Preparation of pyridyl-terminated oligodimethylsiloxane and siloxane-grafted copolymers containing pyridyl groups at the side chain ends

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The preparation of hetero difunctional oligodimethylsiloxanes (ODMSs) was carried out. The ODMSs contained 2-(4-pyridyl)ethyl (Py) or 2-(2,6-di-t-butyl-4-pyridyl)ethyl (DBPy) at one end and a reactive group, such as 3-methacryloxypropyl (MP) or hydrosilyl (H), at the other end. These oligosiloxanes were prepared by anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) initiated with silanolate anions containing pyridyl groups. To obtain the initiators, novel silanol compounds containing Py or DBPy groups were prepared from 4-methylpyridine and 2,6-di-t-butyl-4-methylpyridine, respectively. The average degree of polymerization could be controlled by changing the ratio of D_3 and the initiator. Py-ODMS-MP and DBPy-ODMS-MP were copolymerized with methyl methacrylate or butyl methacrylate to yield the desired graft copolymers containing pyridyl groups at the side chain ends. Also, the hydrosilylation of DBPy-ODMS-H with vinyldimethylsilylated polysulphone (PSF) was carried out to afford PSF/DBPy-ODMS graft copolymer. The gas permeability coefficients of nitrogen, oxygen and carbon dioxide for the copolymer membranes were evaluated.

(Keywords: oligodimethylsiloxane; pyridyl groups; macromonomer; graft copolymer; gas permeability)

INTRODUCTION

Recently, we have investigated the preparation of several kinds of graft copolymers containing oligodimethylsiloxane (ODMS) as the side chain for the development of highly gas and liquid permeable membranes. In our approach, rigid polymers have been selected as the backbone component in order to obtain graft copolymers having high mechanical strength. The backbone polymers used were poly(2,6-dimethyl-1,4-phenylene oxide)[1], ethyl cellulose[2], poly(1-trimethylsilyl-1-propyne)[3,4], poly(1-phenyl-1-propyne)[5,6], polysulphone (PSF)[7,8] and polyimide[9,10]. The graft copolymers were prepared from ODMSs containing reactive end groups, such as hydrosilyl, chlorosilyl, chlorocarbonyl and 3,5-diaminophenyl groups. The graft copolymer membranes possess high tensile strength and thermal stability, due to the rigid backbone components. Also, the introduction of oligosiloxane greatly enhanced the gas permeability, and resulted in ethanol permselectivity at pervaporation of aqueous ethanol even though the starting polymers exhibited water permselectivity. Such permselectivity of gases or liquids must be derived from high flexibility and hydrophobicity of the ODMS component in the side chain.

A pyridyl group is one of the polar substituents and possesses some functional properties; it can be quaternized with alkyl halide or complex with metal. Also, polyvinylpyridine is known to show excellent oxygen selectivity in gas permeation[11], though the permeability is too low to use for the practical application of oxygen-enriching membranes. Therefore, the combination of the functional pyridyl group and flexible ODMS chain is expected to bring about unique properties such as high oxygen-permselectivity. Nemoto *et al.* reported the synthesis of polyorganosiloxane with pyridyl groups in the side chain and the application to a polymer–metal complex catalyst[12].

In this paper, we present the synthesis of ODMS which possesses a pyridyl group at one end and a reactive group at the other end. For this purpose, novel silanol compounds containing a pyridyl group were synthesized and used as the initiator of anionic ring-opening polymerization of hexamethylcyclotrisiloxane. This so-called 'initiator method' conveniently produces hetero functional oligosiloxane[13]. This kind of oligosiloxane can be used as an intermediate for the preparation of siloxane-grafted copolymers having a pyridyl group at the side chain end; therefore, we will describe the preparation of the desired graft copolymers by using the macromonomer method or a polymer reaction.

EXPERIMENTAL

Materials

Chloromethyldimethylsilane, hexamethylcyclotrisiloxane (D_3), 3-methacryloxypropyldimethylchlorosilane and dimethylchlorosilane were purchased from Chisso Cor-

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poration and used without further purification. Tetrahydrofuran (THF) was distilled over sodium, and 4-methylpyridine, 4-methyl-2,6-di-t-butylpyridine, methyl methacrylate (MMA) and butyl methacrylate (BMA) were distilled over calcium hydride. Vinyldimethylsilylated PSF (1.77 vinyl groups per PSF unit) was prepared by metallation of PSF with n-butyllithium followed by termination with dimethylchlorosilane. The detailed procedure for the preparation is described in our previous paper[7].

Preparation of 2-(4-pyridyl)ethyldimethylsilanol (2)

Under an argon atmosphere, 4-methylpyridine (12.0 g, 129 mmol) was dissolved in dry THF (200 ml). To this solution 2.0 M hexane solution of phenyllithium (97 ml, 194 mmol) was added dropwise at −78°C. After stirring for 40 min at −78°C and after a further 1 h at room temperature, chloromethyldimethylsilane (31.4 ml, 258 mmol) was added and the mixture was stirred for 12 h at room temperature. The mixture was evaporated, washed with diethyl ether and filtered to remove lithium chloride. The filtrate was distilled under reduced pressure to afford 17.0 g of 2-(4-pyridyl)ethyldimethylsilane, **1**, as a transparent colourless liquid.

