

Preparations of PDMS-grafted Aromatic Copolyamide Membrane Exhibiting High Durability and Processability

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The syntheses of siloxane-grafted polyamides were carried out by a macromonomer method, in order to develop a highly permeable and durable membrane material for pervaporation. A novel compounds, 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated polydimethylsiloxane (**BAPB-PDMS**), and 3,5-bis(4-amino-3-methylphenoxy)benzyloxypropyl-terminated polydimethylsiloxane (**BAMPB-PDMS**), were synthesized as macromonomers, which consisted of different PDMS segment lengths. The polycondensation of **BAPB-PDMS**s or **BAMPB-PDMS**s with terephthaloyl chloride yielded the desired siloxane-grafted polyamide copolymers, **PA-g-PDMS** and **MPA-g-PDMS**, respectively. The copolymer membranes were prepared by solvent casting method, and the gas permeability and pervaporation property of these membranes were evaluated. **PA-g-PDMS** was insoluble in any solvents after the copolymer was dried *in vacuo*, however, **MPA-g-PDMS** was soluble in solvents, such as tetrahydrofuran, chloroform and dichloromethane. Therefore, **MPA-g-PDMS** exhibited the higher processability than **PA-g-PDMS**. The gas permeability coefficients of these copolymer membranes were increased as increase of PDMS segment length, and these values of **MPA-g-PDMS** were slightly higher than those of **PA-g-PDMS** containing the same PDMS segment length. From the results of pervaporations of the dilute aqueous solutions of organic solvents, it was found that both of **PA-g-PDMS** and **MPA-g-PDMS** exhibited the excellent permselectivity toward several organic solvents, such as alcohols, acetone, tetrahydrofuran, chloroform, dichloromethane and benzene with a high and stable permeation.

Key words: *polydimethylsiloxane / aromatic polyamide / graft copolymer / pervaporation / membrane*

1. INTRODUCTION

Polydimethylsiloxane (PDMS) has the unique properties derived from its siloxane bond, which include the low glass-transition temperature, the low surface energy, the high thermal stability, the biocompatibility. Especially, PDMS cross-linked membrane indicates the highly permeability to most gases and organic liquids. In addition, PDMS membrane has been known to exhibit the organic permselectivity in the pervaporation of aqueous organic solutions [1,2]. However, because the PDMS membrane should be prepared by cross-linking, it is difficult to make a thin film to obtain the high flux of permeation. Therefore, the processability of PDMS is desired to be improved, which would be achieved by the copolymerization with a high T_g component. In our previous work, PDMS-grafted copolyimide or copolyamide membrane was prepared from the diamino-terminated PDMS macromonomers, which exhibited the high gas and liquid permeability [3-7]. Especially, we have developed a siloxane-grafted polyamide (**PA-g-PDMS**) by the polycondensation of 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated polydimethylsiloxane (**BAPB-PDMS**) and terephthaloyl chloride, which exhibited a high organic permselectivity in the pervaporation of aqueous organic liquid solutions with a stable permeation and a durability to organic liquids. However, in the case of **PA-g-PDMS**, when the reprecipitated polymers were filtered and dried *in vacuo*, they became insoluble in all solvents. In other words, this membrane possessed poor processability due to the chemical structure of the backbone component [6].

In this study, a chemical modification of the main chain structure of PDMS-grafted polyamide has been investigated to enhance the processability of the

copolymer, with maintaining the durability to organic components. For this purpose, the introduction of methyl groups into the main chain polyamide component was carried out, in which a new macromonomer, 3,5-bis(4-amino-3-methylphenoxy)benzyloxypropyl-terminated polydimethylsiloxane (**BAMPB-PDMS**) was synthesized instead of **BAPB-PDMS**. Generally, it has been known that the introduction of alkyl group into aromatic polyamides could achieve the improvement of their solubility.

