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Pervaporation Property of Siloxane-Grafted Aromatic Polymer/Silicalite Hybrid Membrane

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It is well known that the hydrophobic silicalite is effective to improve the alcohol-permselectivity in the pervaporation with silicone membrane. In this study, the effect of silicalite on the pervaporation property of novel siloxane-grafted aromatic polymers was evaluated. The synthesis of a 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. Then, PDMS-grafted poly(amide-imide) (PAI-*g*-PDMS) was prepared by polycondensation of PDMS macromonomer with trimellitic dianhydride chloride. The copolymer membrane and the hybrid membrane with silicalite were prepared by solvent casting method, and the pervaporation properties of these membranes were evaluated. As a result, there membranes exhibited the alcohol-permselectivity for the pervaporation of various organic liquid/water mixtures. Especially, the silicalite filled PAI-g-PDMS hybrid membrane exhibited the higher permselectivity of alcohols and acetone than PAI-g-PDMS membrane, which depended on the content of silicalite.

Key words: *poly(amide-imide) / polydimethylsiloxane / graft copolymer / silicalite / hybrid membrane / pervaporation*

1. INTRODUCTION

The pervaporation (PV) technique has been focused in much attention, for example, to remove harmful organic components from the industrial effluents. It is favorable to remove the small amount of organic liquids, such as benzene and dichloromethane, from wastewater by PV technique. Polydimethylsiloxane (PDMS) membrane has been known as one of the few organic-permselective membrane materials [1)], however, it is difficult to make a thin film to obtain the high flux of permeates. Therefore, many studies to improve its mechanical properties have been carried out by inducing a siloxane block or graft copolymer structure.[2)] In our recent study, PDMS-grafted poly(amide-imide) (PAI-g-PDMS) membrane exhibited the ethanol-permselectivity from the dilute aqueous solution of ethanol by pervaporation[3)].

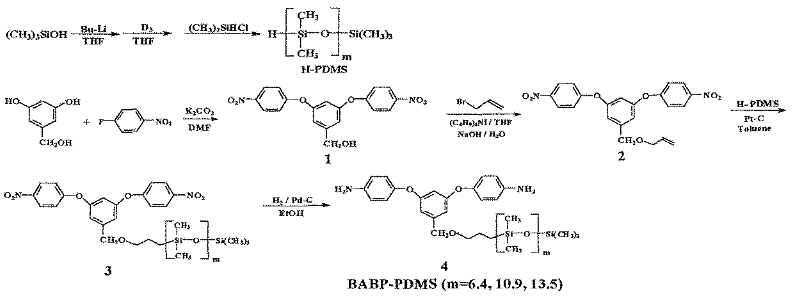
On the other hand, zeolite membranes have been paid a great attention as candidates for the molecular sieving separation membranes and the membrane reactor. Pure silica type MFI zeolite, *i.e.* silicalite, is hydrophobic and capable of selectively adsorbing organic molecules from the aqueous solutions. Thus, the silicalite membrane is known to show a very high ethanol-permselectivity from a dilute aqueous solution of ethanol[4)-5)], which is higher than that of polymer membranes. However, the silicalite membrane is difficult to make a practical module, such as a tube type or a spiral type. In addition, the aggregates of zeolite crystallites often form pinholes in the membrane. Then, the development of zeolite filled PDMS membranes has focused in a renewed interest on the improvement of the performance of these membranes by incorporating highly selective zeolite molecular sieves into polymer membranes. According to the reports by Hennepe *et al.*, the silicone rubber membrane filled with silicalite showed a much improved selectivity and flux in the pervaporation of aqueous organic liquid solutions[6)]. The selectivity, α, of ethanol over water of the silicalite-filed silicone membrane rises from 7 to about 40, when the silicalite content increases from 0 to 70 wt. %. The flux also rises from 0.02 to 0.045 l/m^2-hr, which is implying a facilitated transport of ethanol molecules through the silicalite.

In this study, silicalite filled PAI-g-PDMS composite membrane was prepared by incorporating the silicalite particle into the polymer matrix, which was mechanically strong and thermally stable membrane material. Then, the pervaporation properties of the silicalite-filled PAI-g-PDMS membranes for various organic liquids/water solutions were investigated in detail.

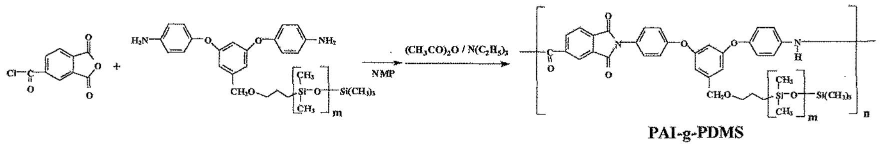
2. RESULTS AND DISCUSSION

2.1 Preparation of PDMS-grafted poly(amide-imide)

The matrix polymer, PAI-*g*-PDMS, was prepared by polycondensation of a reactive PDMS macromonomer, 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated PDMS (BABP-PDMS) with trimellitic anhydride chloride, followed by the chemical imidation. BAPB-PDMS 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 1. The starting



Scheme 1 Synthesis of BABP-PDMS macromonomer.



