Preparation and Pervaporation Performance of 3,3-Bis[4-(4-aminophenoxy)phenyl] Phthalide Based Polyimide Membranes

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ABSTRACT: A series of novel solvent-soluble polyimides based on the diamine of 3,3-bis[4-(4-aminophenoxy)phenyl] phthalide (BAPP) were prepared. The effects of the dianhydride structures on the pervaporation performance of aqueous alcohol mixtures through these polyimide membranes were studied. The BAPP-based polyimide membranes exhibited water permselectivity during all process runs. The permeation rate increased with the addition of bulky groups to the polyimide backbone. The effects of the feed solution concentration, feed solution temperature, and carbon atom number of the feed alcohol on the pervaporation performance were also investigated systematically. Optimum pervaporation results, a separation factor of 22 and a permeation rate of 270 g/m^2 h, were obtained for a 90 wt % feed aqueous ethanol solution through a 3,3′,4,4′-biphenyl tetracarboxylic dianhydride polyimide membrane at 25°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2046–2052, 2005

Key words: membranes; polyimides; separation techniques

INTRODUCTION

More and more liquid mixtures, such as close-boiling-point and azeotropic mixtures, cannot be separated or concentrated by traditional separation processes. For example, an ethanol/water mixture is produced by fermentation, and then separation is more economically beneficial. Specifically, the separation of a ethanol/water mixture is difficult with a conventional distillation process. Because ethanol/water is an azeotropic mixture when the ethanol content is 95.6 wt % and some component is destroyed at a high temperature, much attention has been paid to membrane separation processes for the separation and concentration of such liquid mixtures. A pervaporation separation process offers potentially more economical alternatives for the separation of azeotropic mixtures, isomers, and heat-sensitive mixtures.[1–3] Basically, pervaporation involves passing a mixture solution through a dense membrane by a solution–diffusion mechanism.[4] For the solution–diffusion mechanism, the permselectivity of the membrane must be attributable to the solubility of the solvent toward the membrane and the diffusivity of the mixture in the membrane. For this reason, the development of novel membranes for the separation of aqueous ethanol solutions has attracted more attention.

In the past, hydrophilic polymers such as polyacrylic acid (PAA), poly(vinyl alcohol), sodium alginate, and chitosan were first considered for fabricating pervaporation membranes to separate alcohol mixtures.[5–10] However, excessive swelling lowered the separation factor during the pervaporation separation process. Therefore, polymer crosslinking and grafting were used to modify the polymer structure and improve the pervaporation performance.[11–13] Polyimides (PIs) possess good chemical resistance, mechanical properties, and thermal stability, and so the development of novel PI pervaporation membranes with good separation performance is exceedingly important. There are many PIs used in membrane separation processes such as gas separation and pervaporation.[14–17] Most of the research uses the solvent resistance of PIs to separate aromatic/aliphatic hydrocarbon mixtures[18–20] and organic/water mixtures.[14] The main reason is that some functional groups of PIs have an affinity for aromatic hydrocarbons and can improve the separation properties. In addition, the permeation rate varies when PIs are added with different bulky groups to produce large free volumes.[21]

In this study, a series of solvent-soluble PIs based on the novel and bulky diamine of 3,3-bis[4-(4-aminophenoxy)phenyl] phthalide (BAPP) were prepared. The