In this paper, we have described the syntheses of PDMS-grafted aromatic polyamide, which was derived from a new diamino-terminated PDMS macromonomer, **BAMPB-PDMS**, and the separation characteristics of the obtained copolymer membranes were evaluated by gas permeation and pervaporation experiments. If the obtained membranes are insoluble in various organic solvents with a good processability, the pervaporation technique could be extended to separate many kinds of organic liquid mixtures and become a more promising separation process.

2. EXPERIMENTAL

2.1 Materials

The synthetic procedures of **PA-g-PDMS**, **BAPB-PDMS** and hydrosilyl-terminated PDMS (**PDMS-H**) were described in our previous paper [6]. Terephthaloyl chloride was purified by recrystallization from hexane. Tetrahydrofuran (THF) and toluene were distilled over sodium to remove the small amount of water. All other chemicals were used as received.

2.2 Syntheses of 3,5-bis(4-nitro-3-methylphenoxy)benzyl alcohol (1)

To a solution of 3,5-dihydroxybenzyl alcohol (12.0 g, 85.6 mmol) in 258 ml of DMSO, 5-fluoro-2-nitrotoluene (21.7 ml, 172 mmol) and K_2CO_3 (23.8 g, 172 mmol) were added. After the mixture was stirred at 140°C for 15 h, the reaction mixture was poured into excess iced water to precipitate the product. Then, the product was purified by column chromatography on silica gel with ethyl acetate/hexane (2/5 vol.) to afford 28.2 g of **1** as a yellow liquid. Yield: 79.8 %

1H -NMR δ ($CDCl_3$, ppm): 2.61 (6H, s), 4.72 (2H, d, $J=5.36$ Hz), 6.69 (1H, t, $J=4.39$ Hz), 6.99 (6H, m), 8.07 (2H, d, $J=8.78$ Hz).

IR, ν (KBr, cm^{-1}): 2935 (C-H), 2860, 1578, 1506, 1487, 1342 (NO_2), 1223 (C-O-C), 1032, 847.

2.3 3,5-Bis(4-nitro-3-methylphenoxy)benzyl allyl ether (2)

To a solution of **1** (27.8 g, 67.9 mmol) in 190 ml of THF, allyl bromide (16.4 g, 135 mmol), tetra-*n*-butylammonium iodide (2.5 g, 6.78 mmol) and the solution of NaOH (5.42 g, 136 mmol) in 5 ml of water were added, and the mixture was stirred at room temperature for overnight. Then, the organic products were extracted with chloroform, and purified by column chromatography on silica gel with ethyl acetate/hexane (1/4 by volume) to afford 27.6 g of **2** as a yellow liquid. Yield: 89.0 %.

1H -NMR δ ($CDCl_3$, ppm): 2.60 (6H, s), 4.00 (2H, d, $J=1.46$ Hz), 4.51 (2H, s), 5.27 (2H, dd, $J=1.46, 16.5$ Hz), 5.88 (1H, m), 6.69 (1H, t, $J=4.87$ Hz), 6.99 (6H, m), 8.05 (2H, d, $J=9.26$ Hz).

IR, ν (KBr, cm^{-1}): 3086, 2935 (C-H), 2835, 1605, 1580, 1344 (NO_2), 1236 (C-O-C), 1165, 1117, 845, 750.

2.4 3,5-Bis(4-nitro-3-methylphenoxy)benzyloxypropyl-terminated PDMS (3)

PDMS-H ($m=6.9, 6.99$ g, 11.2 mmol), **2** (5.56 g, 12.3 mmol) and Pt/C powder (5 %, 0.47 g) were mixed in 17.0 ml of dry toluene under an argon atmosphere, and the mixture was stirred at 80°C for overnight. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (100/1 by volume) to afford 11.0 g of **3** as a yellow liquid. Yield: 88.0%.

1H -NMR δ ($CDCl_3$, ppm): 0.02 (6($m+1$)H, s), 0.46 (4H, m), 0.82 (3H, t, $J=6.58$ Hz), 1.22 (4H, m), 1.48 (2H, m), 2.53 (6H, s), 3.40 (2H, t, $J=6.82$ Hz), 4.44 (2H, s), 6.67 (1H, s), 6.84 (5H, m), 7.00 (4H, m), 7.99 (2H, d, $J=8.78$ Hz). Average degree of polymerization of PDMS segment (m) = 7.4.