Yield: 80%; b.p. 65°C/0.8 mmHg. I.r. (KBr, cm^{-1}): 3100, 3050, 2980, 2950, 2120, 1600 (Py), 1560, 1500, 1420, 1315, 1255 (Si–C), 1220, 1175, 1120, 1070, 925 (Si–C), 880, 800, 740. ^1H n.m.r. δ ($CDCl_3$, ppm): 0.09 (6H, d), 0.90 (2H, m), 3.07 (2H, m), 3.80 (1H, m), 6.98 (2H, dd), 8.34 (2H, dd). *m/e*: 165 (M^+), 164 (M^+–H), 150 (M^+–Me), 106, 59. $C_9H_{15}NSi$ (165.33): calc. C 65.38, H 9.16, N 8.47; found C 65.11, H 8.98, N 8.33%.

To refluxing absolute ethanol (80 ml) containing a small pellet of metallic sodium, **1** (15.0 g, 90.7 mmol) was added dropwise. After the evolution of hydrogen had ceased, the reaction mixture was cooled to 0°C and a mixture of sodium hydroxide (11.0 g), methanol (160 ml) and water (16 ml) was added with constant stirring. To this was added again a solution of sodium hydroxide (11.0 g) in water (160 ml). After standing for 30 min, this mixture was poured into a solution of potassium hydrogen phosphate (95.7 g) in excess of ice and water. The organic products were extracted with diethyl ether and distilled under reduced pressure to afford 13.8 g of **2** as a pale yellow liquid.

Yield: 84%; b.p. 39–40°C/0.015 mmHg. I.r. (KBr, cm^{-1}): 3500–2900 (OH), 3100, 3050, 2980, 2950, 1600 (Py), 1560, 1500, 1420, 1315, 1255 (Si–C), 1220, 1175, 1055 (Si–O), 995, 915 (Si–C), 840, 800, 740. ^1H n.m.r. δ ($CDCl_3$, ppm): 0.08 (6H, s), 0.85 (2H, m), 2.30 (1H, s), 2.61 (2H, m), 7.07 (2H, dd), 8.45 (2H, dd). *m/e*: 181 (M^+), 180 (M^+–H), 166 (M^+–Me), 106, 75. $C_9H_{15}NOSi$ (181.33): calc. C 59.61, H 8.35, N 7.72; found C 59.52, H 8.36, N 7.72%.

Preparation of 2-(2,6-di-t-butyl-4-pyridyl)-ethyldimethylsilanol (4)

Under an argon atmosphere, 4-methyl-2,6-di-t-butylpyridine (10.0 g, 49.8 mmol) was dissolved in dry THF (100 ml). To this solution 1.4 M hexane solution of sec-butyllithium (100 ml, 140 mmol) was added dropwise at −78°C. After stirring for 1.5 h at −78°C, chloromethyldimethylsilane (20.0 ml, 164 mmol) was added and the mixture was stirred for 12 h at room temperature. The mixture was evaporated, washed with diethyl ether and filtered to remove lithium chloride. The product was purified by silica gel column chromatography to afford 13.3 g of 2-(2,6-di-t-butyl-4-pyridyl)ethyldimethylsilane, **3**, as a transparent colourless liquid.

Yield: 96%. I.r. (KBr, cm^{-1}): 3100, 2990, 2900, 2130, 1600 (Py), 1562, 1480, 1450, 1415, 1360, 1310, 1250 (Si–C), 1220, 1165, 1070, 1000, 925 (Si–C), 880, 835, 770. ^1H n.m.r. δ ($CDCl_3$, ppm): 0.11 (6H, d), 0.96 (2H, m), 1.35 (18H, s), 2.63 (2H, m), 3.93 (1H, m), 6.94 (2H, s). *m/e*: 277 (M^+), 276 (M^+–H), 262 (M^+–Me), 59. $C_{17}H_{31}NSi$ (277.57): calc. C 73.56, H 11.28, N 5.04; found C 73.07, H 11.42, N 4.83%.

To refluxing absolute ethanol (40 ml) containing a small pellet of metallic sodium, **3** (10.0 g, 36.0 mmol) was added dropwise. After stirring for 1 h, a mixture of sodium hydroxide (4.20 g), methanol (100 ml) and water (10 ml) was added to the solution. To this was added again a solution of sodium hydroxide (4.20 g) in water (100 ml). After standing for 30 min, this mixture was poured into a solution of potassium hydrogen phosphate (36.7 g) in excess of ice and water. The organic products were extracted with diethyl ether and purified by silica gel column chromatography to afford 7.90 g of **4** as a transparent colourless liquid.