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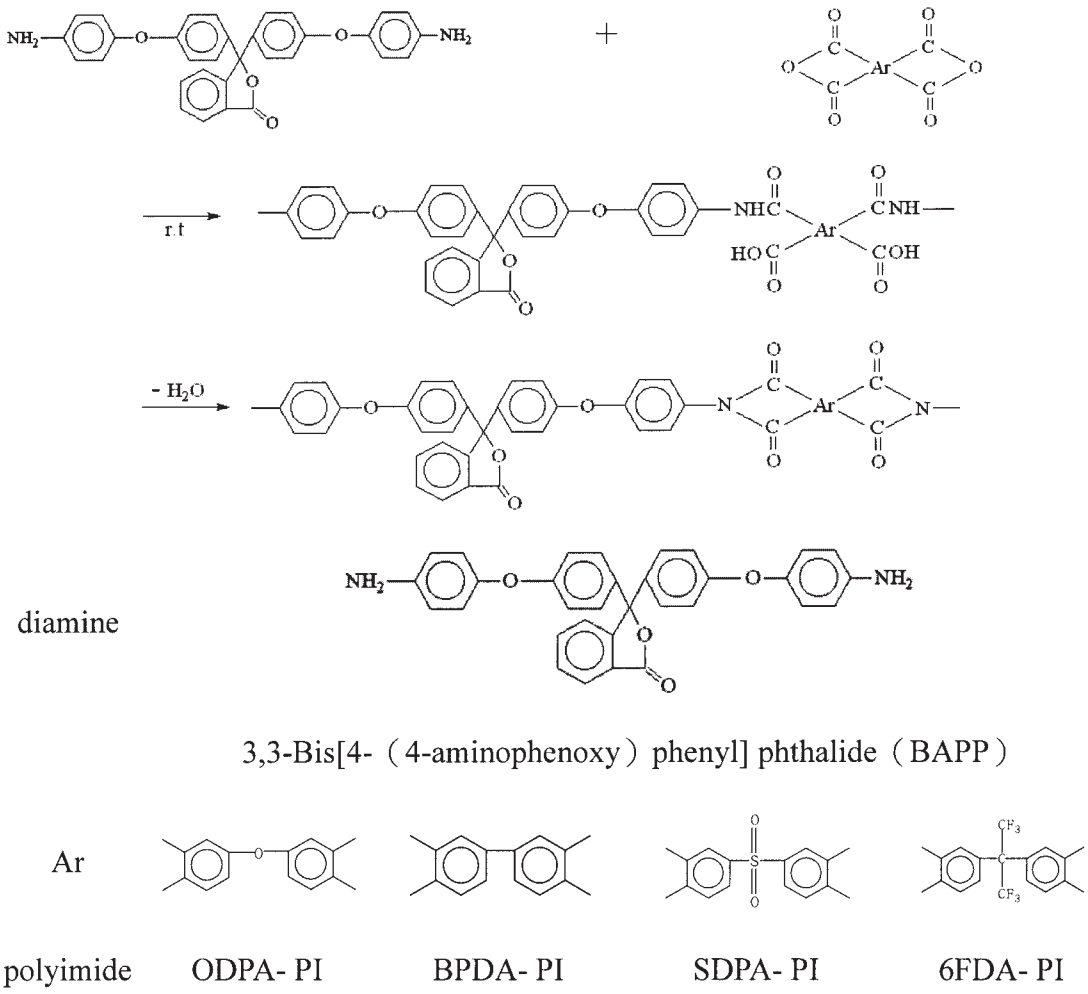

Scheme 1

purpose of this work was to study the effects of the dianhydride structure on the pervaporation performance of PI membranes for aqueous alcohol solution separation. The incorporation effects of the dianhydride on the sorption, diffusion selectivity, and pervaporation performance were investigated. In addition, the effects of the feed composition, the molar volume of the alcohols, and the feed temperature on the pervaporation performance of the prepared PI membranes were also studied.

EXPERIMENTAL

Materials

BAPP and four dianhydrides [i.e., 4,4′-sulfonyl diphthalic anhydride (SDPA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), 4,4′-oxydiphthalic anhydride (ODPA), and 4,4′-hexafluoroisopropylidene diphthalic anhydride (6FDA)] were prepared as described previously.[22] PIs were synthesized conveniently by the two-step polycondensation of a dianhydride and a diamine in an aprotic solvent (*N*,*N*-dimethylacetamide). The synthetic route of the PIs is presented in Scheme 1. All reagent-grade chemicals, such as *N*-methylpyrrolidinone (NMP), methanol, ethanol, *n*-propanol, and *tert*-butanol, were used directly without further purification. Water was deionized and distilled.

Membrane preparation

The aromatic PI polymer was dissolved in NMP to form a 10 wt % homogeneous polymer solution at room temperature. Then, the polymer solution was cast onto a glass plate to a predetermined thickness with a Gardener knife (Braive, Belgium) at room temperature. The cast film was placed in an oven and heated at 80°C for 3 h to evaporate the solvent. The membrane was peeled off from the glass plate and placed in the vacuum oven for 48 h to further remove the residual solvent in the membrane. The average thickness of the polyamide membranes was approximately 40 μm.