IR, ν (KBr, cm^{-1}): 2935 (C-H), 2905, 2860, 1521, 1344 (NO_2), 1260 (Si-C), 1026 (Si-O-Si), 799, 660.

Other compound **3** ($m=12, 15, 18$) was prepared according to the same procedure as above by using **PDMS-H** ($m=12, 15, 18$) instead of **PDMS-H** ($m=6.9$).

2.5 3,5-Bis(4-amino-3-methylphenoxy)benzyloxypropyl-terminated PDMS (BAMPB-PDMS)

3 ($m=7.4, 11.0$ g, 9.85 mmol) was dissolved in 50 ml of ethanol, and Pd/C powder (5 %, 0.21 g) was suspended in the solution. Then, the reaction vessel was purged with hydrogen and the mixture was stirred at room temperature for overnight. After Pd/C powder was filtered off, the product was purified by column chromatography on silica gel with hexane/ethyl acetate

(5/1 by volume) to afford 10.3 g of **BAMPB-PDMS**. Yield: 95.9 %.

1H -NMR δ ($CDCl_3$, ppm): 0.02 (6($m+1$)H, m), 0.46 (4H, m), 0.81 (3H, t, $J=6.82$ Hz), 1.22 (4H, m), 1.48 (2H, m), 2.07 (6H, s), 3.31 (2H, t, $J=6.82$ Hz), 3.49 (4H, s), 4.28 (2H, s), 6.37 (1H, s), 6.47 (2H, s), 6.55 (2H, d, $J=7.31$ Hz), 6.78 (4H, t, $J=8.49$ Hz). Average degree of polymerization of PDMS segment (m) = 7.1.

IR, ν (KBr, cm^{-1}): 3367 (NH_2), 2935 (C-H), 2860, 1616, 1577, 1261 (Si-C), 1236, 1026 (Si-O-Si), 798.

Other **BAMPB-PDMS** ($m=12, 15, 18$) was prepared according to the same procedure as above by using **3** ($m=12, 15, 18$) instead of **3** ($m=7.4$).

2.6 PDMS-grafted polyamide membrane (MPA-g-PDMS)

Under an argon atmosphere, **BAMPB-PDMS** ($m=7.1, 2.21$ g, 2.02 mmol) and terephthaloyl chloride (0.41 g, 2.02 mmol) was dissolved in 4.9 ml of NMP, and the solution was stirred at room temperature for 1 h 20 min. After the reprecipitation of this solution into excess methanol, the obtained polymer was dried at 70°C *in vacuo* and dissolved in THF. Then, the solution was cast on the poly(tetrafluoroethylene) sheet, and the solvent was evaporated at 40°C over a period of 6 h to form a **MPA-g-PDMS** membrane. The obtained membrane was dried for 2 h at 80°C *in vacuo*.

Other **MPA-g-PDMS** membranes were prepared according to the same procedure as above by using different **BAMPB-PDMS** ($m=12, 15, 18$).