Yield: 76%. I.r. (KBr, cm^{-1}): 3500–2900 (OH), 3100, 2980, 2890, 1600 (Py), 1562, 1480, 1450, 1415, 1360, 1310, 1255 (Si–C), 1220, 1165, 1055 (Si–O), 1000, 925 (Si–C), 900, 840, 790. ^1H n.m.r. δ ($CDCl_3$, ppm): 0.15 (6H, s), 1.06 (2H, m), 1.35 (18H, s), 2.18 (1H, s), 2.70 (2H, m), 6.95 (2H, s). *m/e*: 293 (M^+), 292 (M^+–H), 278 (M^+–Me), 218, 75. $C_{17}H_{31}NOSi$ (293.57): calc. C 69.55, H 10.67, N 4.77; found C 69.24, H 10.11, N 4.55%.

Preparation of α-(2-(4-pyridyl)ethyl)-ω-(3-methacryloxypropyl)oligodimethylsiloxane (Py-ODMS-MP, 5)

Sodium hydride (60% dispersion in mineral oil, 0.433 g, 10.8 mmol) was washed with hexane to remove the oil, and suspended in dry THF (20 ml). To this mixture a solution of **2** (1.10 g, 6.07 mmol) in dry THF (10 ml) was added at room temperature. After stirring for 2 h, D_3 (2.70 g, 12.1 mmol) dissolved in dry THF (20 ml) was added. After stirring for 12 h at room temperature, 3-methacryloxypropyldimethylchlorosilane (2.20 g, 10.0 mmol) was added to the solution to introduce a 3-methacryloxypropyl group at the oligomer end. The mixture was evaporated and filtered to remove sodium chloride. The filtrate was purified by silica gel column chromatography to afford 3.00 g of **5** as a transparent viscous oil. The average degree of polymerization, $\bar{m}$, was ~7.3 (theoretical value 7.0), which was determined from the ratio of the ^1H n.m.r. peak intensity of the methyl protons in the ODMS unit (0.11 ppm) to that of the methylene protons next to the pyridyl group (2.64 ppm). The degree of polymerization changed to 3.8 (theoretical value 4.0) by using an equivalent amount of D_3 *versus* **2** in the above reaction.

I.r. (KBr, cm^{-1}): 3100, 3050, 2960, 1720 (C=O), 1640, 1600 (Py), 1560, 1500, 1420, 1315, 1260 (Si–C), 1220, 1160, 1100–1000 (SiOSi), 955, 920 (Si–C), 840, 800. ^1H n.m.r. δ ($CDCl_3$, ppm): 0.11 (s), 0.57 (m), 0.89 (m), 1.70 (m), 2.04 (s), 2.64 (m), 4.10 (t), 5.52 (m), 6.08 (m), 7.11 (dd), 8.47 (dd).

Preparation of α-(2-(2,6-di-t-butyl-4-pyridyl)ethyl)-ω-(3-methacryloxypropyl)oligodimethylsiloxane (DBPy-ODMS-MP, 6a)

A solution of **4** (2.50 g, 8.52 mmol) in dry THF (10 ml) was prepared under an argon atmosphere. To this solution 1.6 M hexane solution of n-butyllithium (5.32 ml, 8.52 mmol) was added at −10°C. After stirring for 1 h, D_3 (3.79 g, 17.0 mmol) dissolved in dry THF (40 ml) was added. After stirring for 12 h at room temperature, 3-methacryloxypropyldimethylchlorosilane (3.31 g, 15.0 mmol) was added to the solution. The mixture was evaporated and filtered to remove lithium chloride. The filtrate was purified by silica gel column chromatography to afford 5.95 g of **6a** as a transparent viscous oil; $\bar{m} = 7.5$ (theoretical value 7.0).

I.r. (KBr, cm^{-1}): 3100, 2960, 2890, 1720 (C=O), 1640, 1600 (Py), 1562, 1480, 1450, 1425, 1360, 1310, 1255 (Si–C), 1220, 1200, 1165, 1100–1000 (SiOSi), 925 (Si–C), 900, 840, 800. ^{1}H n.m.r. δ ($CDCl_3$, ppm): 0.12 (s), 0.58 (m), 0.90 (m), 1.33 (s), 1.80 (m), 2.03 (s), 2.62 (m), 4.21 (t), 5.63 (m), 6.10 (m), 6.90 (s).

Preparation of α-(2-(2,6-di-t-butyl-4-pyridyl)ethyl)-ω-hydro-oligodimethylsiloxane (DBPy-ODMS-H, 6b)

A solution of **4** (1.50 g, 5.11 mmol) in dry THF (10 ml) was prepared under an argon atmosphere. To this solution 1.6 M hexane solution of n-butyllithium (3.20 ml, 5.12 mmol) was added at −10°C. After stirring for 1 h, D_3 (2.27 g, 10.2 mmol) dissolved in 15 ml of dry THF was added. After stirring for 12 h at room temperature, dimethylchlorosilane (2.00 ml, 18.3 mmol) was added to the solution. 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 150°C *in vacuo* for 2 h. The product was purified by silica gel column chromatography to afford 3.30 g of **6b** as a transparent viscous oil; $\bar{m} = 7.2$ (theoretical value 7.0).

