

PREPARATION OF CONDENSATION-TYPE SILOXANE-GRAFTED COPOLYMERS BY USING 3,5-BIS(4-AMINOPHENOXY)BENZYLPROPYL-TERMINATED POLYDIMETHYLSILOXANE MACROMONOMER AND THE PERMEATION PROPERTY AS A MEMBRANE MATERIAL

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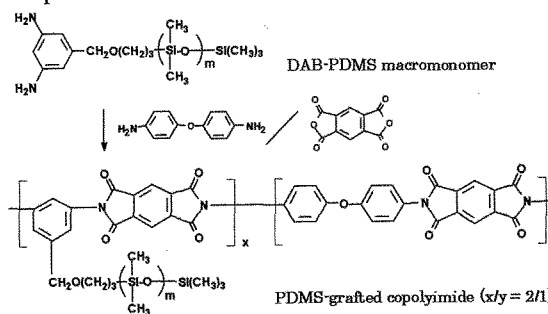
The synthesis of a novel polydimethylsiloxane (PDMS) macromonomer containing aromatic diamino groups at one chain end was carried out to prepare siloxane-grafted copolymers with an aromatic backbone by polycondensation. 3,5-bis(4-aminophenoxy)benzylpropyl-terminated polydimethylsiloxane (BAPB-PDMS) was prepared by hydrosilylation of 3,5-bis(4-nitrophenoxy)benzyl allyl ether with hydrosilyl-terminated PDMS using Pt catalyst, followed by hydrogenation reduction of the terminal dinitro groups. Then, PDMS-grafted copolymers consisted of aromatic backbone were prepared by using BAPB-PDMS as a macromonomer. PDMS-grafted polyimide and poly(amide-imide) were prepared by polycondensation of BAPB-PDMS with pyromellitic dianhydride and trimellitic dianhydride chloride, respectively. The copolymer membranes were prepared by solvent casting method, and the gas permeability and the pervaporation property of these membranes were evaluated. As a result, these membranes exhibited the similar gas permeability to PDMS cross-linked membrane and the ethanol-permselectivity for the pervaporation of aqueous ethanol solution. Key words: polydimethylsiloxane, macromonomer, graft copolymer, membrane, permeability.

1. INTRODUCTION

The pervaporation (PV) technique has been focused in much attention, for example, to remove harmful organic components from the industrial effluent. It is favorable to remove the small amount of organic solvents, such as benzene and dichloromethane, from wastewater by PV technique. For this purpose, it is an important factor that the membrane exhibits the organic-permselectivity, not the water-permselectivity, and the durability against several organic solvents. Polydimethylsiloxane (PDMS) membrane has been known as one of the few organic-permselective membrane materials¹⁾, however, it is difficult to make a thin film to obtain the high flux of permeates. Thus, we have investigated the synthesis of graft copolymers by using diamino-terminated PDMS macromonomer, the main chain component of which was mechanically strong²⁾⁻⁴⁾. Particularly, PDMS-grafted polyimide membrane exhibited the stable and high gas permeability, and also the excellent durability against several organic solvents, which was derived from the main chain component. Actually, the highly selective permeation of organic solvent was observed from the mixtures of water and organic solvents, such as acetone, THF, chloroform and dichloromethane, through this membrane³⁾.

In the previous study³⁾, 3,5-diaminobenzylpropyl-terminated PDMS (DAB-PDMS in Scheme 1) was synthesized as the macromonomer to prepare siloxane-grafted copolyimide. In this study, a new type of reactive terminal group, 3,5-bis(4-aminophenoxy)-

benzylpropyl (BAPB) group, was introduced in the PDMS macromonomer and its polymerization property was investigated. BAPB-PDMS macromonomer is expected to improve the reactivity in polycondensation as compared with DAB-PDMS.

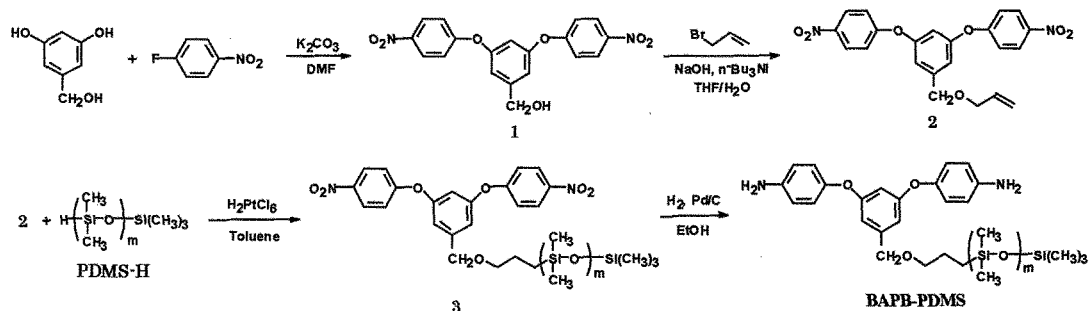


Scheme 1 Graft copolymerization using DAB-PDMS.

