n = 2.12 \times 10^4$, $\overline{M}_w = 3.83 \times 10^4$

4e: $x/y = 58/42$ (mol%), $\overline{M}_n = 2.41 \times 10^4$, $\overline{M}_w = 4.32 \times 10^4$

Preparation of block copolymers

High molecular weight poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dialkylsiloxane) (PTMPS/PDAS) block copolymers were conveniently prepared from TMPS monomer and silanol-terminated poly(dialkylsiloxane)s as shown in *Scheme 4*.



Scheme 4 Preparation of PTMPS/PDAS block copolymers

Into a flask equipped with a reflux condenser and a benzene-filled azeotrope trap was placed a mixture of TMPS monomer, silanol-terminated poly(dialkylsiloxane)s and a few drops of tetramethylguanidine di-2-ethylhexanoate in benzene. After refluxing for 15–20 h, the copolymers obtained were reprecipitated in methanol to remove the catalyst and unreacted starting materials. The structures and compositions of the copolymers were confirmed by ^{1}H n.m.r. spectrometry.

Poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dimethylsiloxane) (PTMPS/PDMS) block copolymer was also prepared as a reference for PTMPS/PDAS block copolymers according to the method of Merker and Scott[6], from TMPS monomer and silanol-terminated PDMS ($\overline{M}_n = 30000$). Copolymers having various compositions of PTMPS and PDMS units were prepared by changing the ratio of TMPS monomer and silanol-terminated PDMS.

Characterization

The composition ratio of PTMPS/PDAS and PTMPS/PDMS block copolymers were determined by ^{1}H n.m.r. spectra recorded on a Hitachi EM-390 90 MHz n.m.r. spectrometer using CCl_4 as the solvent. The number average and weight average molecular weights were determined with a Toyo Soda HLC-802A gel permeation chromatograph. THF was used as the solvent and standard polystyrenes were used for calibrating molecular weight.

Membrane preparation

Chloroform solution containing 5 wt% of the polymer was cast on a polytetrafluoroethylene sheet and the solvent was evaporated over 24 h. For measuring gas permeability the polymer membrane formed was then dried in vacuo and cut into a circular piece 22 mm in diameter. The thickness of the membrane was in the range 50–100 μm.

Measurement of gas permeability coefficients

Gas permeability was measured according to the vacuum method using the apparatus shown in *Figure 1*. Pressure on the permeation side, where the initial pressure was 0.01 mmHg, was measured with a Pirani gauge. The permeability coefficient, *P*, was calculated from the slope of a time–pressure curve, d*p*/d*t*, at steady state.

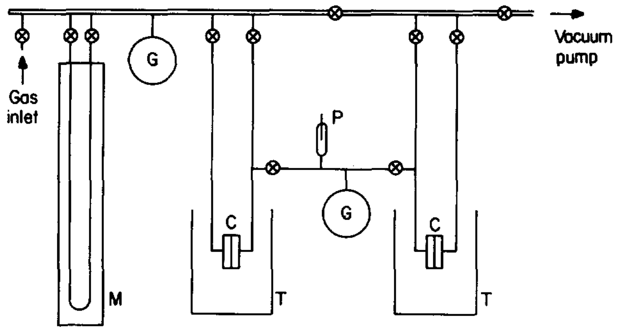


Figure 1 Schematic diagram of the apparatus for gas permeability measurement: C, permeation cell; G, gas reservoir; M, manometer; P, Pirani gauge; T, thermostat; ⊗, stop cock