Characterization

Differential scanning calorimetry was performed on a PerkinElmer DSC-7 differential scanning calorimeter (Wellesley, MA) in flowing nitrogen (60 cm^3/min) at a heating rate of 20°C/min. The thermogravimetric analysis was conducted with a PerkinElmer TGA-7 at a heating rate of 20°C/min. The bulk density was determined with a Mettler–Toledo AX analytical balance (Zurich, Switzerland).

Pervaporation measurements

Pervaporation was reported in an earlier article.[2] The effective area was 10.2 cm^2, and the feed temperature was 15–55°C. The permeation rate was determined by the measurement of the weight of the permeate. The compositions of the feed solution and the permeate were measured by gas chromatography (GC; 8700 T, China Chromatography, Taiwan). The water/alcohol separation factor ($\alpha_{w/A}$) was calculated as follows:

$$\alpha_{w/A} = (Y_W/Y_A)/(X_W/X_A)$$

where X_W and X_A are the weight fractions of water and alcohol in the feed, respectively, and Y_W and Y_A are the weight fractions of water and alcohol in the permeate, respectively.

Sorption measurements

The PI membranes were immersed in aqueous alcohol mixtures for 24 h at different temperatures. They were subsequently blotted between tissue paper for the removal of excess solvent and were placed in the left tube of a twin setup.[23] The system was evacuated while the left tube was heated with hot water and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC.

TABLE I
Properties of the Synthesized Aromatic PIs

Polymer	T_g (°C)	$T_{10\%}$ (°C)[a]	Young's modulus (GPa)	FFV (%)[b]
ODPA-PI	260	514	2.10	7.2
BPDA-PI	290	517	2.45	8.8
SDPA-PI	287	505	2.42	7.3
6FDA-PI	296	576	1.03	13.7

[a] Temperature at which 10% weight loss was recorded with TGA at a 20°C/min heating rate.

[b] FFV = $(V - V_0)/V$; $V_0 = 1.3V_W$ (from Bondi[24]); V = the specific volume of polymer (cm^3/mol); V_0 = the occupied volume of polymer (cm^3/mol); V_W = van der Waal's volume calculated from the group contribution method (cm^3/mol).

TABLE II
Effect of the Polyamide Structure on the Pervaporation Performance of 90 wt % Aqueous Ethanol Solutions

Polymer	Permeation rate (g/h m^2)	Water concentration in the permeate (wt %)	PSI[a]
ODPA-PI	213.3	55.5	2240
BPDA-PI	270.5	67.3	6150
SDPA-PI	318.7	45.9	1912
6FDA-PI	332.2	35.4	1495

Feed solution temperature = 25°C; feed solution concentration = 90 wt % aqueous ethanol solution.

[a] PSI = Permeation rate × $\alpha_{W/A}$.

Degree of swelling

The PI membranes were immersed in different feed mixtures for 24 h at different temperatures. The degree of swelling of the membranes was defined as follows:

$$\text{Degree of swelling} = (W_w - W_d)/W_d \times 100\%$$

where W_d and W_w are the weights of the dry and swollen membranes, respectively.

RESULTS AND DISCUSSION

Properties

The properties of the synthesized PIs are shown in Table I. Young's modulus of the PIs was higher than 1 GPa, and the membrane strength was sufficient. In addition, the glass-transition temperatures (T_g's) of these PIs were 260–296°C, and the 10% weight loss temperatures were 505–576°C in nitrogen. These results indicated that the PI membranes had satisfactory thermal stability during pervaporation. In addition, a symmetric membrane was made with a dry phase-inversion method and was used for pervaporation, sorption, and degree-of-swelling measurements. The average thickness of the polyamide membranes was approximately 40 μm.

