Chemical modification of polysulphone: 2. Gas and liquid permeability of polysulphone/polydimethylsiloxane graft copolymer membranes

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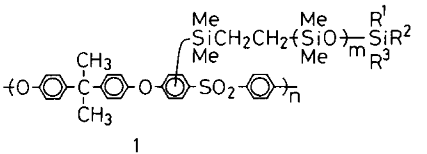
The gas and liquid permeabilities of polysulphone/polydimethylsiloxane (PSF/PDMS) graft copolymer membranes have been investigated. The permeability coefficients to nitrogen, oxygen, hydrogen, methane and carbon dioxide were evaluated. The gas permeability coefficients of the graft copolymer membranes were influenced by the PDMS content of the graft copolymer. In the region of >60 wt% PDMS content, the oxygen permeability coefficient of PSF/PDMS graft copolymer membrane was $(1\text{–}3) \times 10^{-8}\,\mathrm{cm^3\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}}$. In addition, the permeability to methane and carbon dioxide was remarkably enhanced in comparison with PSF membrane. The introduction of PDMS chains greatly increased the diffusion coefficients of methane and carbon dioxide. In the case of pervaporation of aqueous ethanol solution, the preferential permeation of ethanol was observed through the graft copolymer membrane for which the PDMS content was >50 wt%.

(Keywords: polysulphone/polydimethylsiloxane; graft copolymer; gas permeability; pervaporation)

INTRODUCTION

The permeability of polymer membranes to gases and liquids is an important consideration for numerous applications, including membranes for gas separation and pervaporation. Many attempts have been made to find several kinds of membrane materials suitable for gas separation[1–6] and pervaporation[7–14]. Recently, we have also been investigating some kinds of block or graft copolymers containing a polydimethylsiloxane (PDMS) chain[15–21]. The introduction of PDMS into the polymers greatly enhanced the gas permeability and also resulted in ethanol permselectivity at pervaporation of aqueous ethanol solution even though the starting polymers showed water permselectivity.

In our previous paper[22], we presented the synthesis of a polysulphone/polydimethylsiloxane (PSF/PDMS) graft copolymer, whose chemical formula is shown (**1**), by using Pt-catalysed hydrosilylation. That paper also dealt with the thermal properties, solubility and mechanical properties of the graft copolymer. This type of graft copolymer is soluble in several kinds of organic solvents and shows excellent membrane-forming ability, thermal stability and mechanical strength. These properties are derived from the backbone polymer, i.e. PSF.



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In this paper, we describe some results of our investigation into the permeability and separation characteristics of PSF/PDMS graft copolymer membranes for gas permeation and pervaporation of aqueous ethanol solution. The membranes were prepared from several kinds of graft copolymers having different PDMS contents and side-chain end-groups. Detailed study on the copolymer membranes led us to clarify the effects of PDMS content and side-chain end-groups upon the permeation.

EXPERIMENTAL

Materials

PSF/PDMS graft copolymers were prepared by coupling of vinyldimethylsilylated PSFs with hydrosilyl-terminated PDMS oligomers. The detailed procedure for the preparation was described in our previous paper[22], which included the preparations of vinyldimethylsilylated PSF and hydrosilyl-terminated PDMS oligomer. *Table 1* summarizes the chemical structures, the compositions and the glass transition temperatures of the PSF/PDMS graft copolymers used in this work.

Membrane preparation

A chloroform solution containing about 3 wt% of the polymer was cast on a polytetrafluoroethylene sheet and the solvent was evaporated over a period of 24 h to form membranes of 30–60 μm thickness. For the measurement of gas permeability, the polymer membrane formed was then dried *in vacuo* and cut into a circular piece of 22 mm diameter. For the measurement of pervaporation, the membrane was cut into a 50 mm square.

Measurement of gas permeability

Gas permeability was measured according to the

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Table 1 Characterizations of PSF/PDMS graft copolymers