Scheme 2 Synthesis of PDMS-grafted copolymer (PAI-*g*-PDMS) using BABP-PDMS macromonomer.

Table 1 Results of preparations of PAI-*g*-PDMS by using BAPB-PDMS macromonomer.

Sample code	$\overline{m}$ of PDMS [a)]	PDMS content (wt.%)	$\overline{Mn} \times 10^{-4}$ [b)]	$\overline{Mw}/\overline{Mn}$ [b)]
PAI-*g*-PDMS (1)	6.4	52.7	2.87	6.66
PAI-*g*-PDMS (2)	10.9	62.9	1.49	11.2
PAI-*g*-PDMS (3)	13.5	67.4	10.9	2.62

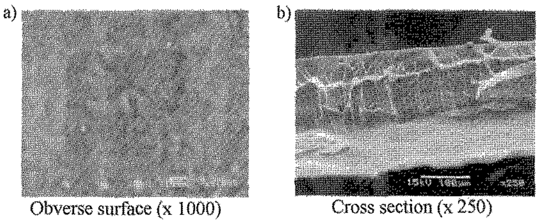
a) The average degree of polymerization ($\overline{m}$) of PDMS, determined on the basis of ^{1}H-NMR spectra.

b) Number-average molecular weight ($\overline{Mn}$) and weight-average molecular weight ($\overline{Mw}$) were determined by gel-permeation chromatography using THF as eluent.

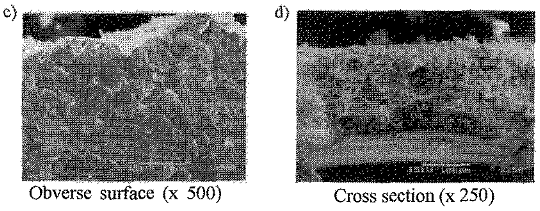
material, H-PDMS, was prepared by a non-equilibrium ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) initiated with trimethylsilanolate anion, and terminating the reaction with dimethylchlorosilane. The average degree of polymerization, *m*, could be controlled by changing the mole ratio of D_3 and the initiator in the polymerization. The three kinds of BAPB-PDMSs were prepared, in which the average degrees of polymerization of PDMS segment were 6.4, 10.9 and 13.5, respectively, as shown in Table 1.

PAI-*g*-PDMS was prepared by the macromonomer methods using BABP-PDMS, as shown in Scheme 2. The obtained PAI-*g*-PDMS was soluble in tetrahydrofuran (THF), dichloromethane, chloroform, benzene, 1-methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF), but insoluble in acetone and alcohols, such as methanol, ethanol, propanol, butanol. Thus, PAI-*g*-PDMS could be used for the separation of various alcohols by pervaporation. On the contrary, the polymers became partially insoluble in NMP and DMF after the thermal imidation. Table 1 summarizes the results of polymerizations including the molecular weights of polymers after the chemical imidation.

Then, PAI-*g*-PDMS membranes were prepared by a solvent-casting method from the NMP solutions. The composite membranes with silicalite were prepared by adding silicalite in the polymer solution in NMP. By changing the composition of the silicalite, three kinds of composite membranes of different silicalite contents were obtained. All of obtained membranes (thickness: 200 - 400 μm) were mechanically strong to be used for pervaporation. Fig. 1 shows the scanning electron microscope (SEM) images of the surface and cross section of the PAI-g-PDMS membrane and silicalite filled PAI-*g*-PDMS composite membrane. In these micrographs, the distribution of silicalite in the polymer matrix was recognized, where silicalite particles were comparatively concentrated in the one side of the membrane.



Obverse surface (x 1000) Cross section (x 250)



Obverse surface (x 500) Cross section (x 250)

Fig. 1 SEM pictures of PAI-g-PDMS membrane (a), (b) and PAI-g-PDMS/silicalite composite membrane (c), (d).

2.2 Pervaporation results of PAI-*g*-PDMS and silicalite filled PAI-*g*-PDMS composite membranes

Pervaporation experiments of aqueous solutions of methanol, ethanol, 1-propanol, 2-propanol and

Table 2 Pervaporation results of aqueous organic solution through PAI-*g*-PDMS and Silicalite filled PAI-*g*-PDMS composite membranes at 50.0℃.

