

# Chemical modification of polysulphone: 1. Synthesis of polysulphone/ polydimethylsiloxane graft copolymer

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In order to improve the gas and liquid permeability of polysulphone (PSF) membrane, a chemical modification of PSF was achieved by introducing a polydimethylsiloxane (PDMS) chain to afford PSF/PDMS graft copolymer. The graft copolymer was prepared by hydrosilylation of vinylsilylated PSF with hydrosilyl-terminated PDMS oligomer. The vinylsilylated PSF was prepared by metallation of PSF with *n*-butyllithium followed by treatment with dimethylvinylchlorosilane. The hydrosilyl-terminated PDMS oligomer was prepared by an anionic ring-opening polymerization of hexamethylcyclotrisiloxane with *n*-butyllithium followed by termination with dimethylchlorosilane. PDMS content of the graft copolymers could be controlled in the range of 18 to 80wt% by changing the silylation rate of vinyltrimethylsilylated PSF or the degree of polymerization of hydrosilyl-terminated PDMS oligomer. Very tough and thin membranes could be prepared from the graft copolymers by using a solvent casting method. Solubility and mechanical properties of the graft copolymer were evaluated in comparison with PSF.

(Keywords: polysulphone; polydimethylsiloxane; graft copolymer; hydrosilylation; stress-strain behaviour)

## INTRODUCTION

In our recent studies<sup>1-6</sup>, we have investigated the development of highly gas and liquid permeable membranes by preparing several kinds of novel graft copolymers containing polydimethylsiloxane (PDMS) as the side-chain. In our approach, relatively rigid polymer materials have been selected as the polymer backbone in order to obtain graft copolymers having high mechanical strength. The backbone polymers used were poly(2,6-dimethyl-1,4-phenylene oxide)<sup>1</sup>, ethylcellulose<sup>2</sup>, poly(1-trimethylsilyl-1-propyne)<sup>3,4</sup> and poly(1-phenyl-1-propyne)<sup>5,6</sup>. We also reported that these graft copolymer membranes possess extremely high gas permeability, tensile strength and thermal stability, and that the selectivity of the membranes during gas permeation was higher than that of PDMS membrane. In addition, during pervaporation of aqueous alcohol solution, preferential permeation of alcohol was observed for the copolymer membranes.

Polysulphone (PSF) is widely used as an important class of engineering plastic which exhibits high glass transition temperature and excellent oxidative, hydrolytic and mechanical stability. Chiou *et al.* have studied the gas permeability of PSF in comparison with that of polycarbonate (PC) and polyethersulphone (PES)<sup>7</sup>, and concluded that the gas transport property of PSF was intermediate between those of PC and PES. Thus, the gas permeability of PSF is too low to use for gas separation. On the other hand, Auman *et al.* have prepared triblock and multiblock copolymers of PSF and PDMS by hydrosilylation of  $\alpha,\omega$ -di(vinylbenzyl) PSF or  $\alpha,\omega$ -di(allyl) PSF with  $\alpha,\omega$ -di(hydrosilyl) PDMS<sup>8-10</sup>. They also reported that these block copolymers showed good degrees of chain extension and phase separation into rubbery PDMS and glassy PSF domains.

Their results prompted us to modify PSF by introducing a PDMS chain as graft chain using polymer reaction for the purpose of improving its gas and liquid permeability. Thus, Pt-catalysed hydrosilylation was applied to the synthesis of a novel PSF/PDMS graft copolymer, which involved the coupling of PSF containing vinyl groups with hydrosilyl-terminated PDMS oligomer. This type of graft copolymer is expected to have excellent membrane-forming ability, thermal stability, mechanical strength and membrane permeability. In this paper, the feasibility of the hydrosilylation reaction for the production of graft copolymer is described. The solubility and the mechanical properties of the products are also disclosed.

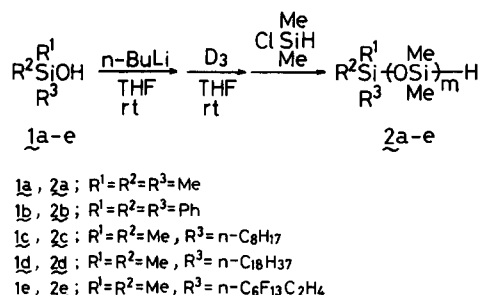
## EXPERIMENTAL

### Materials

PSF was purchased from Union Carbide Corp. (P-1700) and was dried *in vacuo* at 80°C for 24 h before use. All the silicone-containing compounds were purchased from Chisso Corp. Dimethylchlorosilane and dimethylvinylchlorosilane were freshly distilled before use. Tetrahydrofuran was distilled from calcium hydride and sodium to remove the small amount of water present.