Sample no.	Average number of side-chains/PSF unit	$\bar{m}$	Side-chain end-groups[a]			PSF/PDMS (wt%)	T_g (°C)
			R^1	R^2	R^3		
G-1	0.196	22.1	Me	Me	Me	82/18	175
G-2	0.533	22.1	Me	Me	Me	42/58	−105, 168
G-3	1.36	7.2	Me	Me	Me	45/55	151
G-4	1.47	10.5	Me	Me	Me	31/69	142
G-5	1.56	7.2	Me	Me	Me	40/60	150
G-6	1.77	2.0	Me	Me	Me	69/31	170
G-7	1.77	4.3	Me	Me	Me	47/53	157
G-8	1.77	7.2	Me	Me	Me	35/65	148
G-9	1.77	10.5	Me	Me	Me	20/80	131
G-10	2.40	4.3	Me	Me	Me	53/47	152
G-11	2.40	7.2	Me	Me	Me	28/72	141
G-12R	1.77	7.1	Ph	Ph	Ph	34/66	155
G-13R	2.40	4.8	Me	Me	n-C_8H_{17}	40/60	155
G-14R	1.77	7.2	Me	Me	n-C_8H_{17}	34/66	154
G-15R	1.77	6.9	Me	Me	n-$C_{18}H_{37}$	51/49	159
G-16R	1.77	5.5	Me	Me	n-$C_6F_{13}C_2H_4$	51/49	158
G-17R	1.77	7.1	Me	Me	n-$C_6F_{13}C_2H_4$	40/60	154

[a] R^1–R^3 as in **1**

vacuum method. The pressure of the permeability side, for which 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, dp/dt, at steady state.

The diffusion coefficient D was estimated from the observed time lag in permeation, and S was calculated according to the equation based on Fick's and Henry's law[23].

Pervaporation

Pervaporation of ethanol/water mixture through the membrane was carried out by an ordinary method using a stainless-steel cell at 50°C. The permeation area of the membrane was 9.6 cm^2. The feed solution of the ethanol/water mixture was circulated on the upper side of the membrane, and the pressure of the downstream side was kept at about 0.5 mmHg. The composition and flux of the permeating mixture were determined by a gas chromatograph connected directly to the pervaporation cell, in order to avoid the effect of moisture on the determination of pervaporation characteristics. The permeation rate P (in $g\,m\,m^{-2}\,h^{-1}$) was calculated with a correction of the flux for the thickness of the membrane. The separation factor, which was a measure of the preferential permeation of component A, was also defined as the concentration ratio Y_A/Y_B in the permeate divided by the concentration ratio X_A/X_B in the feed. A and B indicate ethanol and water respectively in this paper.

RESULTS AND DISCUSSION

Gas permeability

Figure 1 gives the Arrhenius plots for gas permeation through PSF/PDMS graft copolymer (G-8) membrane. The permeability coefficients of nitrogen (P_{N_2}), oxygen (P_{O_2}), carbon dioxide (P_{CO_2}), methane (P_{CH_4}) and hydrogen (P_{H_2}) were plotted against the reciprocal of temperature ($1/T$). The activation energy E_p in the gas permeation was evaluated from the Arrhenius plots (*Figure 1*) according to the equation:

$$P = P^* \exp(-E_p/RT) \qquad (1)$$

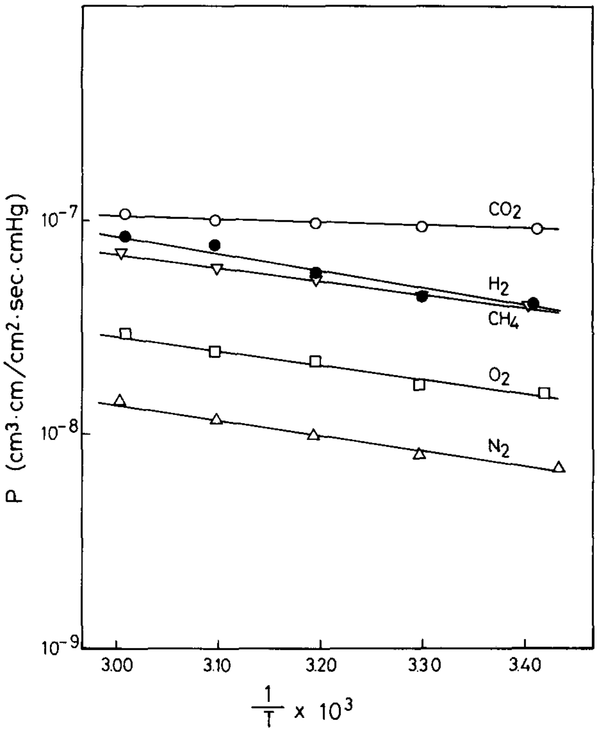

Figure 1 Arrhenius plots for the gas permeability coefficients of PSF/PDMS graft copolymer (G-8) membrane

E_p of each gas permeation through PSF membrane was also determined by the same method. Furthermore, the diffusion coefficient D and the solubility coefficient S were calculated from the observed time lag. The values of E_p, D, S, P and separation factors P/P_{N_2} are listed in *Table 2*.