Code [a)]	Organic liquid	Composition of (wt.%) In feed	Composition of (wt.%) in permeate	α [b)]	J [b)] $\times 10^{-2}$ kg m^{-2}h^{-1}	P [b)] $\times 10^{-6}$ kg m m^{-2}h^{-1}
①	Methanol	9.89	34.2	4.74	2.13	4.48
	Ethanol	9.44	43.2	7.30	2.40	5.03
	1-Propanol	10.1	40.6	6.08	4.08	16.3
	2-Propanol	11.2	44.9	6.46	1.66	6.64
	Acetone	9.13	78.5	36.4	6.82	14.3
②	Methanol	9.81	43.3	7.02	2.18	8.72
	Ethanol	9.89	53.9	10.7	1.94	7.77
	1-Propanol	9.83	63.1	15.7	4.08	8.56
	2-Propanol	10.0	49.7	8.89	2.74	5.76
	Acetone	6.77	81.5	60.7	4.90	19.6
③	Methanol	8.62	40.6	7.25	3.01	11.1
	Ethanol	7.91	49.1	11.2	2.36	8.73
	1-Propanol	6.72	61.7	22.4	2.36	8.73
	2-Propanol	9.84	51.2	8.73	1.67	6.20
	Acetone	9.65	85.3	54.3	7.22	26.7
④	Methanol	9.00	37.9	6.16	3.44	15.5
	Ethanol	8.26	33.0	6.66	3.31	14.9
	1-Propanol	8.16	68.2	24.1	2.64	11.9
	2-Propanol	9.86	61.0	14.3	2.17	9.77
	Acetone	9.14	85.3	57.7	7.67	34.5

a) ① : PAI-*g*-PDMS (m=13.5), membrane thickness : 210 μ m ② : PAI-*g*-PDMS (m=13.5) / *Silicalite* 30.0 *wt.%, thickness* :400 μ m
③ : PAI-g-PDMS (m=13.5) / Silicalite 40.0 wt.%, thickness : 370 μ m ④ : PAI-*g*-PDMS (m=13.5) / Silicalite 50.0 wt.% , thickness : 450 μ m
b) α : separation factor, J : flux, P : permeability coefficient

acetone through the membranes of PAI-*g*-PDMS and silicalite filled PAI-*g*-PDMS composite were carried out, as summarized in Table 2. As a result, these organic liquids were efficiently concentrated from their dilute aqueous solutions through the membranes with high permeability. In the case of PAI-*g*-PDMS membranes, the separation characteristics of these organic liquids increased with increasing the degree of polymerization of PDMS segment in the copolymers. This would be due to not only the high solubility of the organic solvents on the membrane surface but also the high diffusion through the membrane. Therefore, the silicalite-filled membranes were prepared from PAI-*g*-PDMS (3) in Table 1 to compare the PV properties. As seen in Table 2, the separation characteristics of the silicalite filled PAI-*g*-PDMS composite membranes were higher than those of PAI-*g*-PDMS membranes. Especially, 1-propanol, 2-propanol and acetone were efficiently concentrated from these dilute aqueous organic solutions through the silicalite filled PAI-*g*-PDMS composite membranes. For these solvents, the improvement of the selectivity by adding silicalite would be caused by the increase of the selective sorption of these solvents on silicalite. On the other hand, the separation factors of methanol and ethanol decreased with increasing the content of the silicalite, while the permeability coefficients increased. These results attributed to that the small gaps were formed between the polymer and silicalite domains.

2.3 Gas permeability

Gas permeability coefficients of the PAI-*g*-PDMS membrane was evaluated as listed in Table 3 compared with silicalite filled PAI-*g*-PDMS composite membranes, which was prepared by incorporation of silicalite. It was noticed from this table that the gas permeability coefficients of the PAI-g-PDMS membrane was much higher than the composite membrane containing 30 wt.% of silicalite. These results suggested that the incorporation of silicalite into the membrane decreased the diffusion of permeates in the membrane. On the other hand, the composite membrane containing 50 wt.% of silicalite was remarkably higher than PAI-*g*-PDMS membrane and composite membrane loading 30 wt.% of silicalite. It may be attributed that the composite membrane containing 50 wt.% of silicalite forms small gaps between the polymer and silicalite domains.

Consequently, the permeabilities of the composite membranes were affected by the contents of silicalite,

Table 3 Gas permeabilities of PAI-g-PDMS, PAI-g-PDMS/Silicalite (30 wt.%) and PAI-g-PDMS/Silicalite (50 wt.%) composite membranes.

Membranes	Permeability coefficient (Barrer[a)]) H_2	O_2	N_2	CO_2	CH_4	C_2H_6
PAI-g-PDMS (m=13.5)	469	383	172	2060	560	1539
PAI-g-PDMS/silicalite(30 wt.%)	279	196	87	935	255	639
PAI-g-PDMS/silicalite(50 wt.%)	7336	2519	2662	3859	3664	3079

[a)] 1 Barrer = 10^{-10}cm^3(STP) · cm/cm^2 · s · cmHg.

and the appropriate content of silicalite improved the selectivity in the pervaporation.