### Preparation of hydrosilyl-terminated PDMS oligomer

Hydrosilyl-terminated PDMS oligomer 2 was prepared by anionic polymerization of hexamethylcyclotrisiloxane (D<sub>3</sub>) using triorganosilanolate anion as initiator and termination with dimethylchlorosilane. The triorganosilanolate anion was produced from the reaction of triorganosilanol 1 with *n*-butyllithium. The synthetic



Scheme 1 Preparation of hydrosilyl-terminated PDMS oligomer

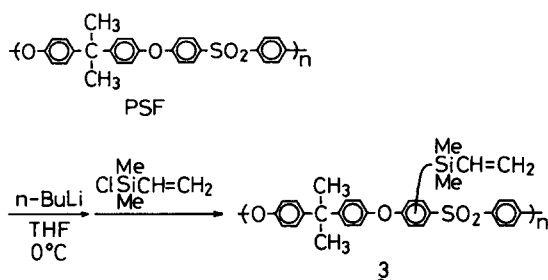
route of the PDMS is shown in Scheme 1. A typical procedure is described below.

A solution of 6.08 g of trimethylsilanol (67.8 mmol) in 80 ml of dry tetrahydrofuran was prepared under an argon atmosphere. To this solution was added 42.4 ml of 1.6 M n-hexane solution of n-butyllithium (67.8 mmol). After stirring for 20 min, 30.0 g of D<sub>3</sub> (135 mmol) dissolved in 180 ml of dry tetrahydrofuran was added. The reaction mixture was stirred for 18 h at room temperature. Then 74 ml of dimethylchlorosilane (680 mmol) was added to halt the anionic polymerization and block the polymer end with a hydrosilyl group. The mixture was evaporated and filtered off to remove lithium chloride. The filtrate was concentrated and low-molecular-weight substances were removed by heating at 200°C *in vacuo* for 6 h to afford 35.7 g of transparent and viscous hydrosilyl-terminated PDMS 2 (84% yield). Average degree of polymerization  $\bar{m}$  of the PDMS was determined by <sup>1</sup>H n.m.r. spectroscopy to be about 7.2 (theor. 7.0). The degree of polymerization could be controlled in the range of 4 to 21 by adjusting the ratio of D<sub>3</sub> and trimethylsilanol in the above reaction.

In this reaction, triphenylsilanol, n-octyldimethylsilanol, n-octadecyldimethylsilanol and 1H,1H,2H,2H-tridecafluoro-n-octyldimethylsilanol were used as the initiator instead of trimethylsilanol to afford hydrosilyl-terminated PDMS oligomers containing other kinds of alkyl groups on the other side of the terminal group. Trimethylsilanol and triphenylsilanol were purchased from Chisso Corp., while the other three triorganosilanols were easily prepared from the reaction of water with n-octyldimethylchlorosilane, n-octadecyldimethylchlorosilane and 1H,1H,2H,2H-tridecafluoro-n-octyldimethylchlorosilane at a diluted state in dry ether.

#### Preparation of vinyl dimethylsilylated PSF

Vinyl dimethylsilylated PSF was prepared as an intermediate to synthesize PSF/PDMS graft copolymer via metallation of PSF with n-butyllithium followed by treatment with vinyl dimethylchlorosilane as shown in Scheme 2. The following describes a typical procedure.



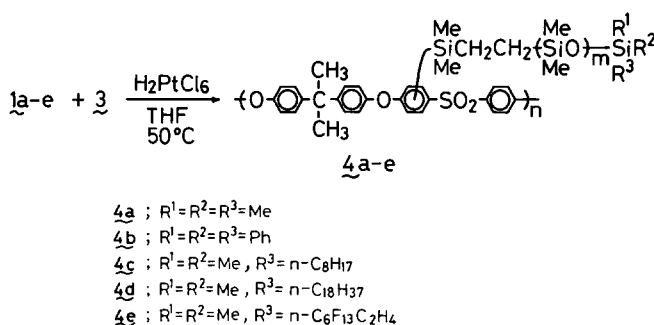
Scheme 2 Preparation of vinyl dimethylsilylated PSF

Some 4.0 g of PSF (9.02 mmol) was dissolved in 300 ml of dry tetrahydrofuran under an argon atmosphere. To this solution was added 11.3 ml of 1.6 M n-hexane solution of n-butyllithium (18.0 mmol) at 0°C, whereupon the colour of the reaction mixture turned red and a polyanion of PSF precipitated as a white solid. After stirring for 5 min at 0°C, 40 ml of dimethylvinylchlorosilane (293 mmol) was added, whence the solution turned colourless and homogeneous. The reaction mixture was poured into 2.0 litres of methanol containing 40 ml of triethylamine, and the resulting polymer was obtained by filtration and reprecipitated several times from its chloroform solution to excess methanol; 5.05 g of vinylsilylated PSF 3 was obtained.

