

# Polysiloxaneimide Membranes for Removal of VOCs from Water by Pervaporation

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**ABSTRACT:** For the separation of volatile organic compounds (VOCs) from water by pervaporation, three polysiloxaneimide (PSI) membranes were prepared by polycondensation of three aromatic dianhydrides of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) with a siloxane-containing diamine. The PSI membranes were characterized using <sup>1</sup>H-NMR, ATR/IR, DSC, XRD, and a Rame-Hart goniometer for contact angles. The degrees of sorption and sorption selectivity of the PSI membranes for pure organic compounds and organic aqueous solutions were investigated. The pervaporation properties of the PSI membrane were investigated in connection with the nature of organic aqueous solutions. The effects of feed concentration, feed temperature, permeate pressure, and membrane thickness on pervaporation performance were also investigated. The PSI membranes prepared have high pervaporation selectivity and permeation flux towards hydrophobic organic compounds. The PSI membranes with 150- $\mu$ m thickness exhibit a high pervaporation selectivity of 6000–9000 and a high permeation flux of 0.031–0.047 kg/m<sup>2</sup> h for 0.05 wt % of the toluene/water mixture. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2691–2702, 2000

**Key words:** pervaporation; polysiloxaneimide membrane; VOCs; sorption selectivity; pervaporation selectivity; permeation flux

## INTRODUCTION

Recently, the presence of volatile organic compounds (VOCs) in ground and drinking water has become a serious environmental and economic problem. Pervaporation seems to be a more effective process to solve this problem, compared with the traditional techniques such as steam/air stripping, distillation, liquid extraction, adsorption, and biological treatment,<sup>1–4</sup> because of the attractiveness such as low energy consumption and a simple separation process.

Organic compounds causing environmental problems can be classified into aromatic or aliphatic hydrocarbons, chlorinated hydrocarbons, alcohols, ketones, acetates, and acids.<sup>5</sup> These organic compounds have larger molar volume and more hydrophobic characteristics compared with water. Therefore, the hydrophobic rubbery polymers such as crosslinked polydimethylsiloxane (PDMS), nitrile–butadiene rubber (NBR), polyvinyltrimethylsilane (PVTMS), polytrimethylsilyl propyne (PTMSP), and ethylene–propylene rubber (EPR) are recommended.<sup>6–11</sup> Particularly, PDMS membranes show both a high sorption selectivity and a high permeability towards organic compounds over water. However, they usually

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**Table I Physical Properties of Organic Compounds Used in Sorption**

Organic Compound	Molar Volume (cm <sup>3</sup> /mol)	Vapor Pressure (mmHg) <sup>a</sup>	Solubility in Water (wt %)	Solubility Parameter <sup>b</sup> (MPa) <sup>1/2</sup>
Water (H <sub>2</sub> O)	18.0	23.8	—	47.8
Ethyl alcohol (EtOH)	58.5	58.7	Miscible	26.5
Isopropyl alcohol (IPA)	76.8	42.6	Miscible	23.5
Acetic acid (AA)	57.1	15.3	Miscible	21.4
Acetone (ACE)	74.0	230.0	Miscible	20.0
Methyl ethyl ketone (MEK)	90.1	90.2	27.50	19.0
Ethyl acetate (EA)	98.5	95.4	8.24	18.1
Methylene dichloride (MC)	63.9	435.9	2.00	20.3
Trichloroethylene (TCE)	90.2	74.3	0.11	19.0
Toluene (TOL)	106.8	28.4	0.0067	18.2
Hexane (HX)	131.6	186.0	Immiscible	14.9

<sup>a</sup> Calculated at 25°C from Vapor-Liquid Equilibria data by using the Antoine vapor pressure equation.<sup>17</sup>

<sup>b</sup> Obtained from CRC handbook.<sup>18</sup>

have poor mechanical strength, and the studies to improve their mechanical properties have been carried out by introducing a siloxane-imide block or graft copolymer structure.<sup>12–16</sup> These studies showed that pervaporation selectivity and permeation flux towards organic compounds decreased with decreasing the fraction of the siloxane group. The observation indicates that polysiloxaneimide homopolymer membranes are expected to show good pervaporation performances, but the pervaporation studies with polysiloxaneimides have not been reported yet.

In this article, three polysiloxaneimide membranes were prepared, and the effects of the nature of organic compounds, membrane thickness, and operation conditions on their pervaporation properties were investigated with their physical and sorption properties.

## EXPERIMENTAL

### Reagents

Tetrahydrofuran (THF) and anhydrous 1-methyl-2-pyrrolidinone (NMP) used as polymerization solvents were purchased from the Aldrich Chemical Co. Polydimethylsiloxane (SIDA, average molecular weight; 800) was obtained from the Shinetsu Co. 3,3',4,4'-Benzophenonetetra carboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) were purchased from the Aldrich Chemical Co., and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was received

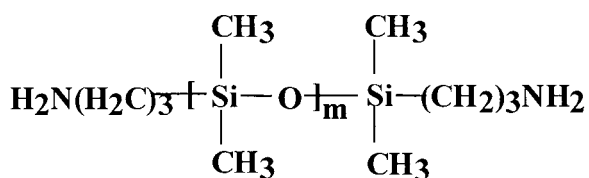
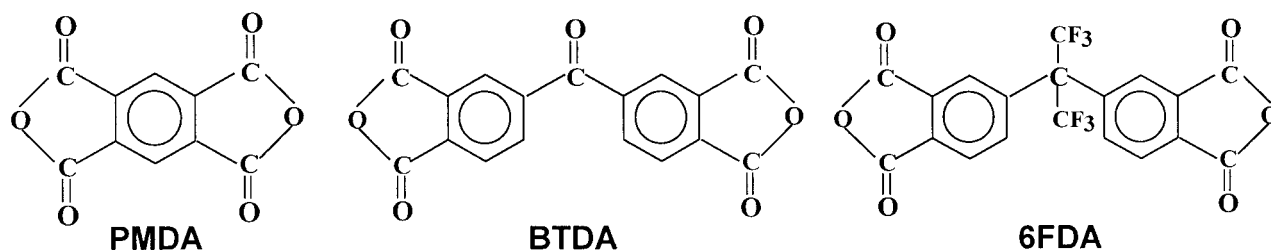
from the Hoechst Co. Before use, BTDA and PMDA were recrystallized by acetic anhydride (Ac<sub>2</sub>O), and 6FDA was dried at 150°C for 24 h in a vacuum oven.