Influence of the PI structure on the pervaporation performance

The pervaporation performances of 90 wt % aqueous ethanol solutions through the aromatic PI membranes are shown in Table II. The permeation rate followed the order of 6FDA-PI > SDPA-PI > BPDA-PI > OPDA-PI. The interaction between the polymer membranes and permeates could be used to explain this phenomenon. The differences in the solubility parameters of the ethanol and aromatic polyamide membranes are listed in Table III. The differences in the solubility parameters of the ethanol and aromatic polyamide membranes followed the aforementioned

TABLE III
Effect of the Solubility Parameter Difference on the Swelling and Solubility for Different Dianhydride PIs

Polymer	Degree of swelling: 10 wt % aqueous ethanol solution (%)	Degree of swelling: 90 wt % aqueous ethanol solution (%)	$\Delta\delta$
ODPA-PI	8.1	17.0	3.0
BPDA-PI	9.2	17.9	2.9
SDPA-PI	10.3	17.8	2.9
6FDA-PI	10.4	24.5	2.3

$\Delta\delta$ = solubility parameter of polymers ($\delta_{polymer}$) − solubility parameter of ethanol ($\delta_{ethanol}$).

trend. Thus, the degree of swelling of the 6FDA-PI membrane (24.5%) was higher than that of the OPDA-PI membrane (17%). These results completely supported the data shown in Table II; that is, the 6FDA-PI membrane had higher affinity for ethanol molecules than the other polyamide membranes, and so the 6FDA-PI membrane had the highest permeation rate. In addition, X-ray diffraction measurements indicated that all the aromatic PIs were essentially amorphous. The free volume of the 6FDA-PI membrane was higher than that of the other aromatic PI membranes. The X-ray diffraction patterns and fractional free volumes (FFVs) of the aromatic PIs are shown in Figure 1 and Table I, respectively. In comparison with the other aromatic PI membranes, the 6FDA-PI membrane with a hexafluoropropane group in the polymer backbone had a higher permeation rate. This could be explained by the fact that the addition of a bulky hexafluoropropane group into the polymer backbone resulted in an aromatic PI with an amorphous structure. Thus, the packing density of the polymer chains decreased during the formation of the membrane. Moreover, the

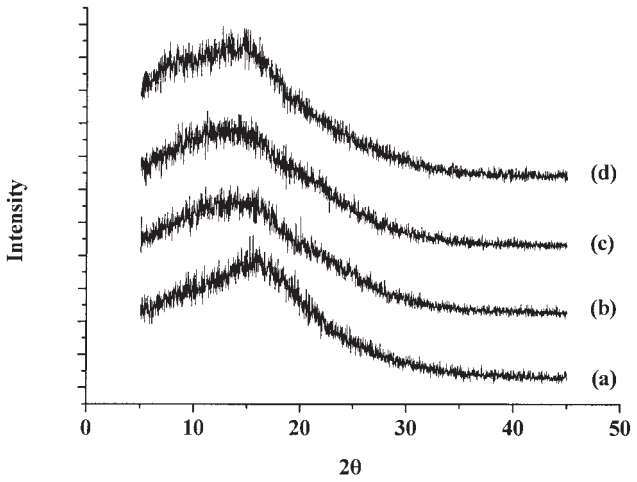

Figure 1 X-ray diffraction patterns of aromatic PIs: (a) SDPA-PI, (b) BPDA-PI, (c) OPDA-PI, and (d) 6FDA-PI.

TABLE IV
Effect of Plasticizing on the Sorption and Diffusion Properties

Polymer	10 wt % α_S	10 wt % α_D	10 wt % α_P	90 wt % α_S	90 wt % α_D	90 wt % α_P
ODPA-PI	2.5	5.76	14.4	5.5	1.1	6.0
BPDA-PI	0.6	18	10.8	9.9	1.2	11.7
SDPA-PI	0.7	17.3	12.1	7.2	1.6	10.5
6FDA-PI	0.7	11.7	8.2	3.1	1.5	4.5

α_P = pervaporation separation factor.
α_D = diffusion separation factor.
α_s = solution separation factor.