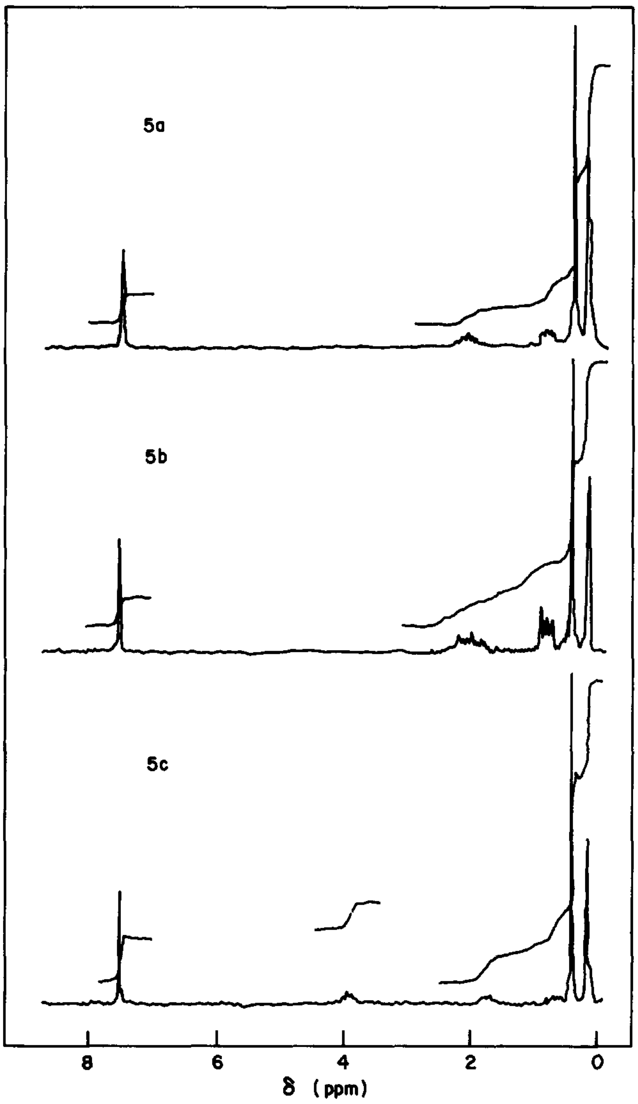


Figure 2 Typical ^{1}H n.m.r. spectra of PTMPS/PDAS block copolymers **5a**, **5b** and **5c** (solvent, CCl_4)

RESULTS AND DISCUSSION

Typical ^{1}H n.m.r. spectra of these copolymers are shown in *Figures 2* and *3*. In the spectra, the signals of methyl and phenylene protons of the silphenylenesiloxane unit were observed at 0.30 and 7.40 ppm, respectively, and signals of methyl protons of the dimethylsiloxane unit at 0.11 ppm. For the copolymers **5a**–**5e**, the proton signals due to the fluorine-containing substituents could be distinguished from those of silphenylenesiloxane and dimethylsiloxane units as shown in *Figures 2* and *3*. The