For sorption and pervaporation tests, 10 volatile organic compounds of ethyl alcohol (EtOH), isopropyl alcohol (IPA), acetic acid (AA), acetone (ACE), methyl ethyl ketone (MEK), ethyl acetate (EA), methylene dichloride (MC), trichloroethylene (TCE), toluene (TOL), and hexane (HX) were purchased from the Junsei Chemical Co. as analytical grade. Distilled water was used. Their physical properties are listed in Table I. Going from top to bottom, the solubility of organic compounds in water decreases, i.e., the VOCs become more hydrophobic.

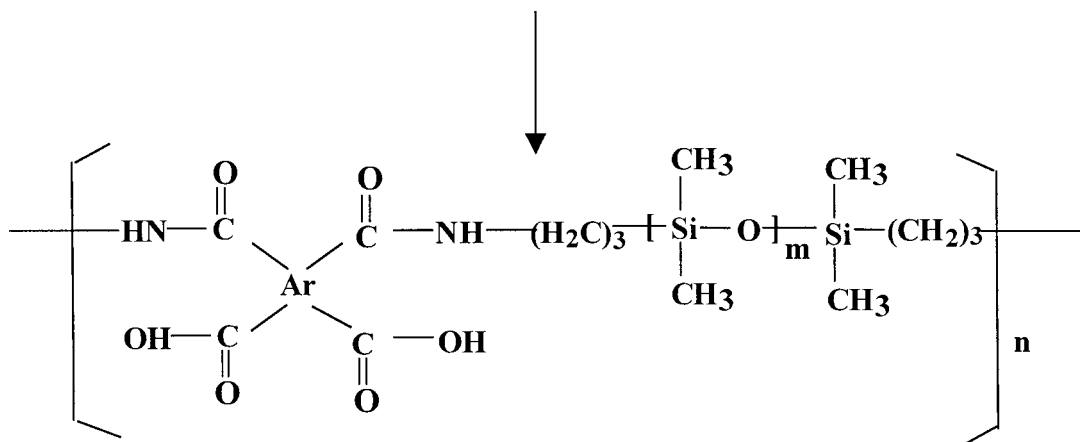
### Preparation of Polysiloxaneimide Membranes

Three series of polysiloxaneimide (PSI) membranes were prepared according to Scheme 1. One-pot imidization and two-pot thermal imidization were used in the preparation of PSI membranes.

In the case of two-pot system, SIDA was dissolved in 30 mL of THF at room temperature for 2 h. After the addition of equimolar amount of three aromatic dianhydrides of 6FDA, BTDA, and PMDA, respectively, the solution was stirred for 20 h to obtain a highly viscous polyamic acid (PAA) as precursor. The reactant content in solution was maintained as 15 wt %. The PAA solution was cast onto a Teflon plate with a predetermined thickness. The plate was completely dried

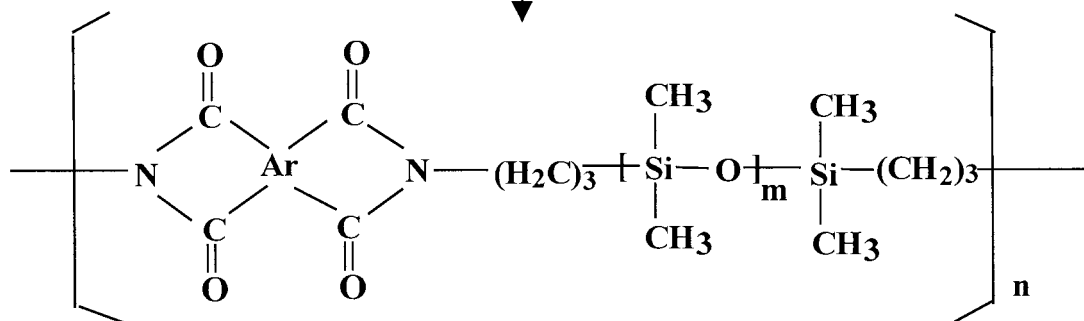


SIDA



Polyamic acid(PAA)

-H<sub>2</sub>O / Imidization



Polysiloxaneimide(PSI)

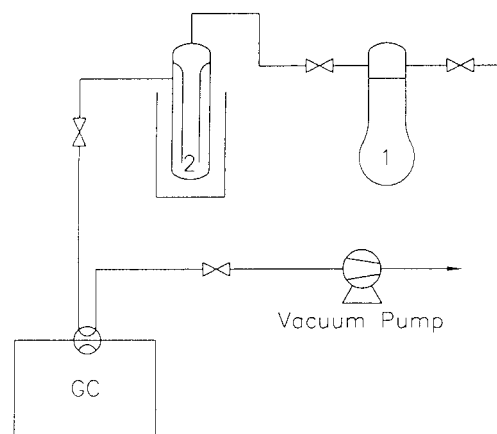
**Scheme 1** Chemical structure of a diamine and three dianhydrides used and synthetic route of the PSI membranes.

at room temperature and then heated at 150°C for 2 h, 200°C for 5 h, and 250°C for 5 h in a vacuum oven. PAA was converted into PSI with a ring closure reaction in the heating process.

In the case of a one-pot system, SIDA and an equimolar amount of dianhydride in 30 mL of THF/NMP (50/50 wt %) cosolvent were stirred for 15 h in a four-necked round flask equipped with a stirrer and a heating system. Then the reflux temperature was increased gradually up to 190°C for 12 h followed by the addition of 10 mL of NMP to the PAA solution. The PSI solution prepared was poured into water with the aid of a homomixer. The precipitated polymers were washed in methanol three times and dried in a vacuum oven. The PSI solution of 10 wt % in THF was cast on a Teflon plate and then dried at elevated temperatures, resulting in the preparation of three series of PSI membranes. The membrane thickness was about 150  $\mu\text{m}$ .