I.r. (KBr, cm^{-1}): 3100, 2960, 2890, 2130 (Si–H), 1600 (Py), 1562, 1480, 1450, 1415, 1360, 1310, 1255 (Si–C), 1220, 1200, 1165, 1100–1000 (SiOSi), 925 (Si–C), 900, 840, 790. ^{1}H n.m.r. δ ($CDCl_3$, ppm): 0.12 (s), 0.90 (m), 1.33 (s), 2.60 (m), 4.90 (m), 6.90 (s).

Copolymerization of 5 or 6a with vinyl monomers

The macromonomer (**5** or **6a**), comonomer (MMA or BMA) and 2,2′-azobisisobutyronitrile (AIBN) were dissolved in dry THF in a polymerization tube. The molar ratio of the macromonomer to the comonomer was fixed at 15/85, and the total concentrations of the monomers and AIBN were 2.0 and 0.05 mol l^{-1}, respectively. After degassing the mixture, the tube was sealed and heated at 60°C for 12 h. The reaction mixture was then poured into excess methanol to precipitate the polymer. The copolymer obtained, **7**, was reprecipitated twice from its toluene solution into excess methanol.

Hydrosilylation of 6b with vinyldimethylsilylated PSF

A solution of vinyldimethylsilylated PSF (0.3 g) and **6b** (1.3 g, $\bar{m} = 7.2$) was prepared by dissolving them in dry THF (10 ml). To this solution 0.2 ml of 0.1 M isopropyl alcohol solution of chloroplatinic acid was added, and the reaction mixture was stirred for 48 h at 70°C. Then, the reaction mixture was poured into methanol (300 ml), and the polymer was reprecipitated several times from its toluene solution to excess methanol to afford 0.55 g of PSF/DBPy-poly(dimethylsiloxane) (PDMS) graft copolymer, **8**. Other **6b**s were reacted with the same vinyldimethylsilylated PSF in a similar procedure as described above.

Characterization

^{1}H n.m.r. was carried out using a Hitachi R-90H FT (90 MHz) n.m.r. spectrometer using $CDCl_3$ as the solvent, and chemical shifts were obtained relative to tetramethylsilane. I.r. spectra and mass spectra were recorded on a Jasco A-202 diffraction grating i.r. spectrometer and a Hitachi M-80A mass spectrometer, respectively. Elemental analysis was carried out using a Perkin–Elmer 240 elemental analyser.

The number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were determined with a Tosoh HLC-802A gel permeation chromatograph equipped with four columns of TSK gels ($G5000H_6$, $G4000H_6$, $G3000H_6$ and $G2000H_6$). THF was used as the solvent, and standard polystyrenes were used for calibrating molecular weight.

Measurement of gas permeability

Toluene solutions containing ~3 wt% copolymer were cast on polytetrafluoroethylene sheets and the solvent was evaporated over a period of 24 h to form 50–80 μm thick membranes. For the measurement of gas permeability, the polymer membranes formed were then dried *in vacuo* and cut into circular pieces (22 nm in diameter).

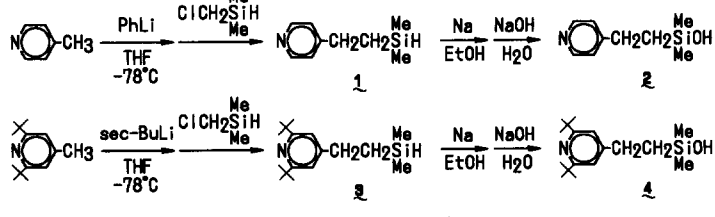
Gas permeability was measured according to the vacuum method[1]. The pressure on the permeation side (initial pressure was ~0.01 mmHg) was measured with a Pirani gauge. The permeability coefficient, P, was calculated from the slope of a time–pressure curve at a steady state.

RESULTS AND DISCUSSION

Preparation of silanol compounds containing pyridyl groups

In order to introduce a pyridyl group at the terminal group of ODMS by the 'initiator method', novel silanol compounds containing pyridyl groups were synthesized as shown in *Scheme 1*. Previously, we attempted to carry out the hydrosilylation of 4-vinylpyridine with dimethylchlorosilane in the presence of Pt catalyst. However, the reaction was unsuccessful, because the catalyst was coordinated with pyridyl group and inactivated. Therefore, an alternative route was investigated.