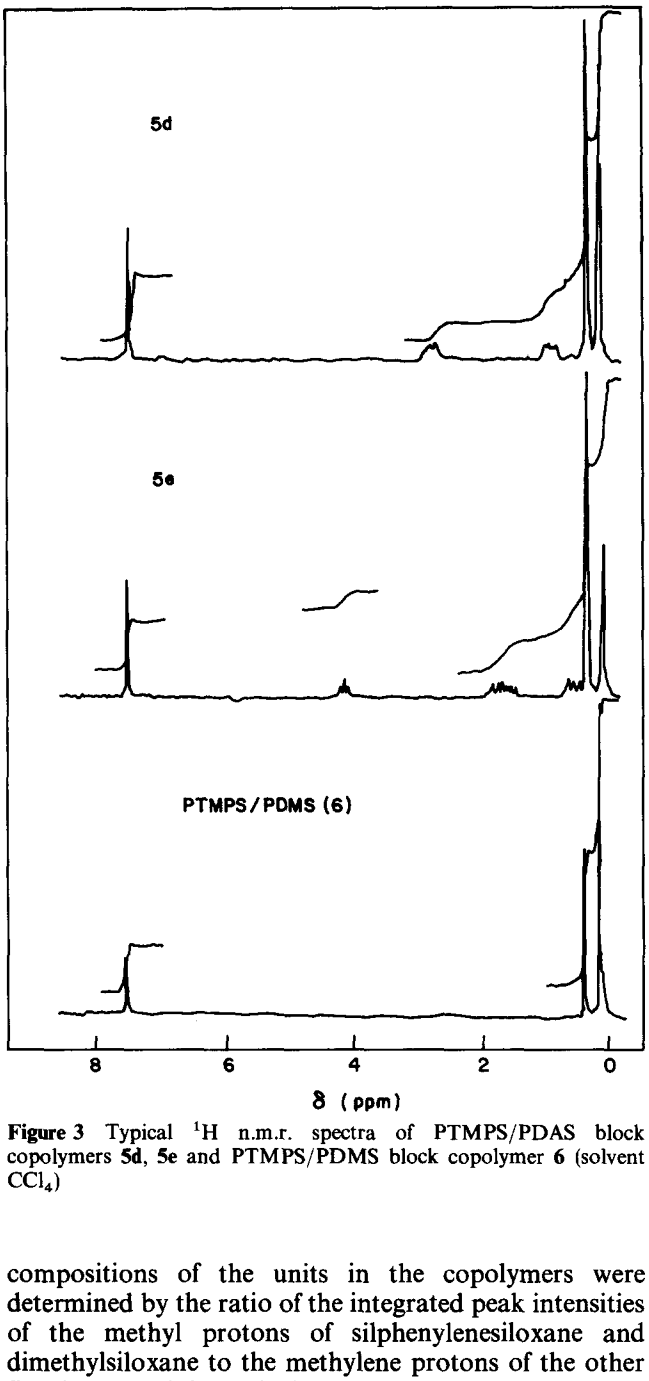


Figure 3 Typical ^1H n.m.r. spectra of PTMPS/PDAS block copolymers **5d**, **5e** and PTMPS/PDMS block copolymer **6** (solvent CCl_4)

compositions of the units in the copolymers were determined by the ratio of the integrated peak intensities of the methyl protons of silphenylenesiloxane and dimethylsiloxane to the methylene protons of the other fluorine-containing substituents.

The observed compositions and molecular weights of PTMPS/PDAS (**5a**–**5e**) and PTMPS/PDMS (**6**) block copolymers are summarized in *Table 1*. The compositions of these copolymers could be varied by changing the ratio of TMPS monomer and silanol-terminated poly(dialkylsiloxane)s (**4a**–**4e**) or PDMS. The compositions agreed with the predicted value from the molar ratio of the starting materials in each case. PTMPS contents of the copolymers could be controlled in the range 20–80 mol%. In this range of PTMPS content, all the copolymers were fibrous, and the melting temperatures were over 130°C, as determined by differential scanning calorimetry (d.s.c.) measurements. The melting temperature of PTMPS homopolymer is 140°C. That of this type of copolymer is known to be influenced by the average degrees of polymerization of the PTMPS segment. Nagase *et al.* investigated the relationship between thermal property and segment length of PTMPS/PDMS block copolymers[7]. They concluded that the longer the PTMPS segment length, the higher was the melting temperature of the copolymers, which was due to the increase in the thickness of chain-folded lamellae of the PTMPS crystalline unit. The average lengths of PTMPS segments are presumed to be over 100 units because the melting temperature is more than 130°C even when the PTMPS content is only 20 mol%. This value of segment length would be reasonable based on the consideration of the high molecular weights of silanol-terminated poly(dialkylsiloxane)s, **4a**–**4e**, and PDMS used in the copolymerizations. The number average molecular weights of those polysiloxanes were more than 20 000. In this copolymerization, the use of silanol-terminated poly(dialkylsiloxane) of a higher degree of polymerization results in the formation not only of longer polysiloxane segments but also of longer PTMPS segments in the resulting block copolymers.