It is noticed from this table that the gas permeability coefficients of PSF/PDMS graft copolymer membrane is quite different from those of PSF membrane but very similar to that of PDMS membrane. It is suggested from the result that the continuous phase of PDMS existed in the copolymer membrane. The gas permeability coefficients of PSF membrane increased in the following order: $P_{H_2} > P_{CO_2} > P_{O_2} > P_{CH_4} > P_{N_2}$. The order at PSF/

Table 2 Diffusion, solubility and permeability coefficients, separation factor and activation energy in gas permeation of PSF and PSF/PDMS graft copolymer (G-8) membranes at 25°C

	PSF					PSF/PDMS graft copolymer (G-8)[a]				
Gas	D (10^{-7} cm^2 s^{-1})	S (10^{-3} cm^3 cm^{-3} cmHg^{-1})	P (10^{-10} cm^3 cm cm^{-2} s^{-1} cmHg^{-1})	P/P_{N_2}	E_p (kcal mol^{-1})	D (10^{-7} cm^2 (s^{-1})	S (10^{-3} cm^3 cm^{-3} cmHg^{-1})	P (10^{-10} cm^3 cm cm^{-2} s^{-1} cmHg^{-1})	P/P_{N_2}	E_p (kcal mol^{-1})
N_2	0.112	1.83	0.205	–	5.56	5.49 (49.0)	7.87 (4.30)	43.2 (211)	–	3.95
O_2	0 271	4.35	1.18	5.76	4.01	11.3 (41.7)	10.2 (2.34)	115 (97.5)	2.66	3.16
CO_2	0.234	30.2	7.06	34.4	1.32	32.0 (136)	21.0 (0.695)	673 (95.3)	15.6	1.29
CH_4	0.047	8.30	0.390	1.90	6.99	19.1 (406)	14.7 (1.77)	280 (718)	6.48	3.05
H_2	0.750	25.7	19.3	94.1	4.35	19.1 (25.5)	16.2 (0.630)	309 (16.0)	7.15	3.98

[a] Numbers in parentheses are values relative to those of PSF (=1)

PDMS graft copolymer membrane differed, as follows: $P_{CO_2} > P_{H_2} > P_{CH_4} > P_{O_2} > P_{N_2}$, which was also similar to that of PDMS membrane. In the case of PSF/PDMS graft copolymer membrane, the change in the solubility coefficient S was relatively small, but the diffusion coefficient D increased 10^2–10^3 times compared with PSF membrane. Such an increase of D is probably due to the increase in free volume of the membrane caused by the flexible PDMS chain. In particular, the diffusion coefficient of methane (D_{CH_4}) of graft copolymer G-8 was 406 times higher than that of PSF membrane, which resulted in the increase of not only P_{CH_4} but also the separation factor to nitrogen P_{CH_4}/P_{N_2} from 1.90 to 6.48. The increase of D_{CO_2} was also greater than that of the other gases such as nitrogen, oxygen and hydrogen. The great increase of D_{CH_4} and D_{CO_2} explains the observed change in the order of P between PSF and PSF/PDMS graft copolymer.

As shown in *Table 1*, a wide variety of PSF/PDMS graft copolymers were prepared, changing the average number and length of side-chain, the side-chain end-group and the composition. The evaluation of the gas permeability coefficients of all the graft copolymers in *Table 1* would lead to clarification of the effect of chemical structure of the graft copolymer upon the gas permeation. The graft copolymer G-2 was phase-separated, which was presumed from the fact that the two glass transition temperatures of PDMS (−105°C) and PSF (168°C) components were observed in d.s.c. measurement. On the other hand, the copolymers containing relatively short PDMS chains up to 10 monomer units (G-3 to G-17R) showed no phase separation because only one transition (130–160°C) derived from the PSF component was observed. Such a difference of membrane structure would affect the gas permeability. In fact, P_{O_2} and P_{O_2}/P_{N_2} of G-2 membrane were 1.68×10^{-8} cm^3 cm cm^{-2} s^{-1} cmHg^{-1} and 2.16, respectively, and those of G-5 membrane were 1.40×10^{-8} cm^3 cm cm^{-2} s^{-1} cmHg^{-1} and 2.54, respectively. For these two membranes, the composition (PDMS content) was nearly the same and the PDMS chain length different. In this case, the permeability coefficients of the two membranes were about the same, but the separation factor of G-5 was higher than that of G-2. This fact indicates that the permeability of the copolymer membrane mostly depends on the composition, but the separation factor is affected by the length of the PDMS chain. Lack of phase separation at the short PDMS branched copolymer would explain these results as the non-phase-separated membrane undergoes the influence of polymer backbone component[4,5].