2.7 Characterizations

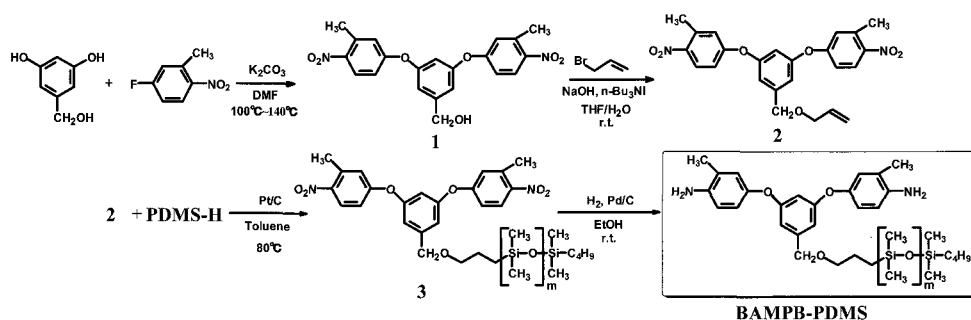
1H -NMR spectra were conducted with a JEOL NM-TH5SK 400MHz FT-NMR spectrometer, and infrared (IR) spectra were recorded with a Shimadzu FTIR-8400 spectrometer. Gel permeation chromatography (GPC) was carried out to determine the number-average (M_n) and weight-average (M_w) molecular weights with a Tosoh HLC-802A instrument by using THF as eluent, equipped with four columns of TSK gels G5000H₆, G4000H₆, G3000H₆ and G2000H₆. The elution was detected by RI and laser light scattering detectors using Tosoh LS-8000. Standard polystyrenes were used to calibrate the molecular weights.

2.8 Measurements of gas permeability coefficients

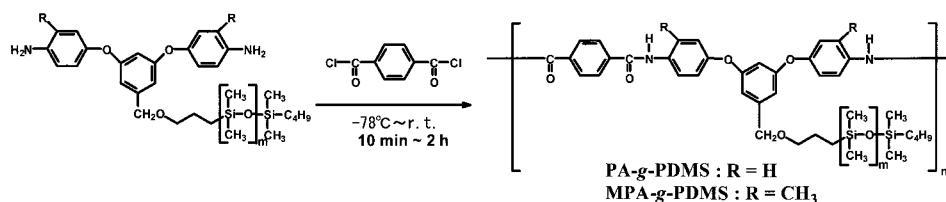
Sample membranes were cut into circular pieces with a diameter of 36 mm and a thickness of 100 – 300 μm . Gas permeabilities of the membranes were measured using the ordinary vacuum method at 30°C with the apparatus, Tsukuba-Rikaseiki K-315N-01, where the permeation area was 7.07 cm^2 . The gas permeability coefficients (P , $cm^3(STP) \cdot cm \cdot cm^{-2} \cdot sec^{-1} \cdot cmHg^{-1}$) were calculated from the slope of the time-pressure curve, dp/dt , in the steady state.

2.9 Pervaporation experiments

Sample membranes were cut into circular pieces with a diameter of 59 mm and a thickness of 100 - 300 μm . 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 below 1.0 mmHg, and the permeation area was 20.0 cm^2 . The



Scheme 1 Synthesis of diamino-terminated PDMS macromonomer.



Scheme 2 Preparations of PA-g-PDMS and MPA-g-PDMS.

permeated vapor was trapped in a vessel cooled with liquid N_2 , and the concentration was determined by gas chromatography. The flux (J , $kg \cdot m^{-2} \cdot h^{-1}$) and the permeability coefficient (P , $kg \cdot m \cdot m^{-2} \cdot h^{-1}$) were calculated from the weight of permeate (w) in the vessel, the permeation time (t), the membrane thickness (L) and the permeation area (A), according to the equations shown below;

$$J = w/At \quad (1)$$

$$P = wL/At \quad (2)$$

The separation factor, α , was defined as the equation below;

$$\alpha = (X_{organic}/X_{water}) / (Y_{organic}/Y_{water}) \quad (3)$$

Where $X_{organic}$ is the mass fraction of organic liquid in permeate, X_{water} is the mass fraction of water in permeate, $Y_{organic}$ is the mass fraction of organic liquid in feed, and Y_{water} is the mass fraction of water in feed.

3. RESULTS AND DISCUSSION

3.1 Preparations of PDMS macromonomers

A new diamino-terminated PDMS macromonomer, **BAMPB-PDMS**, were prepared by hydrosilylation of **2** with hydrosilyl-terminated PDMS oligomer (**PDMS-H**), followed by hydrogenation reduction of the nitro groups, as shown in Scheme 1. The desired PDMS macromonomers, **BAMPB-PDMSs**, with four different PDMS segment lengths. The obtained PDMS macromonomers exhibited the high reactivity in the

Table 1 The results of polymerizations.