### Measurements of Physical Properties

$^1\text{H-NMR}$  spectrometer (Bruker, DRX300) with tetramethylsilane (TMS) as an internal standard material and an ATR/IR spectrometer (Bio-Rad, Digilab, model FTS-80) were used to monitor the progress of reaction and the degree of imidization. Glass transition temperature ( $T_g$ ) was measured by a Different Scanning Calorimeter (Dupont, Model 910) with a heating rate of 10°C/min in an  $\text{N}_2$  atmosphere. Intrinsic viscosity ( $\eta_{\text{int}}$ ) was measured at 30°C in THF by using a Cannon-Fenske viscometer.<sup>19</sup> The value of d-spacing ( $d$ ) of the membrane was examined by an X-ray diffractometer (model D/MAX IIIB Rigaku) with a wavelength ( $\lambda$ ) of 1.54 Å using Bragg's equation ( $n\lambda = 2d \sin \theta$ ). Density of the polymer was studied with the buoyancy technique. The fractional free volume (FFV) was calculated from the density ( $\rho$ ) and van der Waals volume ( $V_w$ ) estimated by the group contribution theory of Van Krevelen and Bondi.<sup>20</sup> Surface free energy was calculated from the Young-Wu equation with the contact angle data measured by sessile drop method on a Ramehart goniometer (Erma Model G-1) using water and methylene iodide as contacting liquids.<sup>21,22</sup> Total surface free energy ( $\gamma^t$ ) is the sum of the dispersion component ( $\gamma^d$ ) and the polar component ( $\gamma^p$ ). The solubility of PSI membranes was measured by immersing in organic compounds at 30°C or elevated temperatures for 48 h.



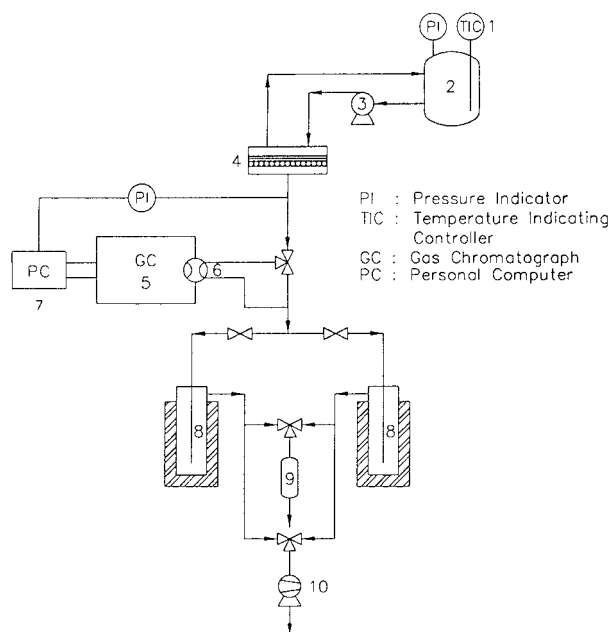
**Figure 1** Schematic diagram of preferential sorption apparatus. 1. Feed tank; 2. cold trap.

### Sorption Experiments

The degree of sorption of PSI membranes for pure organic compounds listed in Table I was obtained as follows. The PSI membrane was immersed in the organic solvents. After the membrane reached an equilibrium state of swelling in a pure organic compound, the membrane was removed from the organic compound. The organic compound on the membrane surface was carefully removed using tissue paper, and the membrane was weighed. After it was dried at 200°C in a vacuum oven, it was weighed again to obtain the sorption amount of the organic compounds in the membrane. The degree of sorption for a pure organic compound,  $\Phi_p$  (wt %), is calculated from the following equation:

$$\Phi_p(\text{wt } \%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

To measure the sorption selectivity and degree of sorption for organic aqueous solutions, the PSI membrane was immersed in aqueous solution containing 0.05 wt % of organic compound at room temperature for 1 week. The schematic diagram of the sorption apparatus is shown in Figure 1. The swollen membrane was weighed, and introduced into trap 1. Trap 1 was heated up to 200°C to evaporate the organic compound in the swollen membrane. The evaporated organic compound from trap 1 was collected in trap 2 with liquid nitrogen. The composition of the condensed liquid mixture in trap 2 was analyzed with an on-line gas chromatog-



**Figure 2** Schematic representation of pervaporation apparatus: 1. temperature indicating controller; 2. feed tank; 3. feed pump; 4. membrane cell; 5. GC; 6. sampling valve; 7. PC; 8. cold trap; 9. vent to atmosphere; 10. vacuum pump.

raphy (GC) connected to trap 2. The sorption selectivity,  $\alpha_{o/w}^s$ , is defined by

$$\alpha_{o/w}^s = \frac{M_o/M_w}{X_o/X_w}$$

where  $M_o$  and  $M_w$  are the weight fractions of the organic compound and water in the membrane, and  $X_o$  and  $X_w$  are those in the feed, respectively.

Their degree of sorption,  $S^m$ , for the organic aqueous solution is calculated from the following equation:

$$S^m(\text{wt } \%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  represent the weights of a dry membrane and a swollen membrane, respectively.

### Pervaporation Experiments

A schematic diagram of the pervaporation apparatus is shown in Figure 2. The composition of the permeate was analyzed by an on-line GC with a TCD detector and a column of Porapak R.

Feed solution in a reservoir was maintained at a constant temperature with an electronic temperature controller. The effective area of membrane in contact with the feed was 13.85 cm<sup>2</sup>, and the pressure at the permeate side was measured with a pressure transducer and maintained at 1–2 mmHg by a vacuum pump. After the permeate pressure was reached to a steady state (about 2–4 h was needed), the permeate vapor was collected in a cold trap with liquid nitrogen for about 3 h. The amount and the composition of the condensed permeate were measured.

The total permeation flux,  $J$ , is calculated from the equation:

$$J(\text{kg/m}^2 \text{ h}) = Q/(A \times T)$$

where  $Q$ (kg) is the total amount of permeate collected through the effective area of the membrane,  $A$ (m<sup>2</sup>), during the experimental time,  $T$ (h), and after the steady state.