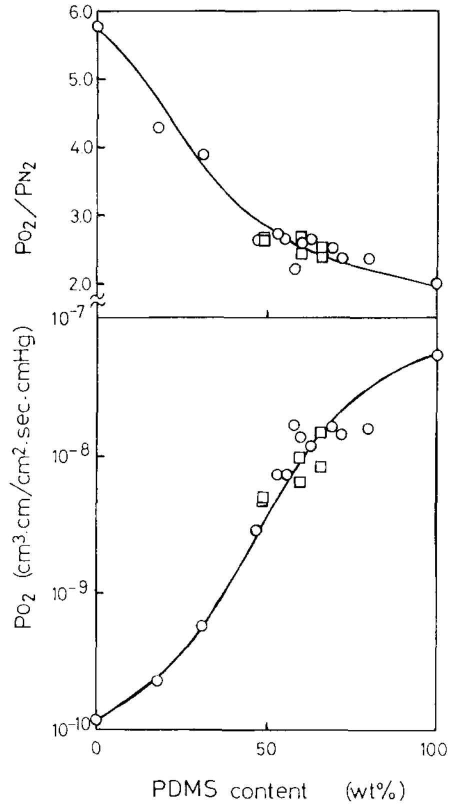

Figure 2 Effect of PDMS content upon the permeability coefficient of oxygen P_{O_2} and the separation factor P_{O_2}/P_{N_2} of PSF/PDMS graft copolymer membranes

In order to clarify the effect of PDMS content on gas permeability coefficients and selectivities, P of oxygen and methane and P/P_{N_2} were plotted against PDMS content of the copolymer membrane (*Figures 2* and *3*). In these figures, the circles indicate the samples G-1 to G-11, and the squares indicate the samples G-12R to G-17R, which contain alkyl or phenyl groups at the side-chain ends. No significant difference was observed between the two kinds of samples, i.e. the gas permeabilities only depended on the PDMS content and not on the side-chain end groups used in this work.

As shown in *Figure 2*, the oxygen permeability coefficient (P_{O_2}) simply increased and the selectivities (P_{O_2}/P_{N_2}) decreased as the PDMS content increased. In the region of >50 or 60 wt% PDMS content, all the permeability coefficients exceeded 10^{-8} cm^3 cm cm^{-2} s^{-1} cmHg^{-1}, which was the same order as for the PDMS

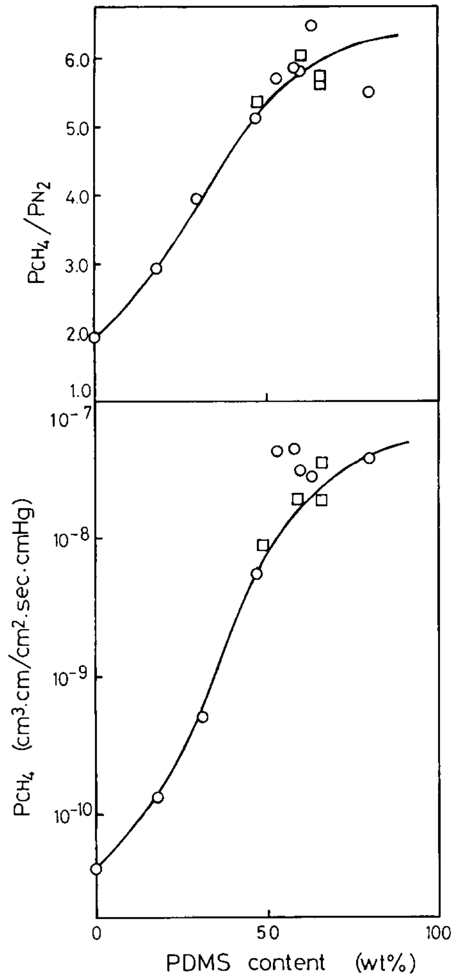

Figure 3 Effect of PDMS content upon the permeability coefficient of methane P_{CH_4} and the separation factor P_{CH_4}/P_{N_2} of PSF/PDMS graft copolymer membranes

