

SEPARATION PROPERTY OF PERVAPORATION MEMBRANE PREPARED FROM POLYDIMETHYLSILOXANE-GRAFTED POLYIMIDE

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In order to evaluate a durable membrane material, which can be used for the separation of several organic solvents by using pervaporation (PV) technique, the separation characteristics of polydimethylsiloxane (PDMS)-grafted polyimide membrane have been investigated. PDMS-grafted polyimide membrane was prepared by casting the poly(amic acid) solution, which was obtained from polycondensation of 3-(3,5-diaminobenzyloxy)propyl-terminated PDMS macromonomer (DAB-PDMS), 4,4'-oxydianiline with pyromellitic dianhydride, followed by thermal imidation. PDMS-grafted polyimide membranes thus obtained are insoluble in various organic solvents. The obtained membrane exhibited an excellent permselectivity toward several organic solvents, such as acetone, THF, chloroform, and dichloromethane in the PV of their aqueous solutions. For example, 0.9 wt.% aqueous CH_2Cl_2 solution was concentrated to 71.3 wt.%, and the separation factor (α) exceeded 274. Furthermore, PDMS-grafted polyimide could be applied to the separation of organic liquids/methanol mixtures without destruction of the membrane form.

Key words: polydimethylsiloxane, PDMS-grafted polyimide, membrane, durability, pervaporation.

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 materials, 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 that consisted of polyimide main chain and PDMS side chain, the main chain component of which was mechanically strong and insoluble in any organic solvent¹⁾. The obtained 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. In particular, the selective permeation of organic solvent was observed from the mixtures of water and organic solvents, such as alcohols, acetone and THF, through this membrane in the PV permeation.

In this study, in order to obtain the more detailed information for the separation characteristics of this kind of PDMS-grafted polyimide membrane, PV experiments of various mixtures of organic solvents with water and methanol through this membrane were carried out. In particular, we investigated the permselectivity and the durability in the permeations of dilute solutions of chlorine-containing solvents, such as dichloromethane and chloroform. Furthermore, the difference of separation factors or permeability coefficients for each organic solvent was examined by using such a durable

organic-permselective membrane, to discuss the relationship between the permeability and the organic species.