The pervaporation selectivity,  $\alpha_{o/w}^p$ , is determined according to the following equation:

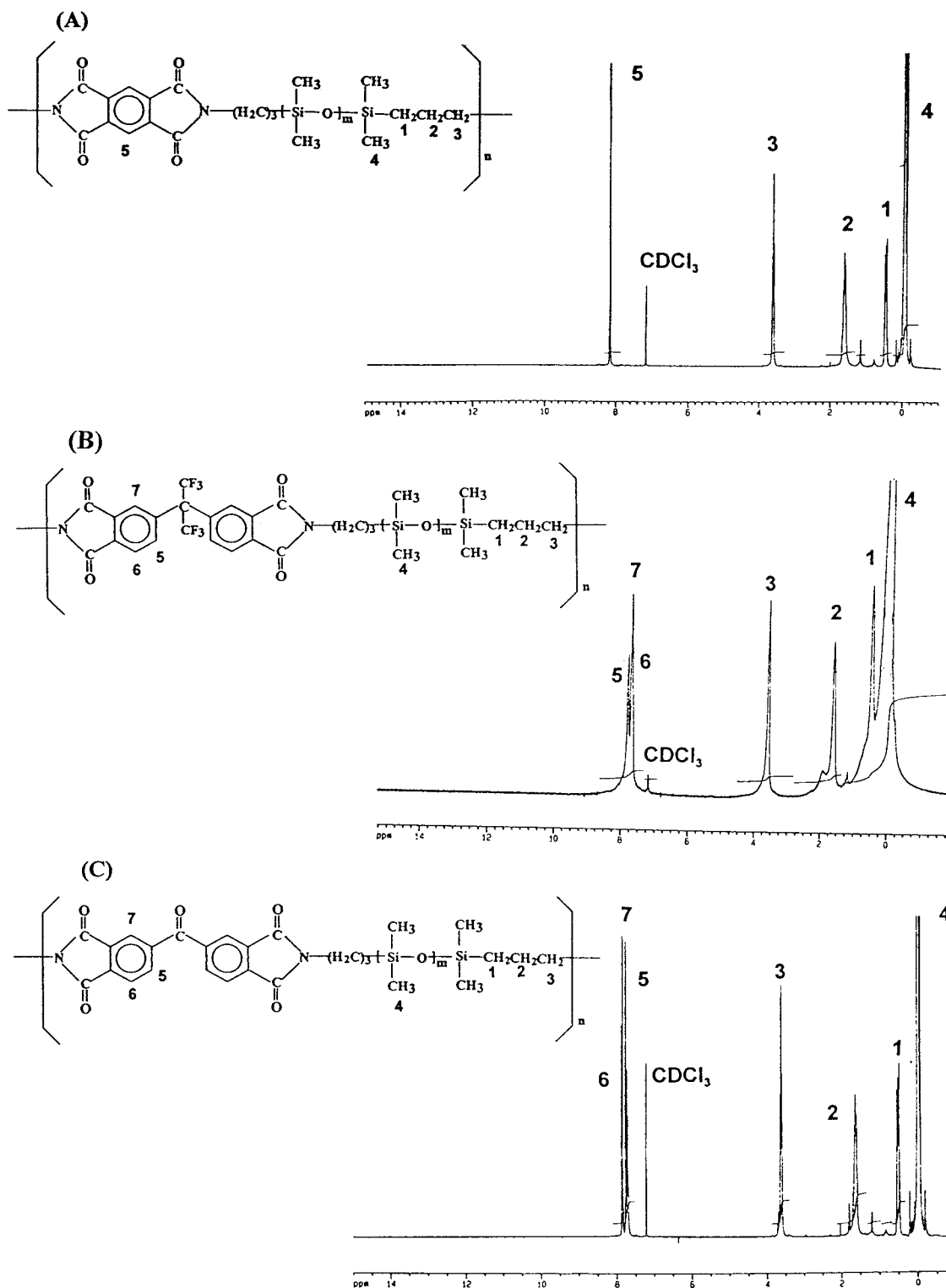
$$\alpha_{o/w}^p = \frac{Y_o/Y_w}{X_o/X_w}$$

where  $Y_o$  and  $Y_w$  represent the weight fractions of organic compound and water in the permeate, and  $X_o$  and  $X_w$  represent those in the feed, respectively.

## RESULTS AND DISCUSSION

### Preparation of Polysiloxaneimide Membranes

The structures of the PSI membranes prepared were characterized by <sup>1</sup>H-NMR, and the spectra are shown in Figure 3. In the spectra, the peak of the protons of —Si(CH<sub>3</sub>)<sub>2</sub>O— unit appears at near 0 ppm and the peaks of three protons of the propyl group are shown in the range of 0–4 ppm. Moreover, the peaks of protons of aromatic dianhydrides of 6FDA, BTDA, and PMDA were observed in 6–10 ppm, respectively. The peak of amide proton cannot be observed in the wide range of 10–14 ppm, indicating that the imidization was completely done. The ATR/IR spectra show the characteristic peaks of the PSI membranes. The absorption peaks of the imide ring are shown at 1780 cm<sup>-1</sup> (carbonyl group, symmetric stretching) and 1718 cm<sup>-1</sup> (carbonyl group, asymmetric



**Figure 3**  $^1\text{H-NMR}$  spectra of the PSI membranes: (A) PMDA-SIDA; (B) 6FDA-SIDA; (C) BTDA-SIDA.

stretching). The peaks of C—N stretching,  $-\text{Si}(\text{CH}_3)_2-$ , and  $-(\text{Si}-\text{O})_n-$  units are observed at  $1396\text{ cm}^{-1}$ ,  $1250\text{ cm}^{-1}$ , and  $1015\text{ cm}^{-1}$ ,

respectively. The two characteristic peaks of amide absorption cannot be observed at  $1650\text{ cm}^{-1}$  (amide I) and  $1545\text{ cm}^{-1}$  (amide II), which

**Table II Intrinsic Viscosities and Glass Transition Temperatures of the PSI Membranes**

Monomer Pair (Dianhydride-Diamine)	Molecular Weight of Repeating Unit (Dalton)	[ $\eta$ ] <sup>a</sup> (dL/g)	$T_g$ (°C)	
			$T_g^1$	$T_g^2$
6FDA-SIDA	1208.21	0.82	-118	-5.40
BTDA-SIDA	1086.20	0.69	-115	13.15 -3.75
PMDA-SIDA	982.09	0.65	-110	

<sup>a</sup> Intrinsic viscosity ( $\eta_{int}$ ) measured in 0.5 g/dL THF solution at 30°C using the equation:  $\eta_{int} = \frac{\sqrt{2}(\eta_{sp} - \ln \eta_{rel})}{C}$

also confirms that PAAs are completely converted to PSIs.