The average number of vinyl dimethylsilyl groups per PSF monomer unit in the product (silylation rate) was calculated to be 1.77, which was determined from the <sup>1</sup>H n.m.r. spectrum. The silylation rate could be varied by changing the ratio of n-butyllithium and PSF in the above reaction.

#### Preparation of PSF/PDMS graft copolymer

PSF/PDMS graft copolymer was prepared by hydrosilylation of vinyl dimethylsilylated PSF 3 with hydrosilyl-terminated PDMS 2 as shown in Scheme 3. A typical procedure is as follows.



Scheme 3 Preparation of PSF/PDMS graft copolymer

A solution of 1.0 g of vinyl dimethylsilylated PSF 3 (1.77 vinyl groups per PSF unit) and 4.2 g of hydrosilyl-terminated PDMS 2 ( $\bar{m}$ =7.2) was prepared by dissolving them in 20 ml of dry tetrahydrofuran. To this solution 50 μl of 0.1 M isopropanol solution of chloroplatinic acid was added, and the reaction mixture was stirred for 24 h at 60°C. Then, the reaction mixture was poured into 700 ml of ethanol, and the polymer was reprecipitated several times from its chloroform solution into excess ethanol; 1.95 g of PSF/PDMS graft copolymer was obtained.

The PDMS content of the graft copolymer was 60 wt%, which was determined by <sup>1</sup>H n.m.r. The PDMS content of the copolymer could be varied by changing the silylation rate of 3 or the degree of polymerization  $\bar{m}$  of 2.

#### Characterization

<sup>1</sup>H n.m.r. was measured by using a Bruker AM-400 (400 MHz) n.m.r. spectrometer using CDCl<sub>3</sub> as the solvent. The number-average and weight-average molecular weights were determined with a Toyo Soda HLC-802A gel permeation chromatograph. Tetrahydrofuran was used as the solvent and standard polystyrenes

**Table 1** Results of preparations of hydrosilyl-terminated PDMS

Sample No.	Triorganosilanol	D <sub>3</sub> /initiator (molar ratio)	$\bar{m}^a$	
			Theor.	Obs.
2a-1	Me MeSiOH Me	1.0	4.0	4.3
2a-2	Me MeSiOH Me	2.0	7.0	7.2
2a-3	Me MeSiOH Me	3.0	10.0	10.5
2a-4	Me MeSiOH Me	6.7	21.0	22.1
2b-1	Ph PhSiOH Ph	2.0	7.0	7.1
2c-1	Me n-C <sub>8</sub> H <sub>17</sub> SiOH Me	1.0	4.0	4.8
2c-2	Me n-C <sub>8</sub> H <sub>17</sub> SiOH Me	2.0	7.0	7.2
2d-1	Me n-C <sub>18</sub> H <sub>37</sub> SiOH Me	2.0	7.0	6.9
2d-2	Me n-C <sub>6</sub> F <sub>13</sub> C <sub>2</sub> H <sub>4</sub> SiOH Me	2.0	7.0	7.1

<sup>a</sup>Theoretical value of  $\bar{m}$  was calculated from the equation  $3(D_3/\text{initiator}) + 1$ , and observed value of  $\bar{m}$  was determined based on <sup>1</sup>H n.m.r. spectrum

were used for calibrating molecular weight. Differential scanning calorimetry (d.s.c.) was carried out by using a Seiko Electronic DSC-20 at a heating rate of 10°C min<sup>-1</sup>.

#### Stress-strain measurements

For the stress-strain measurements, films of the polymers were prepared by casting from about 4 wt% of chloroform solutions in thickness from 0.05 to 0.10 mm. The film samples were dried *in vacuo* for 24 h at room temperature. These samples were then cut into rectangular strips of length 60 mm and width 5 mm. Load-elongation curves were obtained with the following settings on a Toyo Baldwin Tensilon UTM-III: gauge length, 50 mm; crosshead speed, 100 mm min<sup>-1</sup>; a full-scale load, 2 kg.

## RESULTS AND DISCUSSION

### Preparation of hydrosilyl-terminated PDMS oligomer

PDMS oligomers were prepared by the reaction shown in *Scheme 1*. *Table 1* describes the kind of triorganosilanol, the molar ratio of D<sub>3</sub> to initiator (silanolate anion), and theoretical and observed average degree of polymerization of resulting PDMS oligomer. All the triorganosilanols were efficiently converted to silanolate anion by the action of n-butyllithium. As shown in the table, the average degree of polymerization  $\bar{m}$  could easily be controlled by changing the ratio of D<sub>3</sub> to initiator, and the observed  $\bar{m}$  agreed with the theoretical  $\bar{m}$ .