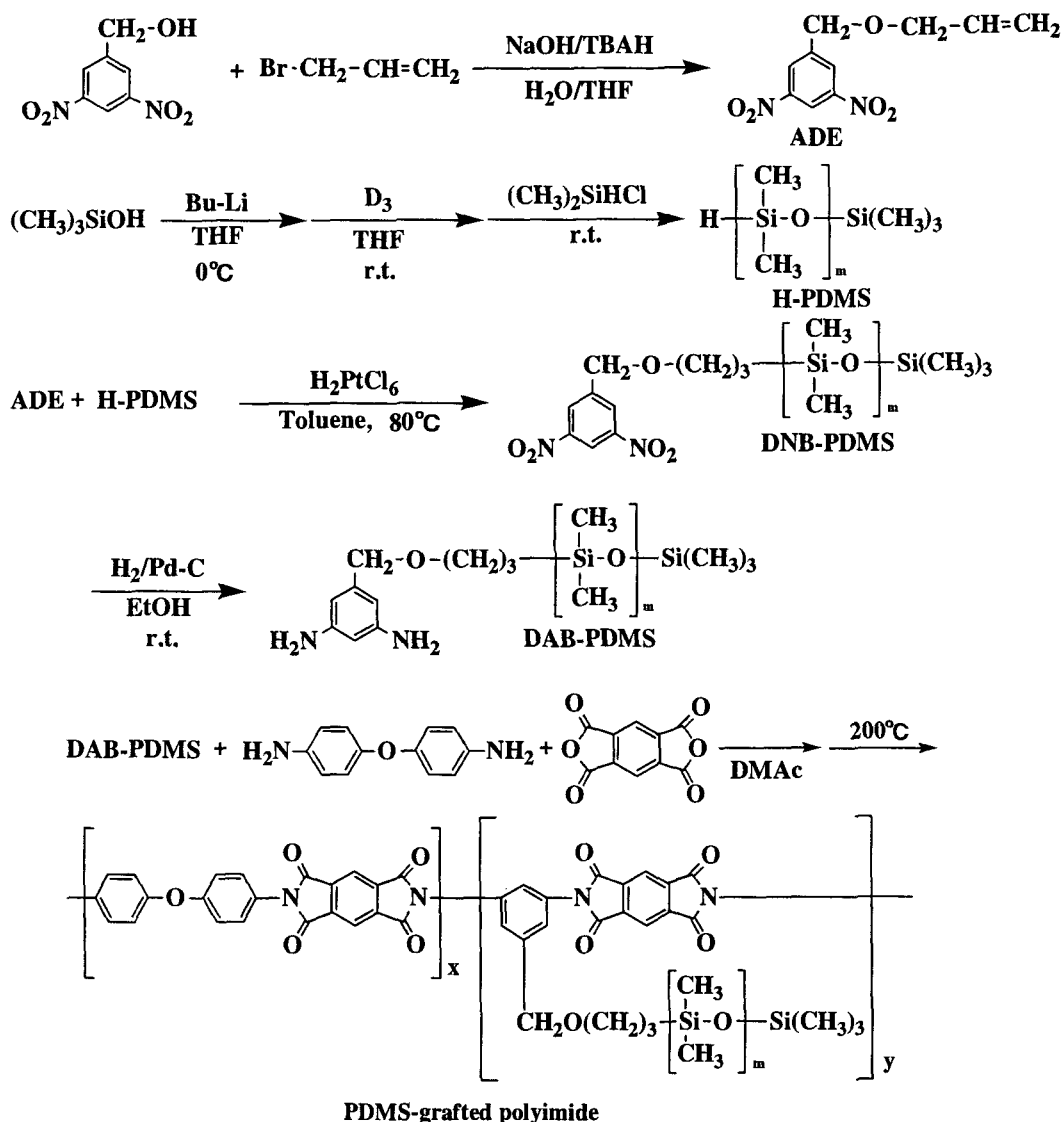
2. EXPERIMENTS

2.1 Preparation of PDMS-grafted polyimide membrane

3-(3,5-diaminobenzyloxy)propyl-terminated PDMS macromonomer (DAB-PDMS)²⁾ (2.0 g, 1.44 mmol) and 4,4'-oxydianiline (0.29 g, 1.44 mmol) was dissolved in 5.0 ml of dry N,N-dimethylacetamide (DMAc) in an argon atmosphere. To this solution, 10 ml of DMAc solution containing pyromellitic dianhydride (0.63 g, 2.88 mmol) was added dropwise, and the mixture was stirred at r.t. for overnight. The solution was spread on a polytetrafluoroethylene sheet, and the solvent was evaporated over a period of 4 days at r.t. Then, the obtained film was heated at 220°C *in vacuo* for 2 h to afford the desired polyimide membrane. The thickness of this membrane was about 100 μm .

2.2 Pervaporation experiment

Sample membranes for the measurement of pervaporation were cut into circular pieces with a diameter of 47 mm. Pervaporation of aqueous organic solutions through the membrane was carried out by the ordinary method using a stainless steel cell, which was dipped in a feed solution kept at 31°C. The pressure of the downstream side was about 5 mmHg. The permeation area of the membrane was 9.6 cm^2 . The permeated vapor was trapped in a vessel cooled with liquid N_2 , and the concentration was determined by gas chromatography. The permeability coefficient, P in $\text{g} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, was calculated from the values of flux and thickness of the membrane. The separation factor, α , which was a measure of the preferential permeation of component A, was also defined as the mass concentration



Scheme 1 Synthesis of PDMS-grafted polyimide.

ratio in the permeate, Y_A/Y_B divided by the mass concentration ratio in feed, X_A/X_B .

3. RESULTS AND DISCUSSION

3.1 Preparation of PDMS-grafted polyimide membrane

The synthetic diagrams of DAB-PDMS and PDMS-grafted polyimide are shown in Scheme 1. PDMS-grafted polyimide membrane was prepared by casting the poly(amic acid) solution obtained from polycondensation of DAB-PDMS, 4,4'-oxydianiline with pyromellitic dianhydride, followed by thermal imidation. The macromonomer, DAB-PDMS, was prepared by hydrosilylation of allyl 3,5-dinitrobenzyl ether with hydrosilyl-terminated polydimethylsiloxane (H-PDMS), followed by catalytic reduction of the two nitro groups, as previously reported². The average degree of polymerization, m , of the PDMS segment of each of H-PDMS, DNB-PDMS and DAB-PDMS is shown in Table 1. In the polycondensation, the equivalent amounts of DAB-PDMS ($m = 18.8$) and 4,4'-oxydianiline were

reacted with pyromellitic dianhydride, as a result, the copolymer composition, x/y , was 50/50 mol%. The PDMS content in the PDMS-grafted polyimide was 70 wt.%, which was calculated from the value of x/y and the molecular weight of the each monomer unit.