transport phenomenon of the aromatic PI membranes is discussed in this section. The sorption experiments were performed to determine the solution separation factor ($\alpha_{solution}$) for the aromatic PI membranes. For pervaporation, the permeability coefficient represents the product of the solution coefficient and the diffusion coefficient. Thus, the pervaporation separation factor ($\alpha_{pervaporation}$) can also be expressed as the product of $\alpha_{solution}$ and the diffusion separation factor ($\alpha_{diffusion}$) as follows:

$$\alpha_{pervaporation} = \alpha_{solution} \times \alpha_{diffusion}$$

The effect of plasticization on the sorption and diffusion properties is shown in Table IV. The effect of $\alpha_{solution}$ dominates the behavior of pervaporation because $\alpha_{pervaporation}$ follows the same trend as $\alpha_{solution}$ but does not follow the trend of $\alpha_{diffusion}$ at a feed higher ethanol concentration (90 wt %). However, the opposite phenomenon was observed at a lower feed ethanol concentration (10 wt %). These phenomena might be due to the fact that the high affinity between the ethanol molecules and the aromatic PI membranes resulted in a more swollen membrane structure. Thus, the water molecules could easily dissolve into the membranes. In general, a swollen membrane structure results in a higher value of $\alpha_{solution}$. According to the results shown in Table III, the degree of swelling of the aromatic PI membranes with a 90 wt % aqueous ethanol solution was higher than that of the membranes with a 10 wt % aqueous ethanol solution; therefore, $\alpha_{solution}$ of the former was higher than that of the latter. These results agreed well with the results from the solution–diffusion study of the aromatic PI membranes, as indicated in Table IV. The optimum pervaporation results were obtained with the BPDA-PI membrane, which yielded a permeation rate of 270.5 g/m^2 h, a separation factor of 22.7, and a pervaporation separation index (PSI) of 6156.

Effect of the feed composition on the pervaporation performance

The effect of the composition of the feed mixtures on the pervaporation performance of the BPDA-PI mem-

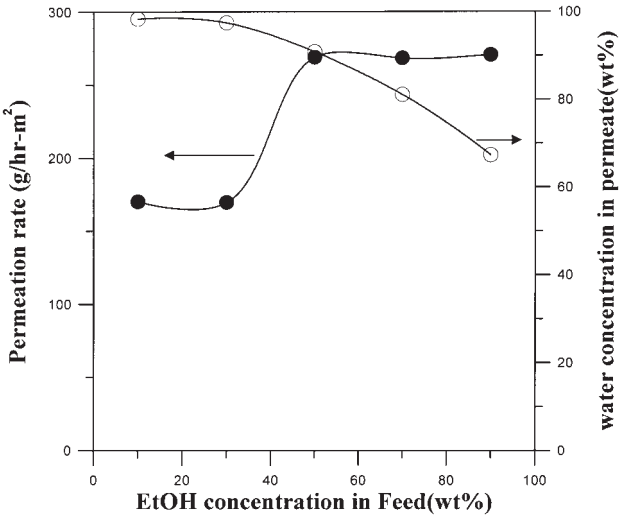

Figure 2 Effect of the feed composition on the pervaporation performance of the BPDA-PI membrane at 25°C.

brane is shown in Figure 2. The permeation rate increased and the water concentration in the permeate decreased as the feed ethanol concentration increased in the range of 10–90 wt %. These results can be explained by the plasticizing effect of ethanol. Generally, the hydrophobic membranes had stronger interactions with alcohol. The degree of swelling of the membranes increased with an increase in the ethanol concentration, as shown in Figure 3, and the results agreed well with the permeation rate of the BPDA-PI membrane, as indicated in Figure 2. When the ethanol concentration in the feed solution was higher, the amorphous regions of the membranes were more swollen. The permeation rate increased suddenly

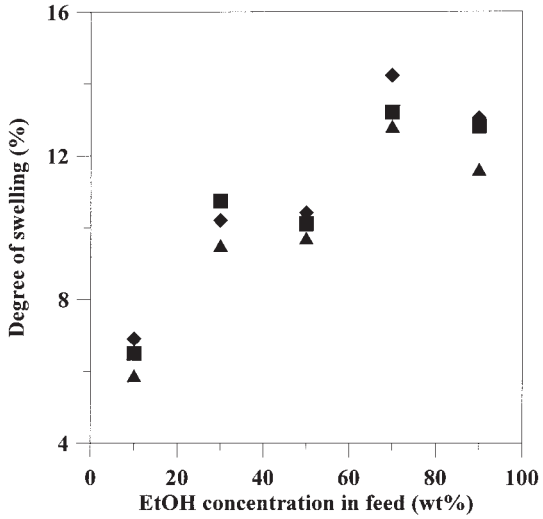

Figure 3 Effects of the feed composition and feed solution temperature on the degree of swelling of the BPDA-PI membrane: (▲) 25, (■) 45, and (♦) 55°C.