### Preparation of vinyl dimethylsilylated PSF

In the reaction shown in *Scheme 2*, protons of phenylene groups of PSF were abstracted by n-butyllithium to afford a polyanion of PSF, which precipitated from the reaction mixture. The metallation of PSF with n-butyllithium was highly sensitive to moisture or other reaction conditions. If the PSF and tetrahydrofuran were insufficiently dried, gelation of the reaction mixture instantly occurred after the addition of n-butyllithium. The optimum reaction temperature was 0°C. At temperatures above or below the optimum, colouring of the reaction mixture hardly occurred, which indicated the absence of PSF polyanion. Further, the polyanion must be quenched within 5 or 10 min by adding an excess amount of vinyl dimethylchlorosilane, because standing of the polyanion for longer periods resulted in partly insoluble product.

*Figure 1* shows the <sup>1</sup>H n.m.r. spectrum of vinyl dimethylsilylated PSF compared with that of PSF. All the proton signals of PSF were assigned as shown in the figure. In the case of vinyl dimethylsilylated PSF, the signals of methyl and vinyl protons of the vinyl dimethylsilyl group (f, g, h) were observed at 0.48 ppm and 5.65–6.48 ppm, respectively. The silylation rate was determined by the ratio of peak intensity at 0.48 ppm (f) to that at 1.70 ppm (e), which were assigned as methyl protons of vinyl dimethylsilyl groups and PSF units, respectively. The signal pattern of phenylene protons between 6.90 and 7.90 ppm changed greatly before and after the introduction of vinyl dimethylsilyl groups, as shown in *Figure 1*. Namely, the signals of phenylene protons of diphenylsulphone unit (c, 6.99 ppm; d, 7.84 ppm) in PSF disappeared and corresponding protons in silylated PSF were observed at higher fields, while those of bisphenol A unit (a, 6.93 ppm; b, 7.24 ppm) were hardly affected. This fact indicates that the vinyl dimethylsilyl group is mainly attached to the phenylene groups connected to sulphonyl groups, and the replacement at bisphenol A unit hardly occurs.

*Figure 2* shows the relationship between amount of n-butyllithium and the silylation rate that is determined by <sup>1</sup>H n.m.r. A linear relationship was observed below 5.0 of n-BuLi/PSF unit. That is, the silylation rate can be controlled by the amount of n-butyllithium. However, the maximum number of silyl groups per PSF unit was about 3 even if the n-butyllithium was used over 5 molar equivalents per PSF monomer unit.

### Preparation of PSF/PDMS graft copolymer

*Table 2* summarizes the results of preparation of PSF/PDMS graft copolymers containing various end-groups in the side-chain, and *Figure 3* shows the <sup>1</sup>H n.m.r. spectra of the graft copolymers **4a-5** and **4c-2**. The signals of methyl protons of PDMS observed at 0.10 ppm are characteristic of the graft copolymers. The composition of the graft copolymer (PSF/PDMS) was determined by the ratio of peak intensity at 1.70 ppm to that at 0.10 ppm, which were assigned as methyl protons of PSF and PDMS monomer units, respectively.

The composition could be controlled by changing the silylation rate of vinyl dimethylsilylated PSF or the degree of polymerization of hydrosilyl-terminated PDMS oligomer as shown in *Table 2*. The remaining excess PDMS oligomer was easily removed by reprecipitation of the product obtained from its chloroform solution into

