Pervaporation Property of Siloxane-Grafted Aromatic Polyamide Membrane

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The synthesis of siloxane-grafted aromatic polyamide was carried out by a macromonomer method, in order to develop a durable membrane material for pervaporation. 3,5-Bis(4-aminophenoxy)benzyloxypropyl-terminated polydimethylsiloxane (BABP-PDMS) was used as a macromonomer. **BABP-PDMSs** with different chain length prepared hydrosilylation were by of 3,5-bis(4-nitrophenoxy)benzyl allyl ether with hydrosilyl- terminated polydimethylsiloxanes using Pt catalyst, followed by hydrogenation reduction of the terminal dinitro groups. The polycondensations of BABP-PDMSs with terephthaloyl chloride or isophthaloyl chloride yielded the desired siloxane-grafted polyamide copolymers (PA-g-PDMS). PA-g-PDMS membranes were prepared by solvent casting method from the NMP solutions, and the pervaporation properties of these membranes were evaluated. As a result, the obtained membrane exhibited an excellent permselectivity toward several organic solvents, such as alcohols, acetone, THF, chloroform, dichloromethane and benzene, in the pervaporation of their aqueous solutions, which was due to the durability of the main chain component of PA-g-PDMS. Key words: polydimethylsiloxane / macromonomer / graft copolymer / membrane / permeability

1. INTRODUCTION

In these years, the pervaporation (PV) technique with a polymer membrane has been focused in much attention for separations of mixtures of several organic liquids and water. Since it is possible to remove organic components from aqueous organic liquid solutions, PV technique is expected for the application to a removal of organic components from waste fluid. For this purpose, it is more important that the membrane exhibits the organic-permselectivity in the permeation of mixtures of organic liquids and water, and the durability against several organic solvents. Polydimethylsiloxane (PDMS) membrane or PDMS-containing copolymer membrane has been known to show a selective permeation of organic liquids in the pervaporation of aqueous organic solutions^{1/3)}. For PV materials possessing the mechanical strength and the durability, we have been studied the syntheses of siloxane-grafted copolymers, the main chain of which consisted of several aromatic polymers⁴⁾⁻⁷⁾.

In the previous study⁶, 3,5-diaminobenzyloxypropyl-terminated PDMS (DAB-PDMS) was synthesized as the macromonomer to prepare siloxane-grafted copolyimide, as shown in Scheme 1. Then, the graft copolymer membrane exhibited the high organic



Scheme 1 Graft copolymerization using DAB-PDMS.

permselectivity in PV of aqueous organic liquid solutions, such as acetone, THF and dichloromethane with a stable permeation⁷⁾. However, the PDMS-grafted copolyimide must be prepared by casting in poly(amic acid) stage, followed by thermal imidation. In other words, this membrane possessed the excellent separation property but less processability due to the chemical structure of backbone component.

In this study, a novel membrane material has been investigated, which possesses the practical properties of permselectivity in PV, durability and processability. The main purpose of this work is to introduce aromatic polyamide into PDMS-grafted copolymer as a backbone component instead of polyimide, which would increase the solubility. Some kinds of aromatic polyamides are soluble in some solvents such as aprotic polar solvents to be easily prepared membranes by solvent-casting method, and insoluble in the other organic solvents to be durable to separating organic components. In addition, a new type reactive terminal of group, 3,5-bis(4-aminophenoxy)benzyloxypropyl (BAPB) group, was introduced in the PDMS macromonomer⁷⁾. This BABP-PDMS macromonomer is expected to improve the reactivity in polycondensation as compared with DAB-PDMS. Thus, in this paper, the synthesis of PDMS-grafted aromatic polyamide was carried out from BABP-PDMS macromonomer, and the separation characteristics of the obtained membranes were evaluated by PV experiments.

2. RESULTS AND DISCUSSION

2.1 Preparation of BABP-PDMS macromonomer

BAPB-PDMS macromonomer was prepared by hydrosilylation of 3,5-bis(4-nitrophenoxy)benzyl allyl ether (2) with hydrosilyl-terminated PDMS oligomer (H-PDMS) followed by hydrogenation reduction of the nitro groups, as shown in Scheme 2. The intermediate



Scheme 2 Preparation of BAPB-PDMS macromonomer.