### Physical Properties of Polysiloxaneimide Membranes

The intrinsic viscosities and glass transition temperature ( $T_g$ )s of the PSI membranes are summarized in Table II. The values of intrinsic viscosities of all the PSI membranes are higher than 0.65 dL/g, which indicates that they have enough molecular weight to be used as a pervaporation membrane. The PSI membranes exhibit two  $T_g$ s below room temperature like siloxane-imide copolymers, which was observed in a previous study.<sup>23</sup> The first  $T_g$ s, in the range of -120 to -110°C, are related to the soft siloxane chain portion, and the second  $T_g$ s in the range of -10 to

15°C are related to the hard imide ring portion. The first  $T_g$ s, which might be affected by the hard imide ring portion, are somewhat higher than that of crosslinked polydimethylsiloxane (-123°C). The PSI membranes showed thermo-plastic elastomeric characteristics with weak mechanical strength, resulting from the segregation of siloxane chains and aromatic imide segments.

Surface free energies, densities, FFVs, and d-spacings of the PSI membranes are presented in Table III. The PSI membranes prepared show very low surface free energies in the order of BTDA-SIDA > 6FDA-SIDA > PMDA-SIDA. The low surface free energy of PMDA-SIDA may be explained in terms of a high siloxane content with a low surface free energy.

The BTDA-SIDA membrane exhibits higher surface free energy compared with the other two membranes, which may be attributed to a polar carbonyl group of BTDA. The PSI membranes with flexible chains of siloxane groups have low densities. The highest density of 6FDA-SIDA is due to high fluorine content. The PSI membranes show high values of FFV. The FFV of 6FDA-SIDA is the highest among three polymers. 6FDA-SIDA has 30.78 wt % of siloxane content and 9.43 wt % of fluorine content, which enhance FFV by lowering surface free energy and cohesive energy.

The solubilities of the PSI membranes observed in various organic compounds are summarized in Table IV. Three PSI membranes of PMDA-SIDA, 6FDA-SIDA, and BTDA-SIDA, prepared by the one-pot system, are soluble in

**Table III Surface Free Energies, Densities, Fractional Free Volumes, and d-Spacings of the PSI Membranes**

Monomer Pair (Dianhydride-Diamine)	Siloxane Content (wt %)	Surface Energy <sup>a</sup> (dyne/cm)			Density ( $\rho$ ) <sup>b</sup> (g/cm <sup>3</sup> )	Fractional Free Volume (FFV) <sup>c</sup>	d-Spacing (Å)
		$\gamma^d$	$\gamma^p$	$\gamma^t$			
	30.78						
	Fluorine Content						
6FDA-SIDA	(wt %) : 9.43	18.05	0.04	18.09	1.093	0.190	8.813
BTDA-SIDA	34.24	22.18	0.43	22.61	1.062	0.168	6.573
PMDA-SIDA	37.87	16.44	0.06	16.50	1.041	0.174	7.169

<sup>a</sup> Calculated from the Young-Wu equation.

<sup>b</sup> Determined by buoyancy method at 25°C:  $\rho = [W(a) \cdot \rho(f)] / [W(a) - W(f)]$ ;  $\rho$ : specific gravity of the solid;  $\rho(f)$ : density of the liquid;  $W(a)$ : weight of the solid in air;  $W(f)$ : weight of the solid in liquid.

<sup>c</sup> Calculated from the equation  $\left(\frac{V - V_o}{V}\right)$  and group contribution method by Bondi and van Krevelen;  $V$ : the specific molar volume at temperature;  $V_o$ : the molar volume occupied by the molecules at 0 K per mol of repeating unit of the polymer.

**Table IV Solubility of the PSI Membrane for Organic Compounds**

Monomer Pair (Dianhydride-Diamine)	Solubility <sup>a</sup> in Organic Compounds											
	NMP	DMA	DMSO	IPA	AA	THF	ACE	MEK	EA	CF	MC	TOL
6FDA-SIDA	±	±	±	-	-	++	++	++	++	++	++	++
BTDA-SIDA (two-pot system)	-	-	-	-	-	-	-	-	-	-	-	-
BTDA-SIDA (one-pot system)	±	±	±	-	-	++	++	++	++	++	++	++
PMDA-SIDA	±	±	±	-	-	++	++	++	++	++	++	++

<sup>a</sup> Solubility: (++) soluble at room temperature; (±) swelling at room temperature; (-) insoluble even on heating.

\* Abbreviations: NMP (1-methyl-2-pyrrolidinone), DMA (*N,N*-dimethylacetamide), DMSO (dimethyl sulfoxide), IPA (isopropyl alcohol), AA (acetic acid), THF (tetrahydrofuran), ACE (acetone), MEK (methyl ethyl ketone), CF (chloroform), EA (ethyl acetate), MC (methylene dichloride), TOL (toluene).