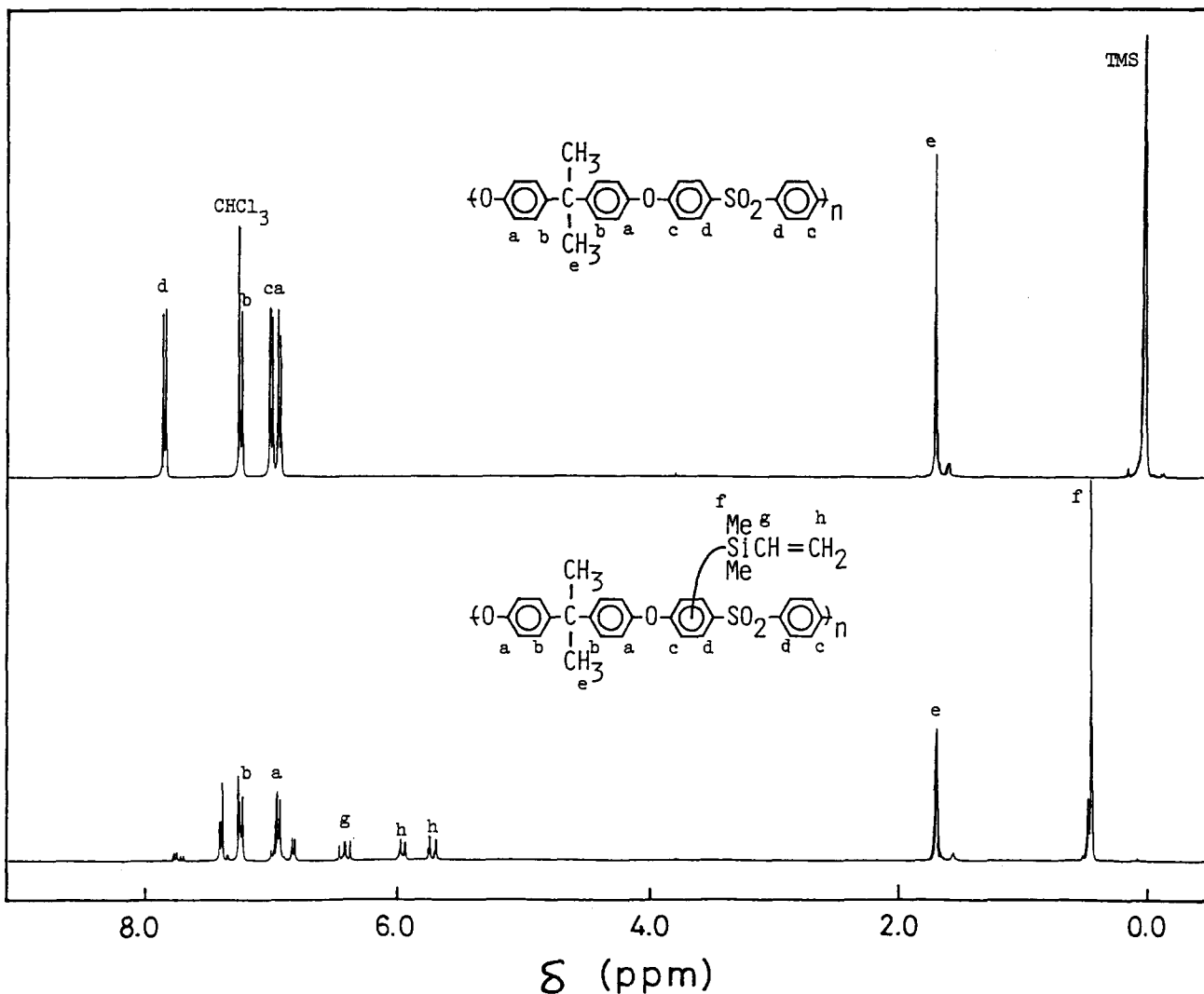


Figure 1 400 MHz <sup>1</sup>H n.m.r. spectra of PSF and vinyltrimethylsilylated PSF (1.77 vinyltrimethylsilyl groups per PSF unit)

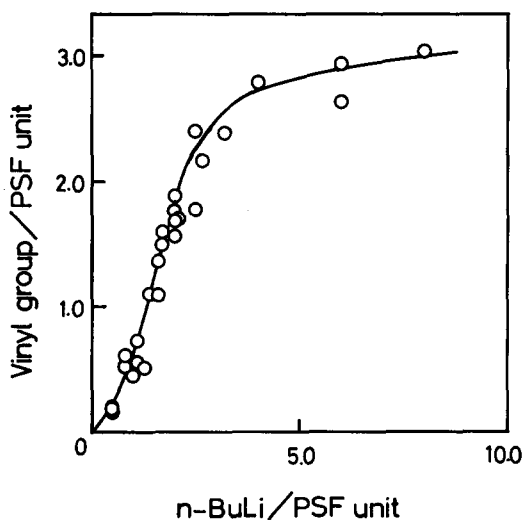


Figure 2 Relationship between amount of n-butyllithium (n-BuLi) and number of vinyltrimethylsilyl groups in the monomer unit of PSF