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

compound, 2, was prepared in good yield from 3,5-dihydroxybenzyl alcohol and p-fluoronitrobenzene followed by etherification with allyl bromide. The starting material, PDMS-H, was prepared by а non-equilibrium ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) initiated with *n*-butyllithium, and terminating the reaction with dimethylchlorosilane. The average degree of polymerization, m, could be controlled by changing the mole ratio of D_3 and *n*-butyllithium in the polymerization. The two kinds of BAPB-PDMSs were prepared, in which the average degrees of polymerization of PDMS segment were 7.3 and 14.8, respectively, as shown in Table 1.

2.2 Preparation of PDMS-grafted polyamides

Four kinds of PDMS-grafted aromatic polyamides, which consisted of different main chain structures and PDMS segment lengths, were prepared by the macromonomer methods using BABP-PDMS, in order to clarify the effect of main chain structure and PDMS segment length on the pervaporation property of the copolymer membranes. The synthetic diagrams of the graft copolymers are shown in Scheme 3. The polycondensation of terephthaloyl chloride or isophthaloyl BAPB-PDMS chloride with in 1-methyl-2-pyrrolidinone (NMP) proceeded smoothly to yield p-PA-g-PDMS or m-PA-g-PDMS after the reprecipitation of the homogeneous reaction mixture into methanol. However, when the reprecipitated polymers were filtered and dried in vacuo for 2 h, they became insoluble in any solvents. Therefore, the polymers were dissolved in NMP immediately after the filtrations to obtain the homogeneous solutions of p-PA-g-PDMS and m-PA-g-PDMS.

Then, the copolymer membranes (thickness: ca. 100 µm) were prepared from these NMP solutions and dried at 60°C for over two days. The obtained PDMS-grafted polyamide membranes were mechanically strong and insoluble in any organic solvents, such as alcohols, acetone, tetrahydrofuran (THF), chloroform, benzene, DMF, DMSO and NMP. Therefore, these copolymers possess an ideal property for PV membrane materials because of the processability and the durability.

2.3 Permeation properties of PDMS-grafted polyamide membranes

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 thermal imidation. It was noticed from this table that the gas permeability coefficients of the PDMS-grafted polyamide membranes were much higher than those of PI

Table 1 Results of preparations of the reactive polydimethylsiloxane (BABP-PDMS).

Run	D ₃ /n-BuLi*	m ^{b)} of H-PDMS		m ^{c)} of	Mn ⁴) of	Mw/Mn ⁴) of	
	(mole ratio)	Theo.	Obs.	BAPB-PDMS	BAPB-PDMS	BAPB-PDMS	
1	2.0	6.0	6.0	7.3	6.75×10 ²	1.20	
2	4.0	12.0	11.5	14.8	1.71×10^{3}	1.14	

a) Mole ratio of D, and n-butyllithium (n-BuLi) in the preparation of H-PDMS. b) Average degree of polymerization (m) of H-PDMS. The theoretical value of m was calculated from the equation,

 $m = 3[D_{3}]/[n-BuL_{3}]$, and the observed value was estimated on the basis of ¹H-NMR spectrum.

c) Average degree of polymerization (m) of BAPB-PDMS, determined by ¹H-NMR spectrum.

d) Number-average and weight-average molecular weights (Mn and Mw) were determined by GPC.

		Gas permeability coefficient, P (Barrer *)					Selectivity, P/PN					
Code	m.*)	N ₂	О,	H,	CO ₂	CH,	C,H	O,N,	H ₂ /N ₂	CO,N,	CH, N,	C,H,N,
p-PA-g-PDMS-1	7.3	14.0	34.8	62.2	191	39.4	88.4	2.49	4.44	13.6	2.81	6.31
p-PA-g-PDMS-2	14.8	53.0	115	141	620	169	479	2.17	2.66	11.7	3.19	9.04
m-PA-g-PDMS-1	7.3	12.3	31.3	59.7	178	36.4	79.8	2.54	4.85	14.5	2.95	6.49
m-PA-g-PDMS-2	14.8	56.7	126	165	672	183	491	2.22	2.91	11.9	3.23	8.66
PI-HP		0.0422	0.183	2.72	1.36	3.14	0.984	4.34	64.5	32.2	74.4	23.3

Table 2 (for nameshility of PDMS mafted notramide membranes at 20%

a) Average degree of polymerization of PDMS segment in the graft copolymer. b) 1 Baner = 1 x 10¹⁰ cm³(STP) · cm · cm³ · sec¹ · cmHg¹

c) PI-HP: Polyimide homopolymer. The structure:

homopolymer membrane. Therefore, it was suggested that the continuous phase of PDMS segment existed in the copolymer membranes.