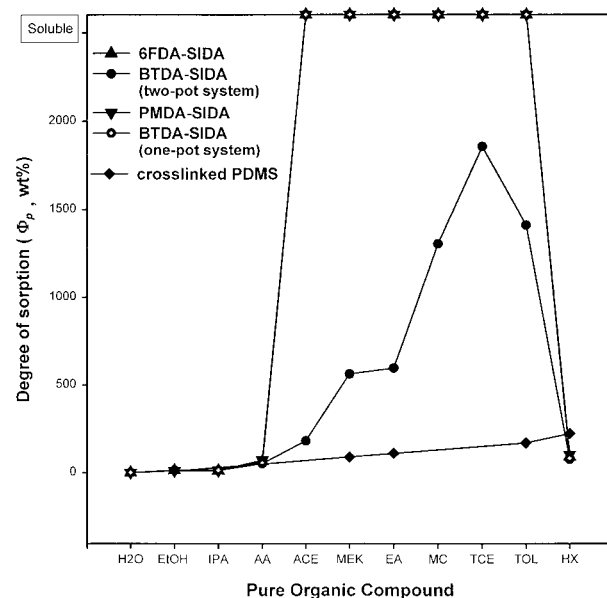
organic compounds such as THF, ACE, MEK, EA, CF, MC, and TOL. The PSI membranes seem to have better affinity toward more hydrophobic organic compounds. BTDA-SIDA membrane prepared by thermal imidization (two-pot system) is insoluble in all the organic compounds used, which is due to the crosslinking between radicals of the methyl group of SIDA and carbonyl group (C=O) of BTDA during the heat treatment in preparing the BTDA-SIDA membrane by a two-pot system.<sup>24</sup> The BTDA-SIDA membrane prepared by the two-pot system swells in the good solvents such as MC, TCE, and TOL because of the crosslinking.

### Sorption and Sorption Selectivity

The degrees of sorption of 10 organic compounds measured for the PSI membranes are shown in Figure 4, where the order of organic compounds in the X-axis is based on the solubility of organic compounds in water in Table I. Because 6FDA-SIDA, PMDA-SIDA, and BTDA-SIDA prepared by the one-pot system are soluble in ACE, MEK, EA, MC, TCE, and TOL, it is difficult to investigate the trend of degree of sorption as a function of the hydrophobicity of the organic compound using 6FDA-SIDA, PMDA-SIDA, and BTDA-SIDA prepared by the one-pot system. To investigate the sorption behavior of the above organic compounds in PSI membranes, BTDA-SIDA prepared by the two-pot system was used for the sorption test, because it is not soluble in the organic compounds. The degree of sorption for BTDA-SIDA prepared by the two-pot system tends to increase with the hydrophobicity of organic compounds, and the degree of sorption of TCE is

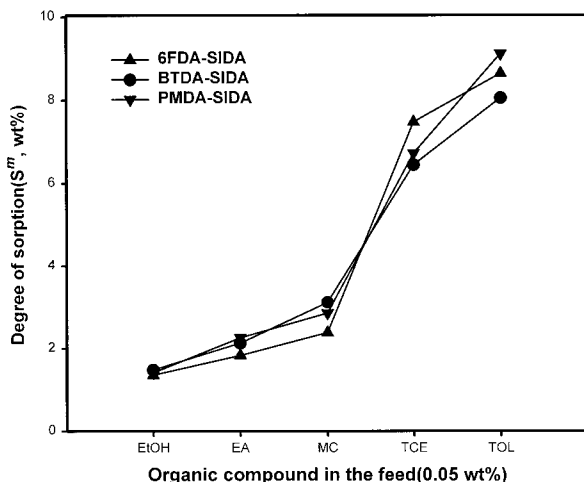
found to be the highest (about 1800 wt %). In Figure 4, the degree of sorption for the crosslinked PDMS membranes<sup>25-28</sup> is also shown, and compared with that of BTDA-SIDA prepared by the two-pot system. The degree of sorption for the crosslinked PDMS membranes increases gradually with the hydrophobicity of the organic compounds. The PSI membranes have a relatively low affinity for HX compared with the crosslinked PDMS membranes. This may be due to the polar imide ring having a weak interaction with the nonpolar HX.

The degrees of sorption and sorption selectivities of 0.05 wt % of the five organic aqueous solu-



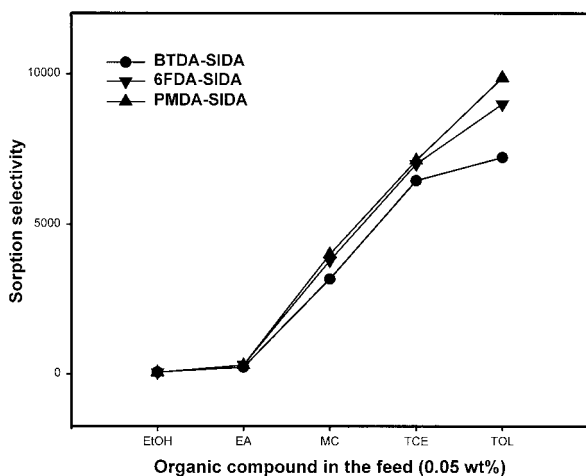
**Figure 4** Degree of sorption of the PSI membranes for pure organic compounds at room temperature.



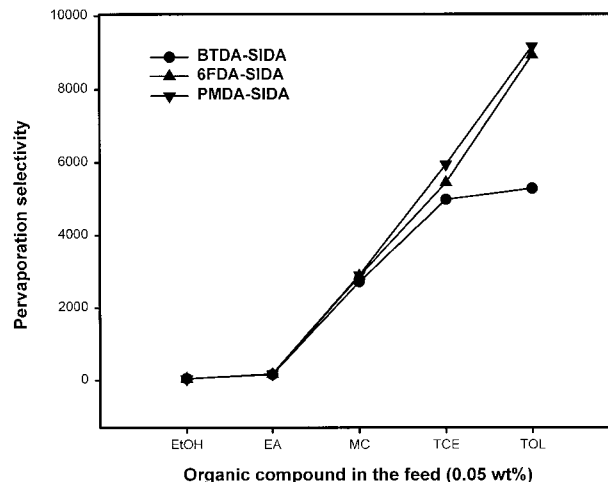


**Figure 5** Degree of sorption of the PSI membranes for 0.05 wt % of organic aqueous solutions at room temperature.

tions of EtOH, EA, MC, TCE, and TOL for the PSI membranes were investigated, and are shown in Figures 5 and 6, respectively. Both the degrees of sorption and sorption selectivity increase with the hydrophobicity of organic compounds from EtOH to TOL. The degree of sorption and sorption selectivity of hydrophilic organic compounds such as EtOH and EA are very low. The sorption of hydrophilic organic compounds for the PSI membranes seems to be severely restricted by their strong interaction with water, i.e., coupling effect. The sorption selectivity increases in the following order: BTDA-SIDA < 6FDA-SIDA < PMDA-