The metallation of 4-methylpyridine was achieved by using phenyllithium as the reagent, and **1** could be prepared in good yield by terminating the reaction with chloromethyldimethylsilane. Phenyllithium was the most



Scheme 1 Preparation of silanol compounds

suitable base for this reaction as compared with other alkyllithium reagents, while the use of n-butyllithium gave a lot of by-products in the metallation of 4-methylpyridine. Then, the hydrosilyl group of **1** could be easily converted to the hydroxysilyl group by the method of Merker and Scott[14] to afford **2**. On the other hand, 4-methyl-2,6-di-t-butylpyridine was also metallized by sec-butyllithium to afford **3** followed by treatment with chloromethyldimethylsilane. In this case, sec-butyllithium was the best reagent for the metallation, while the reaction did not occur by employing n-butyllithium and phenyllithium. The reactivity of 4-methyl-2,6-di-t-butylpyridine was different from that of 4-methylpyridine, owing to the effect of the two t-butyl groups on the pyridine ring. Also, the silanol **4** could be prepared from **3** by the same reaction as in the case of **2** from **1**.

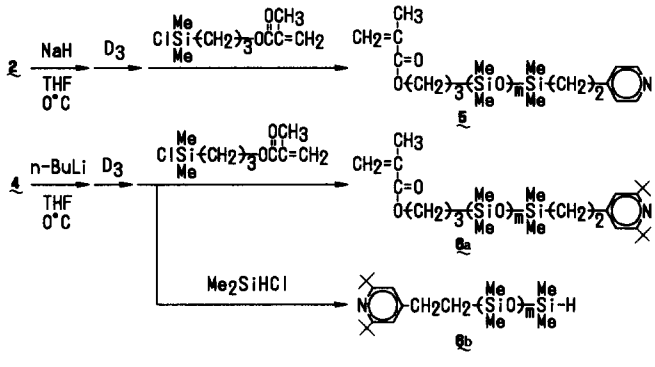
Preparation of pyridyl-terminated ODMSs

Py-ODMS-MP (**5**), DBPy-ODMS-MP (**6a**) and DBPy-ODMS-H (**6b**) were prepared from the two silanols, **2** and **4**, as shown in *Scheme 2*. In general, silanols react with base, e.g. alkyllithium, to afford silanolate anions which act as the initiator in the non-equilibrium polymerization of D_3. However, when **2** was treated with n-butyllithium at 0°C, the product did not initiate polymerization. This may be due to a side reaction between the base and the pyridine ring of **2**. Therefore, sodium hydride (NaH) was used as the base to produce the silanolate anion of **2**, which acted as the initiator of the ring-opening polymerization of D_3 to afford **5** followed by treatment with 3-methacryloxypropyldimethylchlorosilane. On the other hand, in the case of **4**, the desired polymerization occurred by employing n-butyllithium as the base to afford **6a** and **6b** because the pyridine ring did not react with n-butyllithium at 0°C due to steric hindrance by the two t-butyl groups.

The results of preparing **5**, **6a** and **6b** are summarized in *Table 1*. The $\bar{m}$ value for these oligosiloxanes could be controlled by changing the ratio of D_3 to **2** or **4**. The observed $\bar{m}$ agreed with the theoretical value, and the polydispersity ($\bar{M}_w/\bar{M}_n$) was in the range of 1.06–1.12. The g.p.c. curves of these oligosiloxanes are shown in *Figure 1*.

Preparation of graft copolymers

As shown in *Scheme 3*, **5** and **6a** acted as macromonomers which were radically copolymerized with vinyl monomers to afford graft copolymers containing oligosiloxanes as the side chains and pyridyl groups at the side chain ends. Methyl methacrylate and BMA were used as the comonomers. As shown in *Table 2*, five



Scheme 2 Preparation of pyridyl-terminated ODMSs

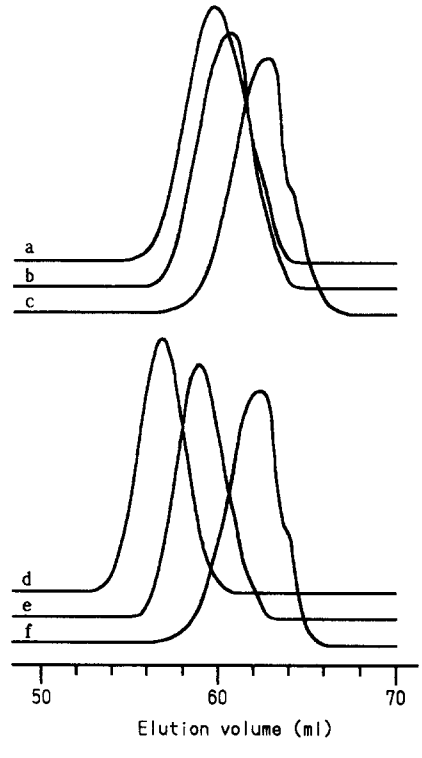
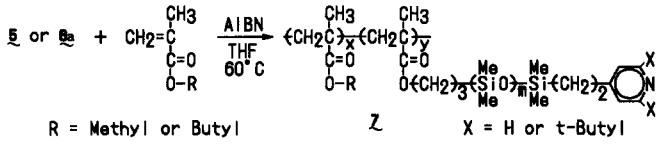