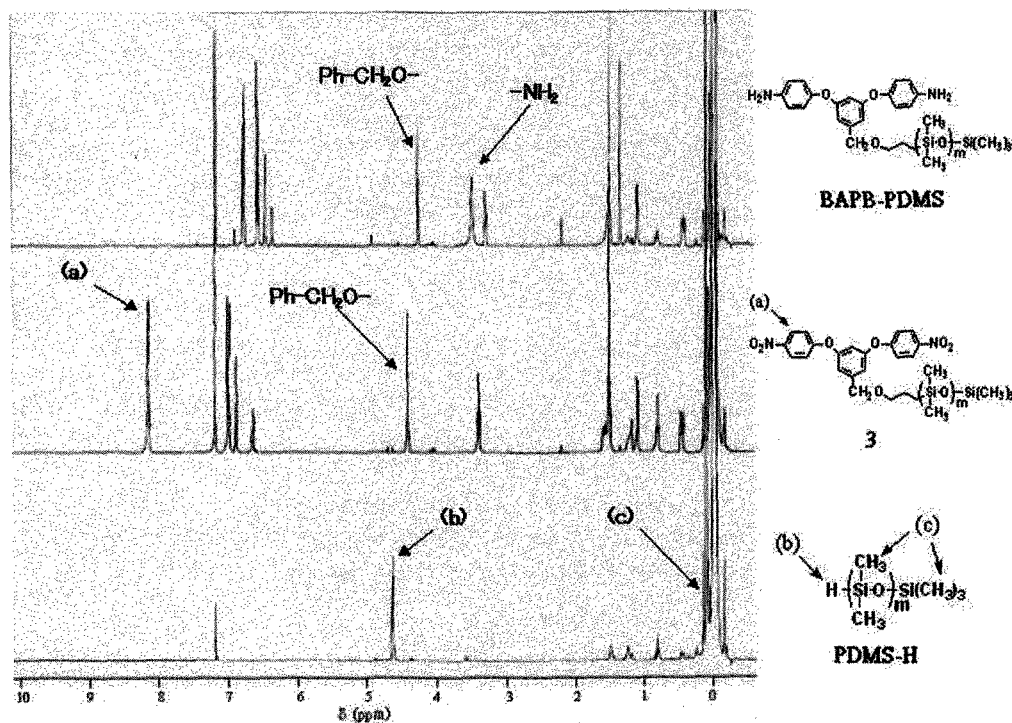
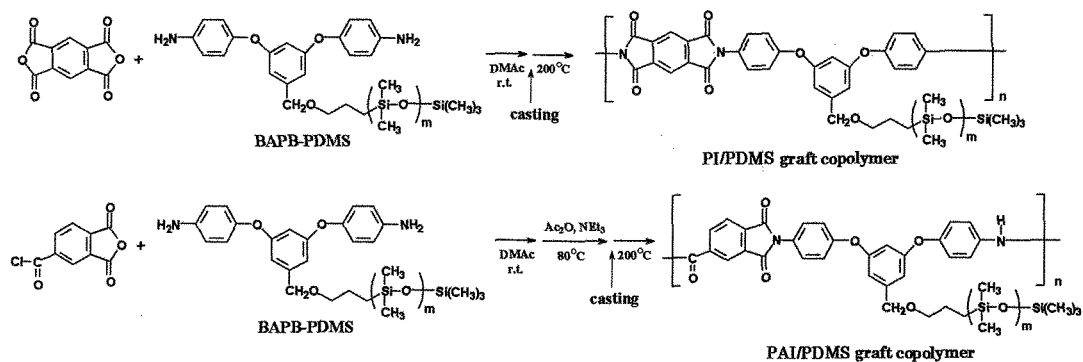
2. RESULTS AND DISCUSSION

2.1 Preparation of BAPB-PDMS macromonomer

BAPB-PDMS macromonomer was prepared by hydrosilylation of 3,5-bis(4-nitrophenoxy)benzyl allyl ether (2) with hydrosilyl-terminated PDMS oligomer (PDMS-H) followed by hydrogenation reduction of the nitro groups, as shown in Scheme 2. The intermediate compound, 2, was prepared in good yield from 3,5-dihydroxybenzyl alcohol and *p*-fluoronitrobenzene followed by etherification with allyl bromide. Fig. 1 shows ¹H-NMR spectra of PDMS-H, 3 and BAPB-PDMS to compare the differences of the terminal groups.