**Figure 6** Sorption selectivity of the PSI membranes for 0.05 wt % of organic aqueous solutions at room temperature.

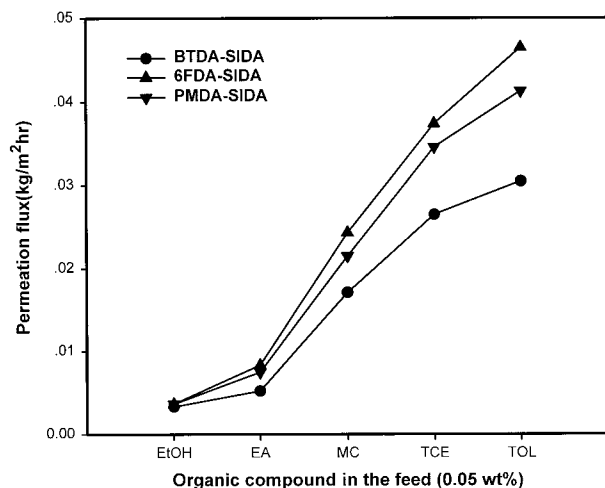


**Figure 7** Pervaporation selectivity of the PSI membranes for 0.05 wt % of organic aqueous solutions at 30°C.

SIDA, which relates with the decreasing order of their surface free energy (Table III). The surface free energy of the membrane may be an important variable for sorption. Interestingly, the degree of sorption and sorption selectivity show the maximum values for the TOL/water mixture, not for the TCE solution exhibiting the highest degree of sorption of pure organic compounds. This result indicates that the sorption selectivity is governed by the combined interactions between the membrane, organic compound, and water.

#### Pervaporation Performances of Polysiloxaneimide Membranes

The pervaporation experiments were carried out with five organic aqueous solutions used in the sorption tests. The concentration of organic compound was 0.05 wt %, and the temperature of the feed solution was maintained at 30°C. The pervaporation selectivity and permeation flux of the PSI membranes of BTDA-SIDA, 6FDA-SIDA, and PMDA-SIDA are shown in Figures 7 and 8, respectively. The pervaporation selectivity and permeation flux for organic aqueous solutions become higher as the organic compound becomes more hydrophobic from EtOH to TOL. These observations may be explained as follows. As more hydrophobic organic compounds such as TOL has a stronger interaction with the PSI membrane, it is preferentially sorbed into the membranes and makes the membrane swell higher. This enhances FFV of the membrane and reduces diffusion resistance. On the contrary, as more hydrophilic



**Figure 8** Permeation flux of the PSI membranes for 0.05 wt % of organic aqueous solutions at 30°C.

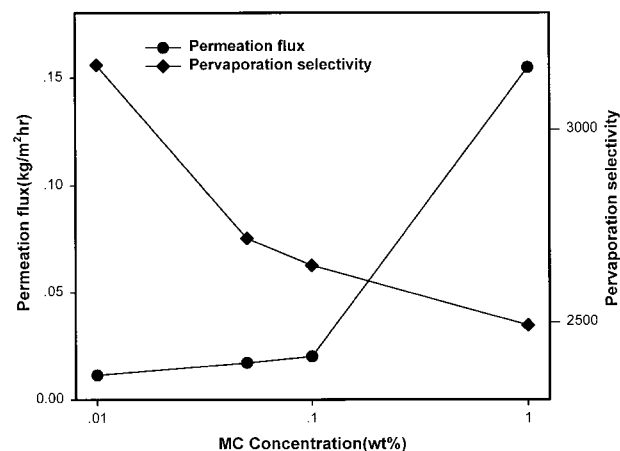
organic compounds such as EtOH has a poorer interaction with the PSI membrane and a stronger affinity for water, it is less sorbed into the membrane and makes the membrane stiffer. This lowers pervaporation selectivity and permeation flux. The pervaporation selectivity toward organic compounds becomes higher in the following order as: BTDA-SIDA < 6FDA-SIDA  $\approx$  PMDA-SIDA. As shown in Figure 8, the permeation flux decreases in the following order as: 6FDA-SIDA > PMDA-SIDA > BTDA-SIDA. Although 6FDA-SIDA membrane has relatively lower sorption selectivity than the PMDA-SIDA membrane, it exhibits the highest permeation flux. This is thought to be related to high FFV and d-spacing. The PSI membranes of BTDA-SIDA, 6FDA-SIDA, and PMDA-SIDA with 150  $\mu\text{m}$  thickness exhibit high pervaporation selectivities of 4980, 5450, and 5950, and the permeation flux of 0.027, 0.038, and 0.034, respectively, for 0.05 wt % of the TCE/water mixture. For 0.05 wt % of the TOL/water mixture, the pervaporation selectivity and permeation flux of the PMDA-SIDA membrane are 9170 and 0.042  $\text{kg/m}^2\text{h}$ , respectively, and those of 6FDA-SIDA membrane are 8930 and 0.048  $\text{kg/m}^2\text{h}$ , respectively. These results suggest that the PSI membranes could be used as membrane materials suitable for the separation of VOCs from water.

#### Effect of Operation Conditions

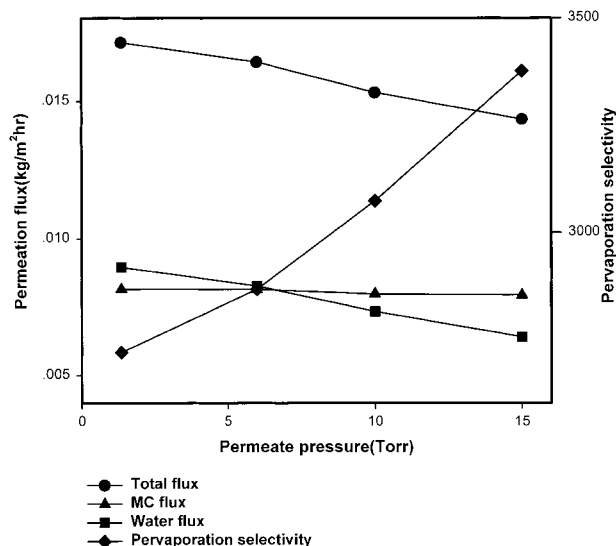
Figure 9 shows the effect of MC concentration in the range of 0.01–1.0 wt % on pervaporation selectivity and permeation flux of BTDA-SIDA