As focused in the gas permeabilities, the gas permeability coefficients of PDMS-grafted copolymer membranes increased as the PDMS segment length became longer. In addition, such difference of the gas permeabilities for each gas would be due to the difference of surface properties. 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 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 membrane exhibited the higher hydrophobicity than PI homopolymer membrane, owing to that the membrane surface would be effectively covered with PDMS side chain, because the organic gas permeabilities of methane and ethane became much higher.

PV experiments of aqueous solutions of alcohols, acetone, THF, chloroform, dichloromethane and benzene through the two membranes of p-PA-g-PDMS-1 and p-PA-g-PDMS-2 were carried out, as summarized in

Table 3. As a result, these organic liquids were efficiently concentrated from their dilute aqueous solutions through the membranes with high permeability. 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. Furthermore, p-PA-g-PDMS-2 (m=14.8) exhibited the higher selectivity than p-PA-g-PDMS-1 (m=7.3) for each organic liquid. Especially, through p-PA-g-PDMS-2 membrane, the saturated solution of dichloromethane in water (1.2 wt.%) was concentrated to over 95 wt.%, which would be due to not only the high permeability but also the durability of the membrane material.

Consequently, it is expected that this PDMS-grafted aromatic polyamide 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 applications to the removal of organic components from wastewater will be in progress by using this kind of membrane material.

3. EXPERIMENTAL

3.1 Synthesis of hydrosilyl-terminated PDMS (PDMS-H) A solution of 1.6 M hexane solution of n-butyllithium (28.1 ml, 45.0 mmol) in 20 ml of dry THF was prepared under an argon atmosphere. After stirring

a . 3:	A 2012	Composi	tion * (wt.%)	Org. Vi	J ¹⁰ x10 ²	P*1x10*	
Code	Organic inquid	in feed in permeate		OL Water	(kg m ⁻² h ⁻¹)	(kg m m ⁻² h ⁻¹)	
p-PA-g-PDMS-1	Methanol	8.80	28.6	4.15	1.44	1.83	
(m = 7.3)	Ethanol	8.11	28.6	4.54	1.56	1.98	
	1-Propanol	7.25	40.4	8.67	5.32	6.76	
	2-Propanol	8.95	31.5	4.68	2.34	2.98	
	Acetone	8,86	64.6	18.8	3.77	4.79	
	Tetrahydrofuran	6.99	85.0	75.4	21.9	27.8	
	Chloroform	0.80	76.2	397	5.92	7.51	
	Dichloromethane	1.20	88.5	634	6.73	8.54	
	Benzene	0.20	59.6	736	3.43	4.36	
p-PA-g-PDMS-2	Methanol	8.80	36,5	5.96	2.50	4.09	
(m = 14.8)	Ethanol	7.97	42.1	8.40	3.24	5.32	
	1-Propanol	8.07	59.2	16.5	6.34	10.4	
	2-Propanol	9.61	48.9	9.00	3.54	5.86	
	Acetone	8.81	78.4	37.6	8.79	14.4	
	Tetrahydrofuran	6.16	88.7	120	41.5	68.0	
	Chloroform	0.80	79.3	451	8.54	14.0	
	Dichloromethane	1.20	96.2	2084	28.6	46.9	
	Benzene	0.20	61.2	787	3.84	6.30	

Table 3 Results of pervaporation of aqueous organic liquid solutions through PDMS-grafted polyamide membranes.

a) Composition of organic liquid in the feed and the permeate.

b) a: Separation factor (organic liquid/water), J: Flux, P: Penneability coefficient.

for 30 min at 0°C, hexamethylcyclotrisiloxane (D₃, 20.0 g, 90.0 mmol) dissolved in 80 ml of dry THF was added, and the reaction mixture was stirred at room temperature (r.t.) for 1.5 h. Then, dimethylchlorosilane (9.95 ml, 90.0 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 21.7 g of PDMS-H as a colorless liquid. Yield: 86.0 %. m = 6.0.

Other PDMS-H (m=11.5) was prepared according to the same procedure as above by using four equivalent amount of D_3 against n-BuLi.