Figure 1 G.p.c. curves of pyridyl-terminated ODMSs: (a) **6a**-1; (b) **5**-2; (c) **5**-1; (d) **6a**-3; (e) **6b**-2; (f) **6b**-1

Table 1 Preparations of pyridyl-terminated reactive ODMSs (**5**, **6a** and **6b**)

Code	Silanol[a]	D_3/silanol[b] (molar ratio)	$\bar{m}$[c] Theor.	$\bar{m}$[c] Obs.	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
5-1	**2**	1.0	4.0	3.8	620	1.11
5-2	**2**	2.0	7.0	7.3	810	1.10
6a-1	**4**	2.0	7.0	7.5	850	1.12
6b-1	**4**	1.0	4.0	4.1	610	1.10
6b-2	**4**	2.0	7.0	7.2	890	1.09
6b-3	**4**	3.0	10.0	10.5	1050	1.06

[a]Silanol compounds containing pyridyl group used as the initiator
[b]Molar ratio of D_3 and silanol in the polymerization
[c]The theoretical value of $\bar{m}$ was calculated from the equation $\bar{m} = 3[D_3]/[\text{silanol}] + 1$, and the observed value of $\bar{m}$ was determined on the basis of the ^1H n.m.r. spectrum
[d]Determined by gel permeation chromatography



Scheme 3 Radical copolymerization of pyridyl-terminated ODMS macromonomers (**5** and **6a**) with vinyl monomers

copolymers were obtained, of which the $\bar{M}_n$ values were $>3 \times 10^4$. *Figure 2* shows a typical ^{1}H n.m.r. spectrum of MMA/Py-DMS graft copolymer (**7-1**) as compared with that of the starting macromonomer (**5-1**). Most of the proton signals were assigned as shown in *Figure 2*. The composition x/y was determined from the ratio of the peak intensity at 3.60 ppm (k) to that at 4.10 ppm

Table 2 Copolymerization of pyridyl-terminated ODMS macromonomers (**5** and **6a**) with vinyl monomers

Code	Macromonomer[a]	$\bar{m}^a$	Vinyl monomer[b]	Vinyl monomer/macromonomer[c] (molar ratio)	Copolymer yield (%)	x/y^d (molar ratio)	$\bar{M}_n{}^e$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n{}^e$
7-1	**5**-1	3.8	BMA	85/15	49	91/ 9	3.31	1.43
7-2	**5**-2	7.3	BMA	85/15	40	93/ 7	5.70	1.41
7-3	**5**-2	7.3	MMA	85/15	35	88/12	3.55	1.55
7-4	**6a**-1	7.5	BMA	85/15	42	90/10	3.12	1.61
7-5	**6a**-1	7.5	MMA	85/15	38	89/11	4.20	1.51

[a]See *Table 1*
[b]MMA, methyl methacrylate; BMA, butyl methacrylate
[c]Molar ratio of vinyl monomer and macromonomer in the copolymerization
[d]Molar ratio of each monomer unit in the copolymer, determined on the basis of the ^{1}H n.m.r. spectrum
[e]Determined by gel permeation chromatography