membrane. As the concentration of MC increases, pervaporation selectivity decreases, but permeation flux increases. The surface free energy of MC (27.2 dyne/cm) is much lower than that of water (72 dyne/cm), and that of the BTDA-SIDA membrane is 22.6 dyne/cm. Therefore, MC is preferentially sorbed into the membrane and water is repelled. The amount of MC sorbed into the membrane increases with increasing the concentration of MC. Accordingly, the membrane becomes more plasticized and swelled by a strong interaction with MC, and the hydrophobicity of the swelled membrane decreases. As a result, water diffuses easily into the MC-swelled membrane, and water uptake in the membrane is enhanced. Thus, pervaporation selectivity decreases, while permeation flux increases.

The pervaporation performance of the BTDA-SIDA membrane for 0.05 wt % of MC/water mixture at 30°C was investigated as a function of permeate pressure, and is illustrated in Figure 10. As the permeate pressure increases from 1.35 to 15 Torr, pervaporation selectivity increases linearly and permeation flux decreases slightly. This may be explained by the difference of saturated vapor pressures. The saturated vapor pressure of MC is 430 mmHg, whereas that of water is 23.7 mmHg. As the permeation pressure increases, the desorption resistance of MC at the permeate side increases slightly with permeate pressure. However, the desorption resistance of water at the permeate side increases largely with increasing permeate pressure. The MC flux is nearly invariant, but water flux decreases linearly with the permeate pressure. Therefore, the pervaporation



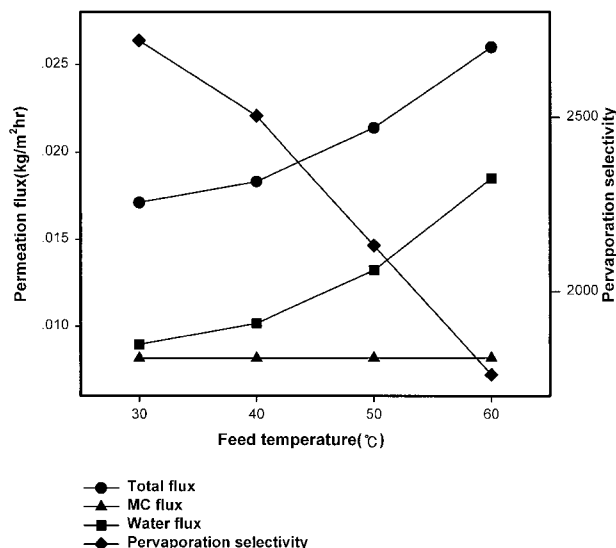
**Figure 9** Effect of the concentration of organic compound on permeation flux and pervaporation selectivity of BTDA-SIDA membrane at 30°C.



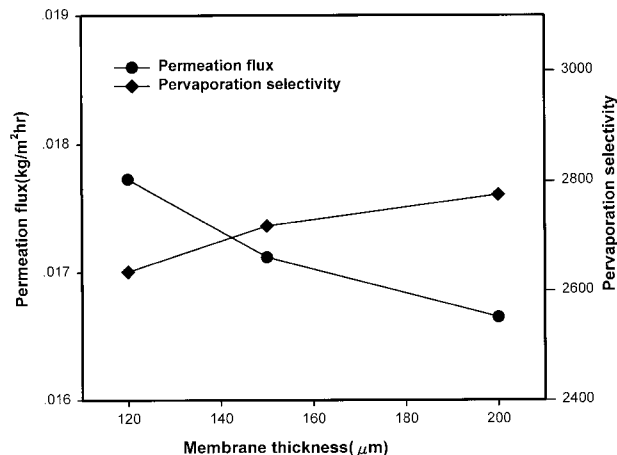
**Figure 10** Effect of permeate pressure on permeation flux and pervaporation selectivity of BTDA-SIDA membrane at 30°C.

selectivity increases, but the permeation flux decreases.

The effect of feed temperature on pervaporation performance of BTDA-SIDA membrane for 0.05 wt % of MC/water mixture is illustrated in Figure 11. The feed temperature varied from 30 to 60°C. As the feed temperature increases, the mobility of polymer chains and the activity of MC increase. The extended mobility of polymeric



**Figure 11** Effect of feed temperature on permeation flux and pervaporation selectivity of BTDA-SIDA membrane.



**Figure 12** Effect of membrane thickness on permeation flux and pervaporation selectivity of BTDA-SIDA membrane at 30°C.

membrane reduces the diffusion resistance towards MC, and the entropy of mixing increases. Accordingly, the permeation flux increases, but pervaporation selectivity decreases.

The effect of membrane thickness on pervaporation performance of the BTDA-SIDA membrane for 0.05 wt % of MC/water mixture is illustrated in Figure 12. As expected, the permeation flux decreases with increasing membrane thickness, while pervaporation selectivity increases slightly.

**CONCLUSIONS**

Three PSI membranes of BTDA-SIDA, 6FDA-SIDA, and PMDA-SIDA were prepared by polycondensation of a SIDA of an  $M_w$  of 800 with three dianhydrides of 6FDA, BTDA, and PMDA. <sup>1</sup>H-NMR and ATR/IR confirm that the PSI membranes fully imidized were successfully synthesized. These membranes show low  $T_{g,s}$  below room temperature, low densities, high FFVs, high d-spacing, and low surface free energy. The PSI membranes exhibited high sorption and sorption selectivity for more hydrophobic organic compounds. With increasing hydrophobicity of organic compound, both pervaporation selectivity and permeation flux increase. The pervaporation properties of the membranes were governed by feed concentration of organic compound, feed temperature, permeate pressure, and membrane thickness. The PSI membranes with 150 μm thickness exhibit a high pervaporation selectivity

of 6000–9000 and a high permeation flux of 0.031–0.047 kg/m<sup>2</sup>h for 0.05 wt % of the toluene/water mixture.

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