Scheme 2 Preparation of BAPB-PDMS macromonomer.

Fig. 1 $^1\text{H-NMR}$ spectra of BAPB-PDMS macromonomer and its intermediates.

Scheme 3 Preparations of PDMS-grafted copolymers using BAPB-PDMS macromonomer.

2.2 Preparation of PDMS-grafted copolymers

Two kinds of graft copolymers, the main chain of which consisted of polyimide (PI) and poly(amide-imide) (PAI), were prepared by macromonomer methods using BAPB-PDMS. The synthetic diagrams of the copolymers are shown in Scheme 3. PI/PDMS graft copolymer was obtained as a membrane (thickness: ca. 100 μm) by casting the poly(amic acid) solution obtained from polycondensation of BAPB-PDMS with pyromellitic

dianhydride in *N,N'*-dimethylacetamide (DMAc), followed by thermal imidation. On the other hand, PAI/PDMS graft copolymer was prepared by polycondensation of BAPB-PDMS with trimellitic anhydride chloride followed by chemical imidation with acetic anhydride and triethylamine. PAI/PDMS copolymer in the reaction mixture was purified by reprecipitation into methanol to afford a soluble polymer as a white powder. Then, the copolymer membrane was

prepared by casting from its N,N-dimethylformamide (DMF) solution, and it was completely imidized by thermal treatment. The obtained PI/PDMS and PAI/PDMS copolymer membranes were insoluble in any organic solvents, such as acetone, tetrahydrofuran (THF), chloroform, benzene, DMF and DMAc. Therefore, these copolymers possess an ideal property for a membrane material because of the processability and the durability.

Table 1 shows the average degree of polymerization, m , of PDMS segments in macromonomer and copolymer, and the molecular weights of polymers before thermal imidation. The siloxane chain lengths of the copolymers were shorter than those of BAPB-PDMS macromonomer in both cases. Probably, the polycondensation would proceed more smoothly in the shorter BAPB-PDMS rather than the longer one. Anyway, BAPB-PDMS, a new type of PDMS macromonomer, gave the high-molecular weight PDMS-grafted copolymers by polycondensation, which lead to durable membrane materials.

Table 1 Molecular weights of copolymers.

Polymer	Length of the siloxane chain (m) ^{a)}		Mn ^{b)}	Mw/Mn ^{b)}
	Macromonomer	Copolymer		
PI/PDMS	25.4	19.4	6.21×10^3	14.3
PAI/PDMS	25.4	21.6	2.07×10^4	7.35

^{a)} Determined by ¹H-NMR spectra.

^{b)} The molecular weights were determined by gel permeation chromatography before thermal imidation.

2.3 Gas permeability of PDMS-grafted copolymers

Gas permeability coefficients of the copolymer membranes were evaluated as listed in Table 2 compared with polyimide homopolymer, which was prepared by polycondensation of 3,5-bis(4-aminophenoxy)benzene with pyromellitic dianhydride, followed by the similar thermal imidation after casting. It was noticed from this table that the gas permeability coefficients of the copolymer membranes were much higher than those of PI homopolymer membrane, which were similar values to those of PDMS membrane. It was suggested from these results that the continuous phase of PDMS segment existed in the copolymer membranes. Actually, the glass transition temperature (T_g) of PDMS segment was detected at around -120°C by differential scanning calorimetry (DSC), which was one of the evidences that PDMS continuous phase was produced in the copolymer.

On the other hand, as focused in the gas permeabilities of organic gases, the gas permeability coefficients of PDMS-grafted copolymer membranes increased in the following order: ethane > ethylene >> methane, whereas the order of PI homopolymer differed as follows: methane >> ethane > ethylene. Such difference of organic gas permeabilities of these membranes would be due to the difference of surface properties between the copolymer and the homopolymer

membranes. Namely, in the case of PI homopolymer with low permeability, the permeability increases as increase of the diffusivity of gases which is affected by the molecular size of permeate. Otherwise, in the permeation through the high permeable copolymer membrane, the solubility of gases in the membrane surface would dominate the gas permeability, because the diffusivity in the membrane is very high and the difference of each gas diffusivities becomes small. Therefore, it was found that PDMS-grafted copolymer membrane exhibited the higher hydrophobicity than PI homopolymer membrane, owing to that the membrane surface would be effectively covered with PDMS side chain.