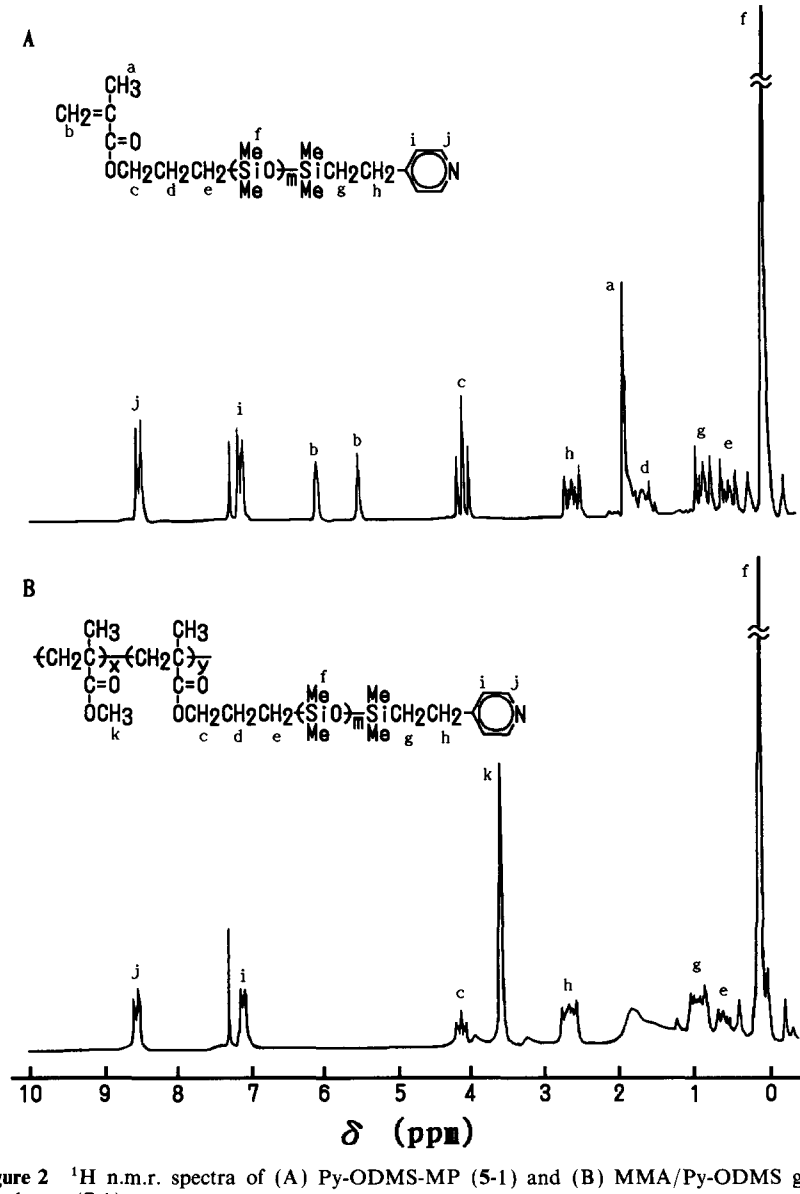


Figure 2 ^{1}H n.m.r. spectra of (A) Py-ODMS-MP (**5-1**) and (B) MMA/Py-ODMS graft copolymer (**7-1**)

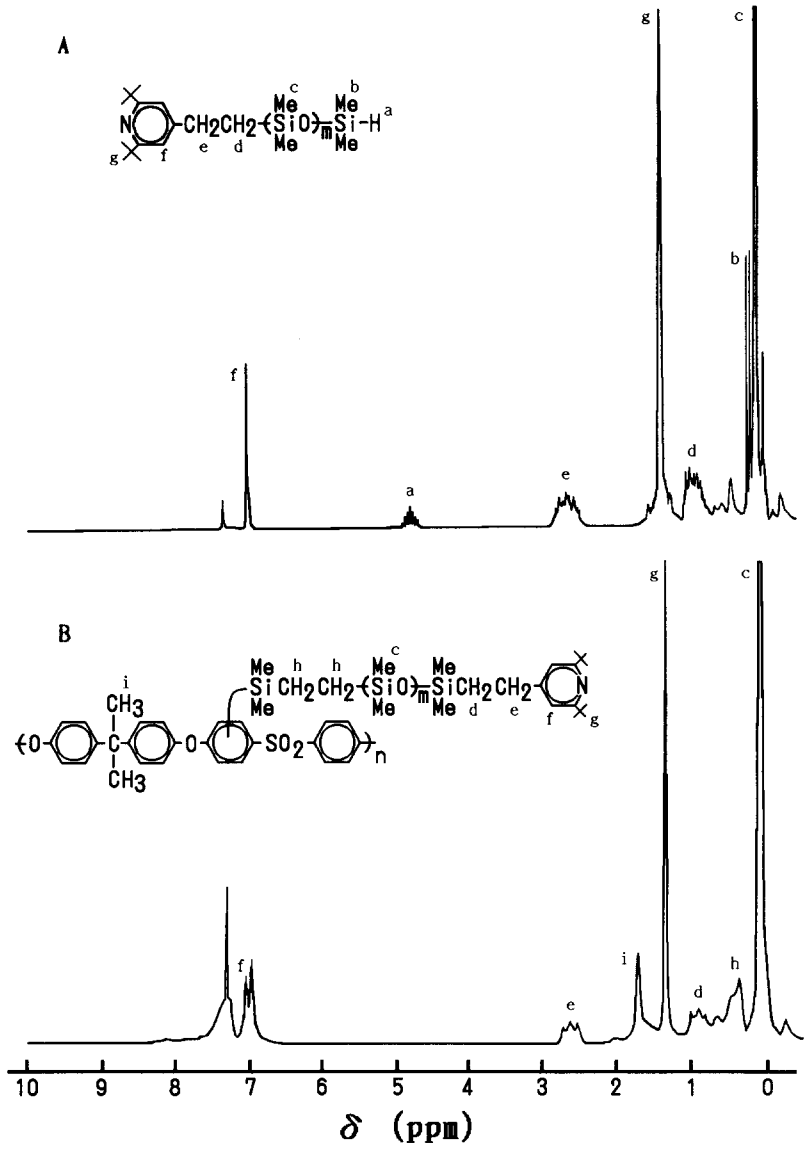
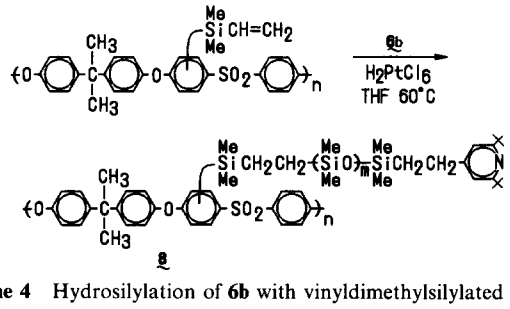


Figure 3 ^{1}H n.m.r. spectra of (A) DBPy-ODMS-H (**6b**-2) and (B) PSF/DBPy-ODMS graft copolymer (**8**-2)

(c). The contents of the macromonomer units (*y* component) in the resulting copolymers were a little less than those of the macromonomer fed into the copolymerization (*Table 2*). This suggests that the comonomers are a little more reactive than the macromonomers. The membranes could be prepared from **7**-1, **7**-4 and **7**-5 by the casting method as described in the Experimental section, however **7**-2 and **7**-3 were too soft to prepare membranes.