Weight average molecular weights of all the copolymers are calculated to be more than 100 000 according to g.p.c. measurements. So very tough and thin membranes could be prepared by casting chloroform solutions of the copolymers. The membranes became softer with decreasing PTMPS content, but the strength of the membranes was sufficient as separation membranes. Membranes prepared from the copolymers containing bulky fluoroalkyl substituents, i.e. **5b**, **5c**, **5d** and **5e**, tend to be stiffer than those prepared from other copolymers when compared at the same PTMPS content. According to the measurement of tensile strength, the values of tensile modulus of copolymers 5b-2, 5c-2, 5d-3 and 5e-2 were in the range 280–400 kg cm^{-2}, and those of copolymers 5a-4 and 6-3 were in the range of 100–140 kg cm^{-2}. In addition, the tensile strength and elongation were in the range 75–85 kg cm^{-2} and 170–220%, respectively, for copolymers 5b-2, 5c-2, 5d-3 and 5e-2, and 45–55 kg cm^{-2} and 310–450%, respectively, for copolymers 5a-4 and 6-3.

Oxygen and nitrogen permeability coefficients P_{O_2} and P_{N_2}, and selectivity P_{O_2}/P_{N_2} of these copolymer

Table 1 Composition and molecular weight of PTMPS/PDAS and PTMPS/PDMS block copolymers

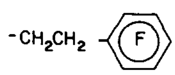
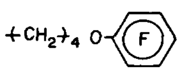
Sample no.	Structure of R	Composition $m/nx/ny$ (mol%)	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w$ ($\times 10^{-4}$)
5a-1	$-CH_2CH_2CF_3$	80/12/8	7.65	14.3
5a-2		64/25/11	10.5	24.8
5a-3		50/30/20	13.5	32.6
5a-4		25/45/30	7.82	15.1
5b-1	$-CH_2CH_2C_8F_{17}$	54/29/17	5.04	13.4
5b-2		39/40/21	8.00	15.2
5b-3		28/45/27	7.50	12.9
5c-1	$-(CH_2)_3-OCF(CF_3)_2$	33/44/23	9.95	19.2
5c-2		25/50/25	9.40	17.1
5d-1		71/17/12	8.48	21.7
5d-2		50/28/22	9.65	21.3
5d-3		44/30/26	13.5	23.9
5e-1		39/45/16	10.8	27.1
5e-2		30/48/22	9.95	25.2
6-1	$-CH_3$	75/25/0	14.1	24.4
6-2		50/50/0	9.88	16.2
6-3		30/70/0	10.6	19.7
6-4		22/78/0	8.26	14.2
6-5		20/80/0	6.96	11.7

Table 2 Oxygen and nitrogen permeability coefficients of PTMPS/PDAS and PTMPS/PDMS block copolymers

Sample no.	P_{O_2} (cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1})	P_{N_2} (cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1})	P_{O_2}/P_{N_2}
5a-1	1.66×10^{-9}	5.37×10^{-10}	3.09
5a-2	4.08×10^{-9}	1.54×10^{-9}	2.65
5a-3	6.51×10^{-9}	2.70×10^{-9}	2.41
5a-4	1.94×10^{-8}	8.51×10^{-9}	2.28
5b-1	5.31×10^{-9}	2.19×10^{-9}	2.42
5b-2	9.82×10^{-9}	4.13×10^{-9}	2.38
5b-3	1.47×10^{-8}	6.26×10^{-9}	2.35
5c-1	1.21×10^{-8}	5.06×10^{-9}	2.39
5c-2	2.76×10^{-8}	1.18×10^{-8}	2.34
5d-1	4.01×10^{-9}	1.58×10^{-9}	2.53
5d-2	7.32×10^{-9}	3.00×10^{-9}	2.44
5d-3	9.63×10^{-9}	3.88×10^{-9}	2.48
5e-1	1.79×10^{-8}	7.72×10^{-9}	2.32
5e-2	1.99×10^{-8}	8.84×10^{-9}	2.25
6-1	1.41×10^{-9}	5.09×10^{-10}	2.77
6-2	5.23×10^{-9}	2.27×10^{-9}	2.30
6-3	2.48×10^{-8}	1.17×10^{-8}	2.12
6-4	3.23×10^{-8}	1.58×10^{-8}	2.04
6-5	4.14×10^{-8}	2.09×10^{-8}	1.98