2.4 Pervaporation results

Preliminary PV experiments of aqueous solutions of ethanol through the PDMS-grafted poly(amide-imide) membrane were carried out, as summarized in Table 2. As a result, ethanol was efficiently concentrated from their dilute aqueous solutions through the membrane with high permeability. Such an organic-permeability of this kind of PDMS-grafted copolymer membrane would be due to the high solubility of the organic solvents on the membrane surface and the high diffusivity through the membrane. In general, the diffusion of water molecule through the polymer membrane must be higher than that of organic molecule, to afford the water-permeability, because the molecular diameter of water is smaller than that of organic molecule. However, the long inter-molecular distance in the PDMS domain would make the diffusivity of organic and water molecules almost same, as a result, the permeability would depend on the difference of solubility of each component on the membrane surface as described in the case of gas permeability of organic gases.

In addition, it is expected that this PDMS-grafted copolymer membranes can be applied to the separations of dilute aqueous solutions of several organic solvents, concerning that the membranes are insoluble in any solvents. The similar PV experiments of several organic mixtures with water are now in progress to clarify the separation characteristics of this membrane material in more detail.

Table 3 Pervaporation results of aqueous ethanol solution through PAI/PDMS membrane (thickness: 120 μm) at 50°C .

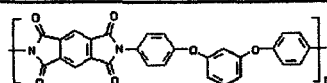
EtOH Composition (wt.%)		Ethanol*	J*	P*
in feed	in permeate	$\alpha_{\text{H}_2\text{O}}$	$\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	$\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
9.3	43.1	7.13	3.90×10^{-2}	5.10×10^{-6}
20.2	59.5	5.86	5.44×10^{-2}	7.13×10^{-6}
41.1	70.5	3.37	6.38×10^{-2}	8.35×10^{-6}

* α : separation factor, J: Flux, P: Permeability coefficient.

Table 2 Gas permeability of copolymer membrane at 30°C .

Polymer	Gas permeability coefficients, $P \times 10^{10} \text{ cm}^3(\text{STP}) \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{cmHg}^{-1}$						
	N_2	O_2	H_2	CO_2	CH_4	C_2H_6	C_2H_4
PI/PDMS	117	248	295	1560	358	990	880
PAI/PDMS	85.6	190	227	991	265	733	635
PI-HP*	0.0422	0.183	2.72	1.36	3.14	0.984	0.807

* Polyimide homopolymer:



3. EXPERIMENTAL

3.1 Synthesis of hydrosilyl-terminated PDMS (PDMS-H)

A solution of trimethylsilanol (5.0 ml, 45.0 mmol) in 50 ml of dry THF was prepared under an argon atmosphere, and 28.1 ml of 1.6 M hexane solution of *n*-butyllithium was added to this solution. After stirring for 30 min at 0°C, hexamethylcyclotrisiloxane (D₃, 50.0 g, 225 mmol) dissolved in 250 ml of dry THF was added, and the reaction mixture was stirred at room temperature for 1.5 h. Then, dimethylchlorosilane (10 ml, 90 mmol) was added in order to terminate the polymerization. The low-molecular-weight substances were removed by heating at 150°C *in vacuo* for 3 h to afford 48.0 g of PDMS-H as a colorless liquid. Yield: 84.8 %.

¹H-NMR δ (CDCl₃, ppm): See Fig. 1.

3.2 Synthesis of 3,5-Bis(4-nitrophenoxy)benzyl alcohol (1)

To a solution of 3,5-dihydroxybenzyl alcohol (1.00 g, 7.14 mmol) in 100 ml of DMF, K₂CO₃ (1.92 g, 13.9 mmol) and *p*-fluoronitrobenzene (1.96 g, 13.9 mmol) were added. After the mixture was stirred for 6 h at r.t., it was poured into excess water to precipitate the product. Then, the product was purified by recrystallization with chloroform/hexane to afford 1.31 g of 1 as a pale yellow powder. Yield: 49.2 %

¹H-NMR δ (DMSO-*d*₆, ppm): 4.48 (2H, d), 5.36 (1H, t), 6.89 (1H, s), 7.04 (2H, d), 7.17 (4H, d), 8.22 (4H, d).