The hydrosilylation of **6b** with vinyldimethylsilylated PSF using chloroplatinic acid as the catalyst was carried out to afford PSF/DBPy-DMS graft copolymer (*Scheme 4*). All the vinylsilyl groups of the vinyldimethylsilylated PSF reacted with the terminal hydrosilyl group of **6b**, therefore, the average number of oligosiloxane side chains in the copolymer was ~1.77 per PSF unit. *Figure 3* shows a typical ^{1}H n.m.r. spectrum of the obtained copolymer (**8**-2) as compared with the starting DBPy-ODMS-H (**6b**-2). The composition of the graft copolymer (PSF unit/ODMS unit) was determined from the ratio of the peak intensity at 1.70 ppm (i) to that at 0.10 ppm (c), which were assigned as methyl protons of PSF and DMS monomer units, respectively. Details of this graft copolymerization have been described in our previous paper[7]. In this reaction, the DBPy end group of **6b** did not inactivate the Pt catalyst because the coordination of DBPy to Pt was protected by the two t-butyl groups. When the DBPy end group changed to the 4-pyridyl group, the hydrosilylation did not proceed.



Scheme 4 Hydrosilylation of **6b** with vinyldimethylsilylated PSF

The results of preparing PSF/DBPy-DMS graft copolymers are summarized in *Table 3*. Three copolymers having different DMS chain lengths were prepared. Tough membranes could be prepared from all the copolymers, being derived from the rigid backbone component, i.e. PSF.

Table 3 Hydrosilylation of **6b** with vinyldimethylsilylated PSF

Code	DBPy-ODMS-H[a] (**6b**)	$\bar{m}^a$	PSF/PDMS[b] (molar ratio)	$\bar{M}_n{}^c$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n{}^c$
8-1	**6b**-1	4.1	14/86	7.72	2.21
8-2	**6b**-2	7.2	8/92	7.90	2.33
8-3	**6b**-3	10.5	5/95	6.87	2.10

[a]See *Table 1*
[b]Molar ratio of PSF and PDMS monomer units in the graft copolymer, determined on the basis of the ^{1}H n.m.r. spectrum
[c]Determined by gel permeation chromatography

Table 4 Gas permeability coefficients of the graft copolymers containing pyridyl groups at the side chain ends

Code	$P_{N_2}{}^a$ ($\times 10^9$)	$P_{O_2}{}^a$ ($\times 10^9$)	$P_{CO_2}{}^a$ ($\times 10^9$)	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
7-1	0.445	1.68	9.38	3.77	21.1
7-4	2.63	7.34	46.7	2.79	17.8
7-5	2.26	6.55	37.7	2.90	16.7
8-1	0.407	1.61	8.43	3.96	20.7
8-2	1.86	5.35	30.3	2.88	16.3
8-3	3.81	9.87	53.3	2.59	14.0

[a]Units: $cm^3(STP)\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$. Temperature: 25°C

Gas permeability

The gas permeability coefficients of nitrogen (P_{N_2}) oxygen (P_{O_2}) and carbon dioxide (P_{CO_2}) were measured for the graft copolymer membranes by the ordinary vacuum method at 25°C. The values are listed in *Table 4*. The gas permeability coefficients increased and the selectivities decreased as the ODMS chain length increased. A similar tendency has been also found in other siloxane-grafted copolymer membranes[1,2,5,8]. The P_{O_2} values for these graft copolymers were in the range of $1-9 \times 10^{-9}\,cm^3(STP)\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$, and the selectivities *versus* nitrogen (P_{O_2}/P_{N_2}) showed relatively high values (2.6–4.0). The high selectivity may be due to pyridyl groups at the side chain ends, although a more detailed study on the membrane structure or on the solubility and diffusivity parameters of the gas permeation is required. The selectivities of **8**-1–**8**-3 were a little higher than those of similar graft copolymer membranes containing the triphenylsilyl group at the side chain end[8] for which P_{O_2} and P_{O_2}/P_{N_2} were $8.37 \times 10^{-9}\,cm^3(STP)\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$ and 2.48, respectively.

Furthermore, the 4-pyridyl group at the chain end was reacted with alkyl halide, e.g. methyl iodide, to obtain 1-methyl-4-pyridinio-terminated ODMS, and unique functional properties developed. Details of these investigations will be discussed in a forthcoming publication.

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