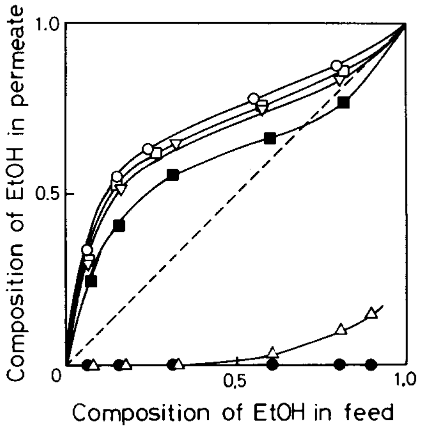

Figure 4 Permeation composition curves of aqueous ethanol solution through PSF (●) and PSF/PDMS graft copolymer membranes: G-1 (△), G-2 (▽), G-5 (□), G-8 (○) and G-14R (■)

membrane. In the case of the gas permeation of carbon dioxide and hydrogen, a similar tendency was observed. This result suggests that a continuous phase of PDMS domain is formed at this large PDMS content region, and hence the selectivities approach the values of PDMS membrane. A similar phenomenon has also been found in other block or graft copolymer membranes containing PDMS segments[1,2,15,17,20]. On the other hand, both P_{CH_4} and P_{CH_4}/P_{N_2} increased as the increase of PDMS content (*Figure 3*). Over 60 wt% PDMS content, the values of P_{CH_4} and P_{CH_4}/P_{N_2} reached over 10^{-8} cm^3 cm cm^{-2} s^{-1} cmHg^{-1} and around 6.0, respectively. This may be due to the fact that the introduction of PDMS chains causes the particular increase of D_{CH_4} compared with the diffusion coefficients of other gases as shown in *Table 2*. This result allows us to expect that this kind of graft copolymer membrane can be used to separate hydrocarbon gases from their mixtures with air or other gases.

Pervaporation

Figure 4 shows permeation composition curves of aqueous ethanol solution at 50°C through PSF and PSF/PDMS graft copolymer membranes having different PDMS contents (G-1, G-2, G-5, G-8 and G-14R). In the case of PSF membrane, only a trace of ethanol was detected in the permeate at every ethanol composition in the feed, i.e. preferential permeation of water was observed. Membrane G-1, of which PDMS content was 18 wt%, also showed water permselectivity. In contrast, preferential permeation of ethanol was observed for the graft copolymer membranes containing over 50 wt% PDMS (G-2, G-5, G-8 and G-14R). The composition of ethanol permeated through the membranes increased with increase of the PDMS content except for the case of G-14R. However, the copolymer membranes of more than 70 wt% PDMS contents were disrupted in the pervaporation experiment when the feed ethanol concentration exceeded 50 wt%. This may be attributed to the large swelling of the membrane caused by the ethanol-rich solution.

Table 3 summarizes typical pervaporation results of about 6–7 wt% aqueous ethanol solution through those polymer membranes. The separation factors of G-2, G-5 and G-8 membranes were about 6 or 7, whereupon the 6–7 wt% feed solution was concentrated to about 30 wt%. The value is very close to that of PDMS membrane[10]. This is one piece of evidence that a continuous phase of PDMS domain is formed in the copolymer membrane. The ethanol permselectivity of PDMS membrane is considered to be due to its large solubility to ethanol and also high diffusitivity in the membrane structure. The separation factor α corresponds to the permeability coefficient *P* of the graft copolymer membrane; that is,

Table 3 Pervaporation results of aqueous ethanol solution through PSF and PSF/PDMS graft copolymer membranes at 50°C

Sample no.	PSF/PDMS (wt%)	EtOH composition (wt%) in feed	EtOH composition (wt%) in permeate	*P* (g m^{-2} h^{-1})	$\alpha^{EtOH}_{H_2O}$
PSF	–	6.11	trace	3.11×10^{-4}	0
G-1	82/18	6.93	trace	4.82×10^{-4}	0
G-2	42/58	6.38	29.8	4.18×10^{-3}	6.23
G-5	40/60	6.65	31.5	4.23×10^{-3}	6.46
G-8	35/65	6.61	33.3	5.52×10^{-3}	7.19
G-14R	34/66	7.22	25.4	1.94×10^{-3}	4.38

the higher P, the greater α. High permeability would be required for high ethanol selectivity, because the diffusivity of water is much greater than that of ethanol. Therefore, the selectivity increased as PDMS content increased according to the increase of diffusivity of the membrane. However, in the case of membrane G-14R, the introduction of octyl groups at the side-chain ends probably causes a decrease of diffusivity because such a long alkyl group would depress the mobility of flexible PDMS chains, which resulted in the decrease of selectivity.

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