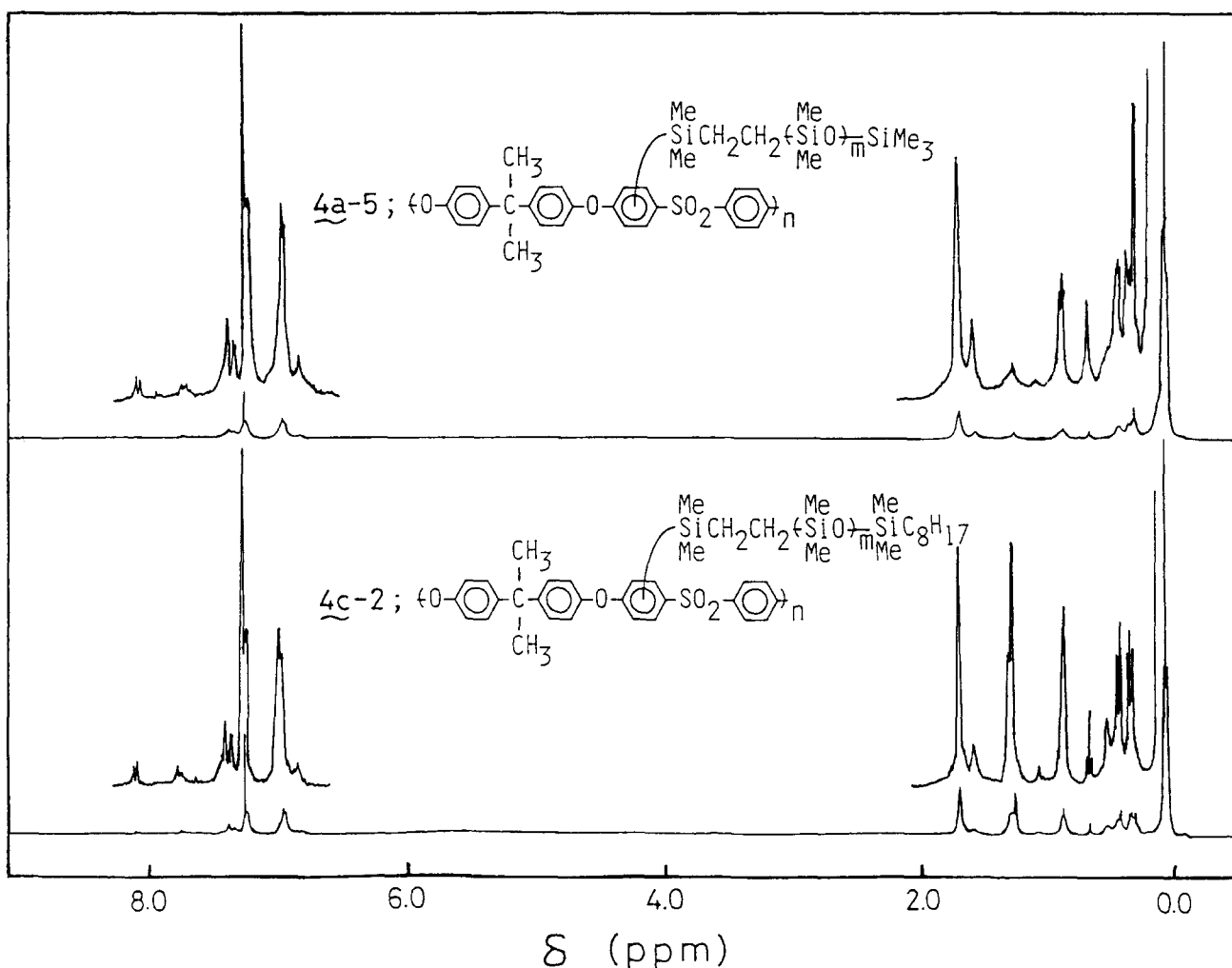
excess ethanol. The PDMS content of the resulting graft copolymers was in the range of 18 to 80 wt%. The theoretical value of the composition in Table 2 was calculated from the silylation rate and the average degree of polymerization  $\bar{m}$ . The observed compositions were

mostly in good agreement with the theoretical values. This result suggested that the vinyl group of vinyltrimethylsilylated PSF completely reacted with the hydrosilyl group of hydrosilyl-terminated PDMS oligomer. However, long PDMS oligomer ( $\bar{m} > 20$ ) and PDMS oligomer containing long alkyl end-group did not completely react with the vinyl group of vinyltrimethylsilylated PSF owing to steric hindrance. The observed PDMS contents of 4a-1, 4a-2, 4d-1 and 4e-1 were smaller than the theoretical values.

Figure 4 shows g.p.c. curves of PSF, vinyltrimethylsilylated PSF and PSF/PDMS graft copolymer. The number-average and weight-average molecular weights of PSF were  $3.66 \times 10^4$  and  $7.76 \times 10^4$ , respectively, and the value of  $\bar{M}_w/\bar{M}_n$  was 2.1. As can be seen from Figure 4, the molecular weights of vinyltrimethylsilylated PSF and PSF/PDMS graft copolymer increased compared with starting PSF. This is one piece of evidence that the silyl group and PDMS chain are surely introduced into PSF. The introduction of a silyl group into PSF probably causes conformational change of the polymer chain in solution, because the bulky silyl group attached to the phenylene group would depress the rotation of the main chain. Thus, such increases of the molecular weights estimated by g.p.c. may be attributed not only to the simple increase of the weight of silyl group or PDMS