3.2 Properties of PDMS-grafted polyimide

The obtained PDMS-grafted polyimide was insoluble in any organic solvents, such as acetone, tetrahydrofuran (THF), dichloromethane, chloroform, benzene, *N,N*-dimethylformamide (DMF), and DMAc. The thermal property of PDMS-grafted polyimide was investigated as compared with polyimide homopolymer, which was prepared by polycondensation of 4,4'-oxydianiline with pyromellitic dianhydride, followed by the similar thermal imidation. For both of polyimides, the glass transition temperature (T_g) was not detected in the range between -150°C and 550°C by differential scanning calorimetry. Fig. 1 shows the thermogravimetric analysis of PDMS-grafted polyimide

and polyimide homopolymer. Polyimide homopolymer was thermally stable, the thermal degradation of which occurred over 500°C. On the contrary, the degradation of PDMS-grafted polyimide started at around 300°C, which would be due to the decomposition of PDMS side chain to produce cyclic siloxane compounds.

In order to investigate the hydrophobicity of the membrane surface, the measurement of contact angle of some solvents on the surface of each polymer membrane was carried out. The values of the contact angle of PDMS-grafted polyimide membrane for water and ethanol were 106° and 18°, respectively. On the other hand, those of polyimide homopolymer membrane for water and ethanol were 96° and 30°, respectively. The contact angles of other organic solvents, such as acetone, THF, chloroform, and dichloromethane, could not be measured, which spread on the membrane in both cases. From these results, it was found that PDMS-grafted polyimide membrane exhibited the higher hydrophobicity than polyimide homopolymer membrane, owing to that its membrane surface would be effectively covered with PDMS side chain.

Table 1 The average degree of polymerization, m , of each polydimethylsiloxane.

Code	m	
	Theo. ^{a)}	Obs. ^{b)}
H-PDMS	15.0	15.3
DNB-PDMS	15.3	19.9
DAB-PDMS	19.9	18.8

- a) The theoretical value of the average degree of polymerization, m , of H-PDMS was calculated from the equation:

$$m = 3 \left(\frac{[D_3]}{[\text{Trimethylsilanol}]} \right) + 1$$
 where the concentrations were those of reagents used in the reaction shown in Scheme 1 to prepare H-PDMS.
- b) Determined by the ratio of proton peaks in the ¹H-NMR spectra.

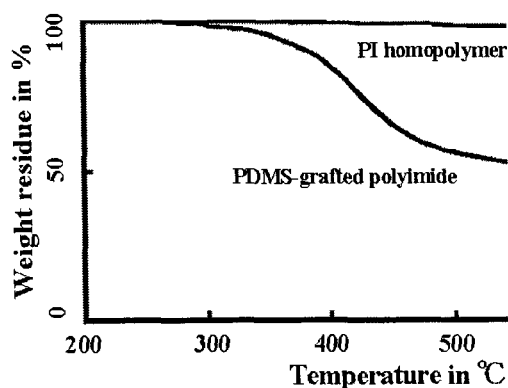


Fig. 1 Thermogravimetry curves for polyimide homopolymer and PDMS-grafted polyimide.

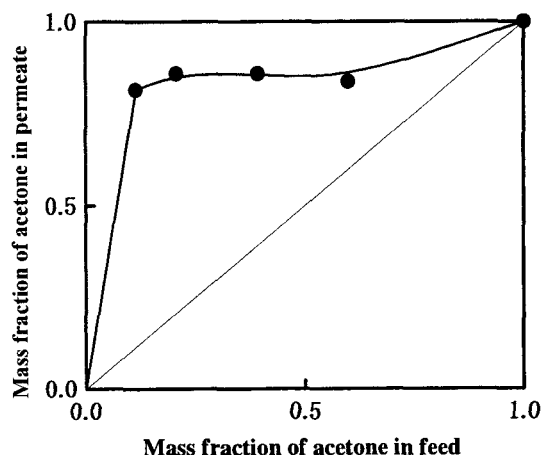


Fig. 2 Permeation composition curves of pervaporation of aqueous acetone solution through the PDMS-grafted polyimide membrane at 31°C.