3. EXPERIMENTAL

3.1 Synthesis of PDMS-H

Under an argon atmosphere, to a solution of trimethylsilanol (6.25 ml, 56.2 mmol) in 50 ml of dry THF, 35.1 ml of 1.6 M hexane solution of *n*-butyllithium was added. After stirring for 30 min at 0℃, hexamethylcyclotrisiloxane (D_3, 50.5 g, 225 mmol) dissolved in 150 ml of dry THF was added, and the reaction mixture was stirred at room temperature (r.t.) for 1.5 h. Then, dimethylchlorosilane (12.4 ml, 112 mmol) was added in order to terminate the polymerization. The low-molecular-weight substances were removed by heating at 150℃ *in vacuo* for 3 h to afford 42.3 g of PDMS-H as a colorless liquid. Yield: 71.9 %.

^{1}H-NMR δ (400MHz, $CDCl_3$, ppm): 0.02 ((6m+3)H, s), 0.11 (6H, m), 4.63 (1H, m).

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

To a solution of 3,5-dihydroxybenzyl alcohol (5.00 g, 35.7 mmol) in 250 ml of DMF, K_2CO_3 (10.0 g, 72.4 mmol) and *p*-fluoronitrobenzene (11.0 g, 78.0 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 10.5 g of **1** as a pale yellow powder. Yield: 77.0 %

To a solution of **1** (5.00 g, 13.1 mmol) in 25 ml of THF, allyl bromide (15.8 g, 131 mmol) and the solution of NaOH (2.1 g, 52.5 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 (1/20 by volume) to afford 4.87 g of **2** as a yellow solid. Yield: 93.0 %

^{1}H-NMR δ (400MHz, DMSO-d_6, ppm): 4.08 (2H, m), 4.58 (2H, s), 5.22 (2H, m), 5.95 (1H, m), 8.32 (4H, m), 7.09 (1H, s), 7.10 (2H, s), 7.28 (4H, m).

3.3 Synthesis of BAPB-PDMS

PDMS-H (5.62 g, 5.23 mmol) and **2** (2.00g, 5.23 mmol) were mixed in 5.2 ml of dry toluene under an argon atmosphere. To this solution, 5%-Pt/C powder (0.39 g, 0.10 mmol) was added, and the mixture was stirred at 80°C for 6 h. The product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/30 by volume) to afford 5.97 g of **3** as a yellow liquid. Yield: 76.4 %

3 (5.97 g, 5.57 mmol) was dissolved in 30 ml of ethanol, and Pd-C powder (5%, 0.17 g, 0.08mmol) 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, 5.03 g of BAPB-PDMS was obtained as a brown liquid. Yield: 89.3%

^{1}H-NMR, δ (400MHz, $CDCl_3$, ppm): 0.02 ((6m+3)H, s), 0.44 (2H, m), 1.53 (2H, m), 3.30 (2H, t, J=6.84Hz), 4.28 (2H, s), 6.37 (1H, t, J=2.20Hz), 6.40 (2H, d, J=1.95Hz), 6.57 (4H, m), 6.78 (4H, m).

3.4 Preparations of the membranes

Under an argon atmosphere, BAPB-PDMS (4.00 g, 2.80 mmol) and trimellitic anhydride chloride (0.59 g, 2.80 mmol) was dissolved in 8.0 ml of anhydrous NMP. After the solution was stirred for 4 h at r.t., 0.53 ml of acetic anhydride and 0.78 ml of triethylamine were added and it was stirred for 2 h at 80℃. The mixture was poured into excess methanol to precipitate the polymer. The obtained polymer was filtered, dried and dissolved in NMP, and the solution was cast on the Teflon sheet, and the solvent was evaporated over a period of 24 h at 80℃ to form a membrane. Then, the membrane was heated for 2 h at 200℃ *in vacuo*.

The synthesis of silicalite was carried out according to the literature[7]. The polymer solution was cast on the Teflon sheet, followed by the addition of silicalite into the NMP solution. Then, the solvent was evaporated over a period of 24 h at 80°C to form a membrane. Then, the membrane was heated for 2 h at 200°C *in vacuo*.

3.5 Measurements of gas permeability coefficients

Gas permeability was measured using the ordinary vacuum method at 30℃ 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.

3.6 Pervaporation experiments

Pervaporation through the membranes was carried out using a stainless steel cell, which was dipped in a water bath kept at 50℃. The pressure of the downstream side was kept at about 1.0 mmHg. The permeation area of the membrane was 19.6 cm^2. The permeated vapor was trapped in a vessel cooled with liquid N_2, 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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