Code	m^a	Yield (wt%)	$M_w^b \times 10^4$	M_w/M_n^b	$M_w^c \times 10^4$
PA6	6.8	76.2	2.54	1.77	-
PA12	12.5	85.3	2.47	1.78	-
PA15	15.7	84.5	2.35	1.82	-
PA18	18.6	86.1	1.28	1.50	-
MPA6	7.5	88.9	2.82	2.13	3.15
MPA12	11.8	87.2	2.52	1.74	9.39
MPA15	15.1	81.5	2.96	1.66	3.87
MPA18	17.9	85.3	2.60	1.68	3.89

a) Average degree of polymerization of PDMS segment.

b) Number-average and weight-average molecular weight (M_n and M_w) were determined by GPC based on polystyrene standards. (Eluent: THF)

c) Weight-average molecular weights (M_w) were determined by laser light scattering method. (Eluent: THF)

polycondensation with diacid chloride, which would be due to the reactivity of p-aminophenyl groups in the terminal component.

3.2 Preparations of graft copolymer membranes

PDMS-grafted aromatic polyamides of different main chain structures and PDMS segment lengths were prepared by a macromonomer method using **BAPB-PDMS** and **BAMPB-PDMS**, respectively. The polycondensation of **BAPB-PDMS** or **BAMPB-PDMS** with terephthaloyl chloride gave **PA-g-PDMS** and **MPA-g-PDMS**, as shown Scheme 2. The molecular weights of the obtained copolymers are summarized in Table 1, which were estimated by GPC and Laser light scattering method. Both PA and MPA copolymers have high molecular over 2×10^4 . In addition, M_w of MPA, which was estimated by GPC, was lower than M_w by laser light scattering. Usually, the branch type polymers such as MPA become compact in their solutions. For sample codes, **PA-g-PDMS**'s with different lengths of PDMS segment were expressed as PA6, PA12, PA15 and PA18, and **MPA-g-PDMS**'s were as MPA6, MPA12, MPA15 and MPA18.

When the reprecipitated **PA-g-PDMS** were filtered and dried *in vacuo* for 2 h, they became insoluble in any solvents. Thus, the copolymers were dissolved in NMP immediately after the reprecipitation to obtain the homogeneous solutions of **PA-g-PDMS**. Then, the copolymer membranes were prepared from these NMP solutions and dried *in vacuo*. On the other hand, the obtained **MPA-g-PDMS** was soluble in THF, dichloromethane and chloroform, after they were completely dried *in vacuo*, but insoluble in acetone, ethanol, DMF, NMP and DMSO. Furthermore, all of the graft copolymer membranes were mechanically strong and became insoluble in any solvents after they were dried *in vacuo*.

Consequently, **PA-g-PDMS** and **MPA-g-PDMS** seem to possess an ideal property for pervaporation membrane materials because of the durability to organic liquids. Furthermore, the solubility of **MPA-g-PDMS** successfully improved by the introduction of methyl

Table 2 Gas permeability coefficients of PA-g-PDMS and MPA-g-PDMS membranes at 30°C.

Code	$m^{(a)}$	Gas permeability coefficient, P (Barrer) ^(b)				
		N ₂	O ₂	H ₂	CO ₂	C ₂ H ₆
PA6	6.8	11.1	29.4	55.9	170	75.9
PA12	12.5	66.8	147	172	759	602
PA15	15.7	76.0	167	200	892	680
PA18	18.6	138	291	333	1573	1302
MPA6	7.5	37.5	86.6	122	491	312
MPA12	11.8	82.3	178	232	960	744
MPA15	15.1	113	240	293	1263	1054
MPA18	17.9	143	302	345	1611	1361
PDMS ^(c)	-	470	927	940	4652	4200

a) Average degree of polymerization of PDMS segment in the graft copolymer.

b) 1 Barrer = $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{cmHg}^{-1}$.

c) The data of PDMS membrane according to the literature [8].

group into the backbone component, as compared with that of PA-g-PDMS.