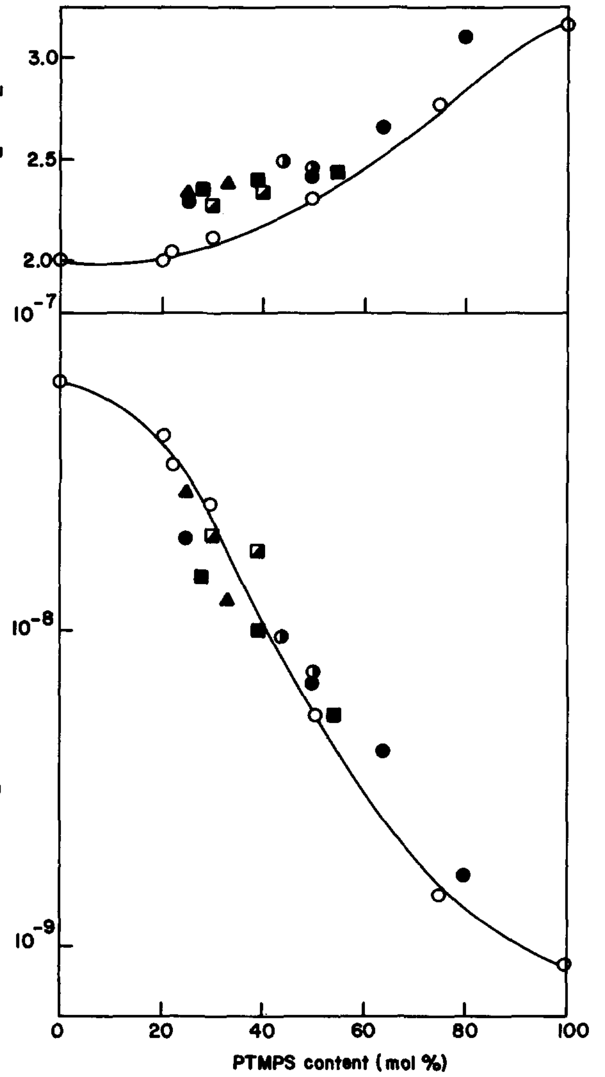


Figure 4 Plots of oxygen permeability coefficient P_{O_2} and selectivity P_{O_2}/P_{N_2} against PTMPS content of PTMPS/PDAS block copolymers **5a** (●), **5b** (■), **5c** (▲), **5d** (◑) and **5e** (▨) and PTMPS/PDMS block copolymer **6** (○)

membranes at 25°C are listed in *Table 2*. The values of P_{O_2}, P_{N_2} and P_{O_2}/P_{N_2} of a membrane prepared from PTMPS homopolymer were 8.80×10^{-10}, 2.79×10^{-10} and 3.15 respectively. Hence P_{O_2} and P_{N_2} of the copolymer membranes increased as PTMPS content decreased, i.e. as polysiloxane content increased. This tendency has been observed for other kinds of block or graft copolymers containing the polysiloxane chain. Ichikawa *et al.* synthesized PTMPS/PDMS block and graft copolymers containing various segment lengths and investigated the relationship between gas permeability and polymer structure[8]. They suggested that for PTMPS/PDMS block copolymers having long segments, values of P_{O_2} and P_{O_2}/P_{N_2} for the copolymers approached nearer and nearer to those of PDMS with increasing PDMS content.