**Table 2** Results of preparations of PSF/PDMS graft copolymers

Sample no.	Vinyl group <sup>a</sup> per PSF unit of 3	$\bar{m}^b$ of 2	Side-chain end-groups			PSF/PDMS (wt%)		$\bar{M}_n$ ( $\times 10^{-4}$ )	$\bar{M}_w$ ( $\times 10^{-4}$ )
			R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Theor.	Obs.		
4a-1	0.196	22.1	Me	Me	Me	60/40	82/18	4.52	18.6
4a-2	0.533	22.1	Me	Me	Me	34/66	42/58	6.82	28.8
4a-3	1.47	10.5	Me	Me	Me	28/72	31/69	7.16	40.1
4a-4	1.77	4.3	Me	Me	Me	45/55	47/53	6.73	36.8
4a-5	1.77	7.2	Me	Me	Me	31/69	35/65	5.27	34.4
4a-6	1.77	10.5	Me	Me	Me	24/76	20/80	5.65	35.7
4b-1	1.77	7.1	Ph	Ph	Ph	31/69	34/66	7.85	34.6
4c-1	2.40	4.8	Me	Me	n-C <sub>8</sub> H <sub>17</sub>	37/63	40/60	6.54	32.1
4c-2	1.77	7.2	Me	Me	n-C <sub>8</sub> H <sub>17</sub>	31/69	34/66	8.21	39.2
4d-1	1.77	6.9	Me	Me	n-C <sub>18</sub> H <sub>37</sub>	31/69	51/49	4.93	23.5
4e-1	1.77	7.1	Me	Me	n-C <sub>6</sub> F <sub>13</sub> C <sub>2</sub> H <sub>4</sub>	31/69	40/60	5.54	27.0

<sup>a</sup> Average number of vinyl dimethylsilyl groups in PSF unit of vinyl dimethylsilylated PSF, 3<sup>b</sup> Average degree of polymerization of hydrosilyl-terminated PDMS oligomer, 2**Figure 3** 400 MHz <sup>1</sup>H n.m.r. spectra of PSF/PDMS graft copolymers (4a-5 and 4c-2)

chain incorporated but also to the above conformational change. In addition, broadening of the molecular-weight distribution was observed after silylation and grafting although the reason for the broadening has not yet been clarified. As shown in *Figure 4b*, the lower-molecular-weight component does not increase on silylation of PSF, suggesting that the main chain of PSF is not cleaved by

the action of *n*-butyllithium. Actually, the same g.p.c. curve of PSF was observed after reaction with *n*-butyllithium followed by treatment with methanol instead of vinyl dimethylchlorosilane.

#### Characterization

Glass transition temperatures ( $T_g$ ) of these graft

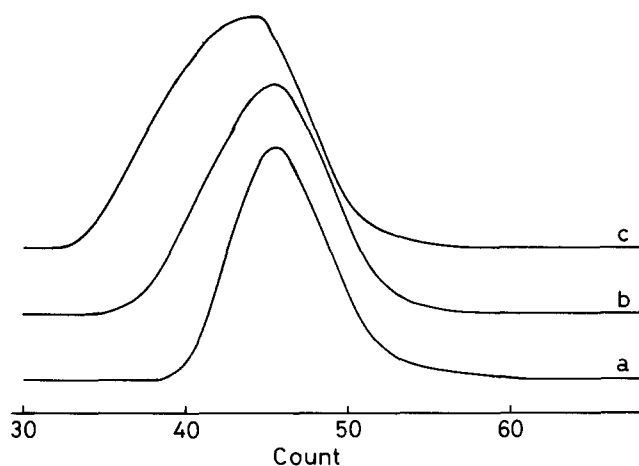


Figure 4 Comparison of g.p.c. curves of (a) PSF, (b) vinyl dimethylsilylated PSF vinyl dimethylsilyl groups per PSF unit = 1.77) and (c) PSF/PDMS graft copolymer (4a-5)

Table 3 Comparisons of solubility among PSF, vinyl dimethylsilylated PSF and PSF/PDMS graft copolymer

Solvent	PSF	Vinyl dimethylsilylated PSF <sup>a</sup>	PSF/PDMS graft copolymer <sup>b</sup>
Tetrahydrofuran	S	S	S
1,4-Dioxane	S	S	S
Diethyl ether	I	P	S
Methylene chloride	S	S	S
Chloroform	S	S	S
Carbon tetrachloride	I	S	S
Benzene	P	S	S
Toluene	I	S	S
m-Xylene	I	S	S
n-Hexane	I	I	S
Cyclohexane	I	I	S
Methanol	I	I	I
Ethanol	I	I	I
n-Butanol	I	I	S
Acetone	I	I	S
Acetonitrile	I	I	I
Acetic acid	I	I	I
Ethyl acetate	I	S	S
Pyridine	S	S	S
N,N-Dimethylacetamide	S	S	I
N,N-Dimethylformamide	S	S	I
Dimethylsulphoxide	I	I	I