3.3 Separation characteristic in pervaporation

Fig. 2 shows the permeation composition curves of aqueous acetone solution through the PDMS-grafted polyimide membrane by using the PV technique. The preferential permeation of acetone from its aqueous solution was observed at each composition in the feed. This is one of the evidences that a continuous phase of the PDMS domain is formed in the PDMS-grafted polyimide membrane, and the membrane surface is covered with the hydrophobic PDMS chain.

The typical PV results of dilute aqueous solutions of organic liquids through the PDMS-grafted polyimide membrane are summarized in Table 2, listing with the numerical values of the separation factor, α , and the permeability coefficient, P . Acetone, THF, chloroform, and dichloromethane were used as organic liquids in these experiments. As a result, each organic solvent was efficiently concentrated from their dilute aqueous solutions through the membrane. Such an excellent organic-permeability of this kind of PDMS-grafted membrane would be due to the high solubility of the organic solvents on the membrane surface and the high diffusion through the membrane. In general, the diffusion of water molecule through the polymer membrane must be faster 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 diffusion rates 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.

The PV experiments of methanol solutions containing organic liquids, such as acetone, THF, chloroform and benzene, were also conducted to compare the permeabilities of these organic liquids. By using methanol as a co-solvent, the homogeneous solutions of these organics were prepared even in any

concentration, whereas chloroform and benzene dissolved in water less than 1.0 wt.%. In this experiment, the concentrations of organic liquids were fixed at about 10 wt.%. As shown in Table 3, the selective permeations of acetone, THF, chloroform and benzene were observed rather than methanol through this membrane, which was also durable to the permeation of these mixtures. The order of permeabilities of these solvents was as follows: benzene > THF, acetone, chloroform > methanol. This order is approximate to that of the solubility parameters of these solvents. Therefore, the permselectivity of these organic components through this membrane was mostly affected by the difference of solubility to the membrane surface. The similar PV experiments of several organic mixtures are now in progress to clarify the separation characteristics of this

membrane material in more detail.

In conclusion, it is expected that this PDMS-grafted polyimide membrane can be applied to the separations of not only a dilute aqueous solution of some organic contaminations, but also several organic mixtures to remove or recover one component.

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Table 2 Results of PV experiments of aqueous organic liquid solutions through PDMS-grafted polyimide membrane.

Organic liquid	Composition in wt. %		α ^{a)}	J ^{b)} kg·m ⁻² ·h ⁻¹	P ^{c)} kg·m·m ⁻² ·h ⁻¹
	Feed	Permeate			
Acetone	11.5	81.4	34.2	0.49	9.60 × 10 ⁻⁵
THF	6.9	94.9	251	0.92	2.06 × 10 ⁻⁴
CHCl ₃	0.8 ^{d)}	85.9	755	0.57	1.28 × 10 ⁻⁴
CH ₂ Cl ₂	0.9	71.3	274	0.33	7.40 × 10 ⁻⁵

a) The separation factor, α , calculated according to the following equation:

$\alpha = (X_{\text{Org}}/X_{\text{water}})/(Y_{\text{Org}}/Y_{\text{water}})$, where X_{Org} is the composition of organic liquid in permeate, X_{water} is the composition of water in permeate, Y_{Org} is the composition of organic liquid in feed, and Y_{water} is the composition of water in feed.

b) Total flux of permeates.

c) Permeability coefficient.

d) The saturated concentration of chloroform in water, described in the literature.³⁾

Table 3 Results of PV experiments of methanol solutions containing organic liquids through PDMS-grafted polyimide membrane.

Organic liquid	Composition in wt. %		α ^{a)}	J ^{b)} kg·m ⁻² ·h ⁻¹	P ^{c)} kg·m·m ⁻² ·h ⁻¹
	Feed	Permeate			
Acetone	10.7	20.5	2.15	0.32	6.66 × 10 ⁻⁵
THF	9.9	23.2	2.75	0.42	8.74 × 10 ⁻⁵
CHCl ₃	12.6	41.0	4.82	0.36	7.49 × 10 ⁻⁵
CH ₂ Cl ₂	12.4	24.7	2.32	0.36	7.49 × 10 ⁻⁵

a) The separation factor, α , calculated according to the following equation:

$\alpha = (X_{\text{Org}}/X_{\text{water}})/(Y_{\text{Org}}/Y_{\text{water}})$, where X_{Org} is the composition of organic liquid in permeate, X_{water} is the composition of methanol in permeate, Y_{Org} is the composition of organic liquid in feed, and Y_{water} is the composition of water in feed.

b) Total flux of permeates.

c) Permeability coefficient.