3.2 Syntheses of 3,5-bis(4-nitrophenoxy)benzyl alcohol (1) and 3,5-bis(4-nitrophenoxy)benzyl allyl ether (2)

To a solution of 3,5-dihydroxybenzyl alcohol (3.00 g, 21.4 mmol) in 100 ml of DMF, K_2CO_3 (5.92 g, 42.8 mmol) and *p*-fluoronitrobenzene (6.04 g, 42.8 mmol) were added. After the mixture was stirred at r.t. for 6 h, it was poured into excess water to precipitate the product. Then, the product was purified by recrystallization with chloroform/hexane to afford 7.17 g of 1 as a pale yellow powder. Yield: 87.7 %

¹H-NMR δ (CDCL₃-d₆, ppm): 1.87 (1H, t, J=5.74Hz), 4.73 (2H, d, J=5.13Hz), 6.75 (1H, s), 6.93 (2H, s), 7.10 (4H, m), 8.22 (4H, m).

To a solution of 1 (5.84 g, 15.3 mmol) in 25.0 ml of THF, allyl bromide (18.5 ml, 153 mmol), tetra-*n*-butyl-ammonium iodide (0.561 g, 1.53 mmol) and the solution of NaOH (2.10 g, 52.5 mmol) in 5 ml of water were added, and the mixture was stirred at r.t. for overnight. Then, the organic products were extracted with chloroform and purified by column chromatography on silica gel with chloroform/hexane (1/4 by volume) to afford 7.01 g of 2 as a yellow solid. Yield: 88.4 %.

¹H-NMR δ (DMSO-d₆, ppm): 4.00 (2H, d, J=1.47Hz), 4.51 (2H, s), 5.27 (2H, dd, J=12.4, 26.1Hz), 5.88 (1H, m), 6.99 (1H, s), 7.02 (2H, s), 7.23 (4H, m), 8.25 (4H, m).

3.3 Synthesis of 3,5-bis(4-nitrophenoxy)benzyloxypropyl terminated PDMS (3)

PDMS-H (m = 6.0, 3.32 g, 5.92 mmol) and Pt-C powder (5 %, 0.277 g) and 2 (3.00 g, 7.11 mmol) were mixed in 7.11 ml of dry toluene under an argon atmosphere. After 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 4.37 g of 3 as a brown liquid. Yield: 75.3 %. m = 7.3.

¹H-NMR δ (CDCL₃-d₆, ppm): 0.01 ((6m+6)H, m), 0.45 (4H, m), 0.81 (3H, t, J=6.59Hz), 1.23 (4H, m), 1.54 (2H, m), 3.53 (2H, t, J=6.83Hz), 4.33 (2H, s), 6.65 (1H, s), 6.88 (2H, d, J=1.71Hz), 6.99 (4H, m), 8.14 (4H, m).

3.4 Synthesis of 3,5-bis(4-aminophenoxy)benzyloxypropyl terminated PDMS (BAPB-PDMS)

3 (m = 7.3, 4.37 g, 4.44 mmol) was dissolved in 50 ml of ethanol, and Pd-C powder (5 %, 0.189 g) was suspended in the solution. Then, the reaction vessel was purged with hydrogen and the mixture was stirred at r.t. for overnight. 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 4.20 g of BAPB-PDMS. Yield: 99.1 %

¹H-NMR δ (CDCL₃-d₆, ppm): 0.01 ((6m+6)H, m), 0.45 (4H, m), 0.83 (3H, m), 1.23 (4H,m), 1.50 (2H, m), 3.30 (2H, t, J=4.56Hz), 3.50 (4H, s), 4.28 (2H, s), 6.38 (1H, s), 6.48 (2H, d, J=2.20Hz), 6.60 (4H, m), 6.77 (4H, m).

3.5 Preparation of PDMS-grafted polyamide membrane

Under an argon atmosphere, BAPB-PDMS (m = 7.3, 1.16 g, 1.22 mmol) and terephthaloyl chloride (0.248 g, 1.22 mmol) was dissolved in 4.88 ml of NMP, and the solution was stirred at r.t. for 2 h. After the reprecipitation of this solution into excess methanol, the obtained polymer was dissolved in NMP. Then, the solution was cast on the Teflon sheet, and the solvent was evaporated at 60°C over a period of 48 h to form a membrane. $Mn = 1.64 \times 10^5$, $Mw = 4.31 \times 10^5$ (by GPC).

IR, ν (KBr, neat, cm⁻¹) :3317 (-CO-NH-), 2960 (-CH₃), 2928, 2872 (-CH₂-), 1647 (C=O), 1603 (-NH-), 1508 (C=C), 1448 (-CH₃), 1410 (-C-N-), 1259 (C-O-C), 1020 (Si-O-Si), 797 (Si-(CH₃)₃) 685 (Si-H), 517 (Si-H)

Other membranes were prepared according to the same procedure as above by using different monomers.

3.6 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.

3.7 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 28.3 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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