3.3 Gas permeability of copolymer membranes

Gas permeability coefficients of the copolymer membranes for nitrogen, oxygen, hydrogen, carbon dioxide and ethane were evaluated as listed in Table 2, as compared with those of PDMS crosslinked membrane, which had been reported in the literature [8]. It was noticed from this table that the gas permeability coefficients of PA-g-PDMS and MPA-g-PDMS membranes were almost in the same order of PDMS membrane. Therefore, it was suggested that the continuous phase of PDMS segment existed in the copolymer membranes. The difference of the gas permeabilities for each gas would be due to the surface property of the copolymer membranes. In the gas permeation through such high permeable copolymer membranes, 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 diffusivities of each gas becomes small. It was found from these results that PDMS-grafted copolymer membranes possessed highly hydrophobic surface that was effectively covered with PDMS side chain, where the organic gas permeability's of ethane became significantly high. In addition, the gas permeability coefficients of PDMS-grafted copolymer membranes increased as the increase PDMS segment length.

Furthermore, Table 2 also indicated that the permeability coefficients of each gas of MPA-g-PDMS tended to be slightly higher than those of PA-g-PDMS containing the same PDMS segment length. This

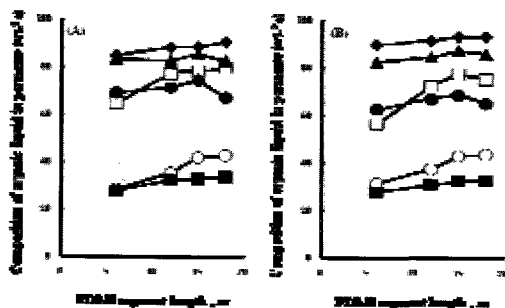


Fig. 1 Effect of PDMS segment length on the composition of organic liquid in permeate of the pervaporation of dilute solutions of organic liquids in water through PA-g-PDMS (A) and MPA-g-PDMS (B) membrane.

◆: THF in water, ▲: Dichloromethane in water, □: Acetone in water, ●: Chloroform in water, ■: Benzene in water, ○: Ethanol in water.

tendency would be derived from the difference of aggregations of main chain components because of the main chain structures. Actually, the density of MPA-g-PDMS membrane was a little lower than that of PA-g-PDMS membrane, which would result in the higher diffusivity of MPA-g-PDMS than PA-g-PDMS.

3.4 Results of pervaporation

Pervaporation experiments of dilute aqueous solutions of ethanol, acetone, THF, dichloromethane, chloroform and benzene through PA-g-PDMS and MPA-g-PDMS membranes were carried out. The results were shown in Fig. 1, where the feed concentrations of ethanol, acetone, THF, dichloromethane, chloroform and benzene solutions in water were 8.0~9.9, 8.8~9.8, 6.1~9.3, 0.80, 2.0 and 0.20 wt.%, respectively. As a result, these organic liquids were efficiently concentrated from their dilute aqueous solutions through these membranes with high and stable permeation. Such an organic-permselectivity 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. The separation property of MPA membrane was similar to that of PA membrane. In addition, the separation factors of organic solvents were different each other, which would be due to the different solubility of each solvent on the membrane surface. The organic liquid permeability of THF, dichloromethane, chloroform and acetone were much higher than those of benzene and ethanol. Furthermore, the pervaporation characteristics of these membranes were about same, even if the PDMS segment lengths were different.

In conclusion, we succeeded in the preparation of new siloxane-grafted aromatic polyamides, which possessed a good processability and durability for pervaporation membrane. These copolymer membranes exhibited the excellent permeability not only the gases but also organic components from aqueous organic liquid solutions. Therefore, it is expected that MPA-g-PDMS membranes can be used for the removal of toxic organic components from the waste-water, etc., due to their mechanical strength and durability for the application of PV technology.

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