3.3 Synthesis of 3,5-Bis(4-nitrophenoxy)benzyl allyl ether (2)

To a solution of 1 (6.00 g, 15.7 mmol) in 30 ml of THF, allyl bromide (13.6 ml, 157 mmol), tetra-*n*-butylammonium iodide (0.580 g, 1.57 mmol) and the solution of NaOH (5.02 g, 62.8 mmol) in 5 ml of water were added, and the mixture was stirred for overnight at r.t. Then, the organic products were extracted with chloroform and purified by column chromatography on silica gel with chloroform/hexane (1/3 by volume) to afford 5.93 g of 2 as a yellow solid. Yield: 89.4 %.

¹H-NMR δ (DMSO-*d*₆, ppm): 4.00 (2H, d), 4.52 (2H, s), 5.23 (2H, m), 5.90 (1H, t), 7.00 (1H, d), 7.04 (2H, d), 7.24 (4H, d), 8.27 (4H, d).

3.4 Synthesis of 3,5-Bis(4-nitrophenoxy)benzyloxypropyl terminated PDMS (3)

PDMS-H (11.5 g, 8.45 mmol) and 2 (3.50 g, 8.29 mmol) were mixed in 10 ml of dry toluene under an argon atmosphere. To this solution, 0.17 ml of 0.1 M isopropanol solution of chloroplatinic acid was added, and the mixture was stirred at 80°C for 6 h. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (20/1 by volume) to afford 14.5 g of 3 as a brown liquid. Yield: 92.2 %.

¹H-NMR δ (CDCl₃, ppm): See Fig. 1.

3.5 Synthesis of 3,5-Bis(4-aminophenoxy)benzyloxypropyl terminated PDMS (BAPB-PDMS)

3 (13.6 g, 8.23 mmol) was dissolved in 50 ml of ethanol, and Pd-C powder (5%, 0.22 g) was suspended in the solution. Then, the reaction vessel was purged with hydrogen and the mixture was stirred for 16 h at r.t. After Pd-C was filtered off, the product was purified by column chromatography on silica gel with hexane/ethyl acetate

(5/1 by volume) to afford 12.9 g of BAPB-PDMS. Yield: 97.0%

¹H-NMR δ (CDCl₃, ppm): See Fig. 1.

3.6 Preparation of PI/PDMS graft copolymer membrane

Under an argon atmosphere, BAPB-PDMS (4.000 g, 2.797 mmol) and pyromellitic dianhydride (0.6100 g, 2.797 mmol) was dissolved in 10 ml of DMAc, and the solution was stirred for overnight at r.t. The solution was cast on the Teflon sheet, and the solvent was evaporated over a period of 24 h at 50°C to form a membrane. Then, the membrane was heated for 2 h at 200°C *in vacuo*.

3.7 Preparation of PAI/PDMS graft copolymer membrane

Under an argon atmosphere, BAPB-PDMS (4.000 g, 2.797 mmol) and trimellitic anhydride chloride (0.5896 g, 2.797 mmol) was dissolved in 10 ml of DMAc. After the solution was stirred for 4 h at r.t., 3.9 ml of triethylamine and 2.6 ml of acetic anhydride were added and it was stirred for 1 h at 80°C. The mixture was poured into excess methanol to precipitate the polymer. The obtained polymer was filtered, dried and dissolved in DMF, and the solution was cast on the Teflon sheet, and the solvent was evaporated over a period of 24 h at 50°C to form a membrane. Then, the membrane was heated for 2 h at 200°C *in vacuo*.

3.8 Measurements of gas permeability coefficients

Sample membrane was cut into circular pieces with a diameter of 35 mm. Gas permeability was measured using the ordinary vacuum method at 30°C with the apparatus, Tsukuba-Rikaseiki K-315N-01. Permeability coefficients were calculated from the slope of the time-pressure curve, dp/dt , in the steady state.

3.9 Pervaporation experiments

Sample membranes were cut into circular pieces with a diameter of 55 mm. Pervaporation of aqueous ethanol solution through the membrane was carried out using a stainless steel cell, which was dipped in a water bath kept at 50°C. The pressure of the downstream side was kept at about 1.0 mmHg. The permeation area of the membrane was 19.6 cm². The permeated vapor was trapped in a vessel cooled with liquid N₂, and the concentration was determined by gas chromatography. The separation factor, α , which was a measure of the preferential permeation of component A, was defined as the mass concentration ratio in permeate, Y_A/Y_B , divided by the mass concentration ratio in feed, X_A/X_B .

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