Figure 4 shows the effect of PTMPS content on P_{O_2} and P_{O_2}/P_{N_2} of the copolymer membranes. In this figure and *Figure 5*, plots for PTMPS/PDMS block copolymers are shown by open circles and plots for copolymers **5a**–**5e**, which contain fluoroalkyl substituents, by filled or half-filled circles. Most of the data for P_{O_2} *versus* PTMPS content of the copolymers are on the same line. This result indicates that P_{O_2} of the copolymer is determined by PTMPS content and is independent of the kinds of substituents. When PTMPS contents are below 40 mol%, P_{O_2} of every copolymer membrane is over 10^{-8} cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1}, which is the same order of P_{O_2} as that of poly(dimethylsiloxane) membrane. On the other hand, the values of selectivity P_{O_2}/P_{N_2} of the copolymers **5a**–**5e** are higher than those of PTMPS/PDMS copolymers for all PTMPS contents. These results clearly indicate that the introduction of fluorine-containing substituents increases the selectivity P_{O_2}/P_{N_2}. Such an increase may be attributed to the

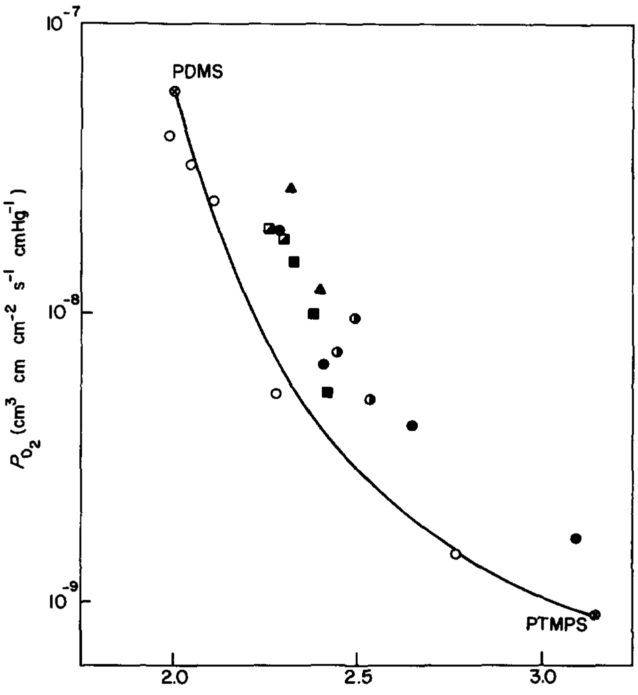


Figure 5 Relationship between oxygen permeability coefficient P_{O_2} and selectivity P_{O_2}/P_{N_2} of PTMPS/PDAS block copolymers **5a** (●), **5b** (■), **5c** (▲), **5d** (◑) and **5e** (▨) and PTMPS/PDMS block copolymer **6** (○)

increase of solubility in the side chains of the copolymer **5a**–**5e**. Kajiyama *et al.* have studied the gas permeability of the polymer/liquid crystal composite membrane[9]. They observed an increase in selectivity P_{O_2}/P_{N_2} on introduction of fluorocarbon monomer, perfluorotributylamine, into the composite membrane, and suggested that such a fluorocarbon monomer acted as an oxygen carrier in the membrane.

Figure 5 shows the relationship between P_{O_2} and P_{O_2}/P_{N_2} for the block copolymer membranes. It is obvious from this figure that the larger the oxygen permeability coefficient, the smaller is the selectivity. But the selectivities of PTMPS/PDAS copolymers **5a**–**5e** are evidently higher than those of PTMPS/PDMS block copolymers when compared at the same permeability coefficients. The difference between fluorine-containing substituents is not so clear even when total fluorine contents and the nature of the substituents were considerably changed. These results suggest that the terminal trifluoromethyl group or pentafluorophenyl group is sufficient to improve membrane performance in this copolymer system. Some of the PTMPS/PDAS block copolymers containing the fluoroalkyl group, 5b-3, 5c-1, 5c-2 and 5e-1, showed excellent oxygen permeability and selectivity, with values of P_{O_2} and P_{O_2}/P_{N_2} more than 10^{-8} cm^3 (s.t.p.) cm cm^{-2} s^{-1} cmHg^{-1} and 2.30, respectively. These values allow these membranes to be candidates for oxygen-enriching membranes in medicine and engineering.

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