S, Soluble; P, Partially soluble; I, Insoluble

<sup>a</sup> Average number of vinyl dimethylsilyl group per PSF unit was 1.77

<sup>b</sup> The composition of PSF/PDMS was 35/65 wt% (4a-5)

copolymers from 4a-3 to 4e-1 were observed at around 130–160°C on the d.s.c. measurement even though the PDMS contents were more than 50 wt%, and no other transition was observed. In the case of 4a-2,  $T_g$  values of PDMS chain and PSF chain were observed at  $-105^\circ\text{C}$  and  $168^\circ\text{C}$ , respectively. The  $T_g$  of starting PSF was  $178^\circ\text{C}$ . Therefore, the high  $T_g$  of PSF chain was maintained and no phase separation occurred in the graft copolymer containing relatively short PDMS chains up to 10 monomer units.

Table 3 indicates the comparison of solubility among PSF, vinyl dimethylsilylated PSF and PSF/PDMS graft copolymer. The solubility of the chemically modified PSF was different from that of PSF. PSF is soluble only in a few solvents, as listed in the table. However, vinyl dimethylsilylated PSF became soluble in other solvents such as carbon tetrachloride, benzene, toluene,

xylene and ethyl acetate. Further, the graft copolymer was soluble even in diethyl ether, n-hexane, cyclohexane, n-butanol and acetone. Consequently, introduction of such a silyl group or PDMS chain altered the solubility. PSF/PDMS graft copolymer became soluble in relatively less polar organic solvents.

#### Mechanical properties

Figure 5 shows the stress-strain behaviour obtained on elongation of the sample specimens directly to rupture. The sample numbers correspond to those used in Table 2. A complete difference in stress-strain curves between PSF and PSF/PDMS graft copolymer was observed. From the curves, Young's modulus, tensile strength and elongation of these samples were calculated and are listed in Table 4. The introduction of PDMS chains into PSF caused a decrease of tensile strength and increase of elongation except in the case of 4a-1 with a small content of PDMS. This fact suggests that the graft copolymer becomes soft owing to more than 50 wt% of flexible PDMS component. Interestingly, the tensile strength of the copolymer containing long alkyl groups in the side-chain end (4c-2, 4e-1) was greater than that of 4a-5 or 4a-6 for which the side-chain end was only methyl group. Such a long alkyl group in the side-chain end may enhance the mechanical strength of the graft copolymer membrane. This is probably due to the depression of mobility of PDMS side-chain by such long alkyl groups, which results in the increase of stiffness of the copolymer membrane.

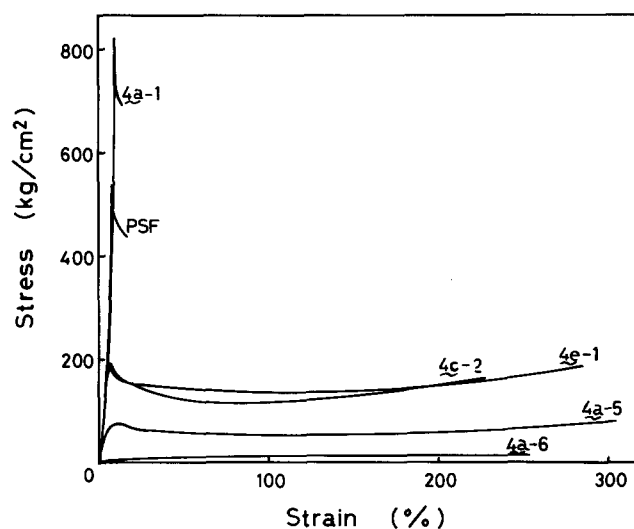


Figure 5 Stress-strain curves of PSF/PDMS graft copolymer membranes compared with PSF membrane

Table 4 Young's modulus, tensile strength and elongation of PSF and PSF/PDMS graft copolymers

Sample no.	PSF/PDMS (wt%)	Young's modulus ( $\text{kg cm}^{-2}$ )	Tensile strength ( $\text{kg cm}^{-2}$ )	Elongation (%)
PSF	—	989	437	16.8
4a-1	82/18	625	690	12.8
4a-5	35/65	617	79.0	305
4a-6	20/80	16.7	15.5	253
4c-2	34/66	1330	162	228
4e-1	40/60	1290	187	284

This kind of graft copolymer membrane shows higher gas permeability coefficient and is ethanol permselective in the separation of aqueous ethanol solution by the pervaporation technique. Details of these investigations will be discussed in a forthcoming publication.

#### ACKNOWLEDGEMENTS

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