TABLE V
Effect of Aqueous Alcohol Mixtures on the Pervaporation Performance of BPDA-PI Membranes

Aqueous alcohol mixture (90 wt %)	Permeation rate (g/h m²)	Water concentration in the permeate (wt %)	Separation factor
Methanol	729.9	12.1	1.3
Ethanol	270.5	67.3	53
n-Propanol	226.4	75.8	30
i-Propanol	160.8	97.4	492

Feed solution temperature = 25°C.

when the ethanol concentration of the feed solution was higher than 40 wt %. Hence, the polymer chain became more flexible and reduced the energy required for molecular transport through the membranes; therefore, the permeation rate increased and the water concentration in the permeate increased as the feed ethanol concentration increased.

Pervaporation of aqueous alcohol mixtures through the BPDA-PI membrane

The pervaporation performances of 90 wt % aqueous alcohol solutions through the BPDA-PI membrane are shown in Table V. Table V shows that the separation factor increased and the permeation rate decreased as the number of carbon atoms in the alcohol increased. It is widely accepted that permeation through polymeric membranes follows a solution–diffusion mechanism. Thus, the size of the permeating species and the interaction between the feed component and the membrane are important in both solution and diffusion processes. The differences in the solubility parameters of the membrane and alcohol, the degrees of swelling, and the molar volumes for different alcohols are summarized in Table VI. The separation factor

TABLE VI
Effect of the Solubility Parameter Difference Between the BPDA-PI Membrane and Alcohol on the Degree of Swelling

Aqueous alcohol mixture (90 wt %)	Degree of swelling (%)	$\delta_{membr} - \delta_{alcohol}$ [a]	Molar volume (mL/mol)[b]
H_2O	2.57	24.7	18.0
Methanol	14.2	6.3	40.7
Ethanol	18.0	2.9	58.7
n-Propanol	12.2	1.7	75.1
i-Propanol	8.2	0.2	77.0

[a] $\delta_{PI2\text{-}BPDA}$ = 23.24 by Hoy's method (δ member = solubility parameter of membrane; α alcohol = solubility parameter of alcohol).

[b] Feed solution composition = 90 wt % aqueous ethanol solution.

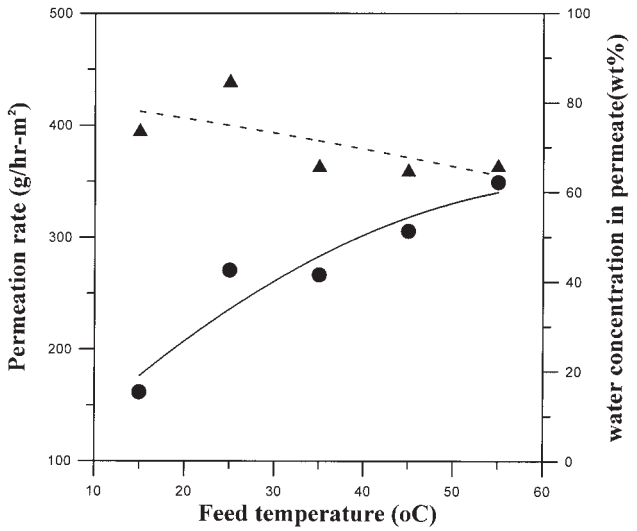

Figure 4 Effect of the feed solution temperature on the pervaporation performances of 90 wt % aqueous alcohol mixtures through the BPDA-PI membrane: (●) permeation rate and (▲) water concentration in the permeate.

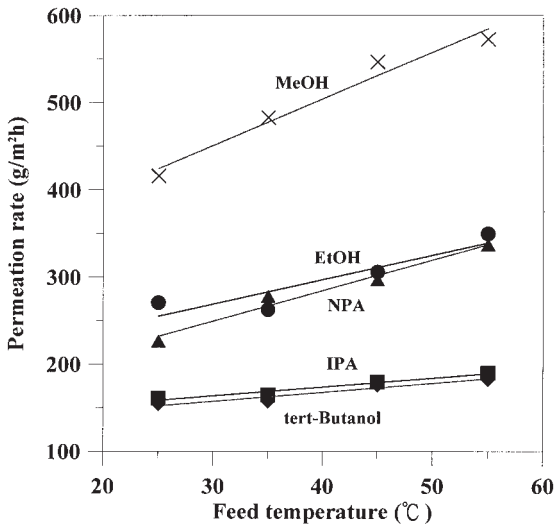

Figure 5 Effect of the feed solution temperature on the permeation rate of 90 wt % aqueous alcohol mixtures through the BPDA-PI membrane: (×) methanol, (●) ethanol, (▲) *n*-propanol, (■) *i*-propanol, and (♦) *tert*-butanol.

depended on the molar volume of alcohol. In addition, the differences in the solubility parameters of the membrane and alcohol were in the order of *i*-propanol < *n*-propanol < ethanol < methanol < water. That is, the affinity between the membranes and alcohols was higher than the affinity between the membranes and water. Hence, the BPDA-PI membrane had the lowest degree of swelling in water. However, the degree of swelling decreased as the difference in the solubility parameters of the larger alcohol series (*n*-propanol and *i*-propanol) decreased. These phenomena might be due to the fact that the steric hindrance of the larger alcohol series (*n*-propanol and *i*-propanol) was higher than that of the small alcohol series (methanol and ethanol). Consequently, this result shows that the solubility of the alcohols for the BPDA-PI membrane was higher than that of water, but the diffusivity of water across the membranes was much higher than that of the alcohols.

Effect of the feed solution temperature on the pervaporation performance

The effect of the feed solution temperature on the pervaporation performances of 90 wt % aqueous alcohol mixtures through the BPDA-PI membrane is shown in Figure 4. The permeation rate increased and the water concentration in the permeate decreased as the feed solution temperature increased. These phenomena might be due to the fact that the polymer chain motion, polymer chain flexibility, and degree of swelling increased with a higher feed solution temperature, and this reduced the separation factor. These results correspond to the data of the degree of swelling very well, as shown in Figure 3. Moreover, the activation energy for the permeation of an aqueous alcohol solution through the BPDA-PI membrane was obtained from an Arrhenius plot. The results are shown in Figure 5 and Table VII. The activation energy of a 90 wt % aqueous alcohol solution through the BPDA-PI membrane was 1.2–3.0 kcal/mol. The activation energy decreased as the molar volume of the alcohol increased. These results are demonstrated by the fact that the degree of swelling of the BPDA-PI membrane in the small alcohol system was higher than that in the larger alcohol. Thus, the BPDA-PI membrane in the former system was more heat-sensitive than that in the latter system.

CONCLUSIONS

A series of BAPP-base PI membranes via dry phase inversion were successfully prepared. The PI membranes had satisfactory thermal stability in the pervaporation process. The pervaporation results showed that water was preferentially permeated during all process runs. The BAPP-base PI membrane had higher

TABLE VII
Permeation Activation Energy (E_P) for Various Alcohol Solutions Through the BPDA-PI Membrane

Aqueous alcohol mixture (90 wt %)	E_P (kcal/g mol)
Methanol	3.0
Ethanol	3.1
n-Propanol	2.5
i-Propanol	1.1
t-Butanol	1.2

affinity to alcohol because of the addition of hydrophobic groups to the polymer backbone. The solubility of the alcohols for the BPDA-PI membrane was higher than that of water, but the diffusivity of water across the membrane was much higher than that of the alcohols. A separation factor of 22 and a permeation rate of 270 g/m^2 h were obtained for a 90 wt % feed aqueous ethanol solution through the BPDA-PI membrane at 25°C.

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