# Development of Polyimide Membranes for the Separation of Water Vapor from Organic Compounds

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**ABSTRACT:** Attempts were made to develop solvent-resistant polyimide capillary membranes with integrally skinned asymmetric structure to be used for the treatment of wood dryer emissions or vacuum pyrolysis aqueous effluents. Model mixtures of 1-propanol (1-PrOH)/$H_2O$ and acetic acid (AA)/$H_2O$, with concentrations of 10–90 wt % of organic components, were used as vaporous feeds. Solvent-resistant membranes with good mechanical and excellent vapor separation properties were prepared from polyimides based on PMDA and BPDA by the dry/wet phase-inversion technique. Molecular structure largely influences membrane properties. For the asymmetric polyimide membranes studied, a tendency similar to that of homogeneous dense membrane was found. Membranes prepared from polyimides with diamine and dianhydride moieties, both containing rigid backbone and aromatic rings, displayed higher permeability and selectivity. Test conditions exhibited influences on membrane separation performance. Membranes prepared from copolyimide BPDA–50DDS/50ODA and PMDA–50DDS/50ODA exhibited the best mechanical and chemical properties as well as water vapor separation properties, which are considered to be of practical usefulness for applications of these membranes in the removal of water from water/organic mixtures. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 139–152, 2002

**Key words:** solvent-resistant; polyimide; vapor permeation; water vapor separation; membrane; wood drying; vacuum pyrolysis; emissions

## INTRODUCTION

Green biomass contains up to 50–65% water and must be dried to 10–30% before combustion or pyrolysis.[1] During the biomass drying process, organic compounds such as formic acid, acetic acid, methanol, and ethanol are formed and re-

leased, causing environmental problems in the form of gaseous emissions to the air or liquid effluents into natural watercourses. Hence, their treatment is required. Similarly in the vacuum pyrolysis process, when water-containing feedstocks, such as urban wastes and biomass are treated,[2,3] a large quantity of water is produced and released, requiring treatment before discharge. On the other hand, some organic compounds released during wood drying and pyrolysis processes are valuable and may be recovered.

There are many processes for the treatment of wastewater. An alternative approach is membrane separation. In this category, vapor permeation is the most attractive because the emissions, either from the wood drying process or from the pyrolysis by-product streams, already exist in the vapor state. Moreover, vapor permeation has the advantage of increased membrane life compared with that of pervaporation, where membranes are in contact with solutions of various organic compounds and, therefore, can be easily attacked by some organics and are prone to swell.

The desired gas or vapor separation membranes should have high permeability and selectivity as well as good mechanical, thermal, and chemical stability. Although there are great amounts of data concerning gas permeation through polymeric membranes, most research has mainly focused on air or natural gas separations, typically $CO_2/CH_4$ and $O_2/N_2$,[4] where the operation of membranes is primarily performed at room temperature.

Polyimides, with their excellent thermal, mechanical, and chemical properties, have been widely investigated in the microelectronic and aerospace industries and have also attracted much attention as gas separation membrane materials since the 1970s.[5,6] It has been known that the molecular structure of polyimides largely influences membrane separation properties. Systematic investigation of the effect of molecular structure on dense polyimide membranes has been made and some significant relationships between the chemical structure and the gas separation properties of polymers have been established, which significantly contributed to advancement of membrane material design for the separation of gas mixtures. The tailor-made polyimide membranes based on 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) were reported to exhibit both higher permeabilities and selectivities than those of many other glassy polymers.[7,8] However, when water vapor is one of the components of gas mixtures, the structure–property relationships of membranes become very complicated, given that water molecules may interact with the polymer to act as a plasticizer or with other water molecules to form clusters.[9] Although 6FDA-based polyimide membranes show good gas separation properties, they are not necessarily good for water and water vapor separation because of their typically hydrophobic properties.[10]

Polyimide polymers, in which both dianhydride and diamine moieties contain sulfonyl connector groups, are reported to exhibit improved solubility characteristics.[11] They are good film-forming materials for preparation of asymmetric and composite gas separation membranes. Furthermore, better water or water vapor sorption in and diffusion through membranes are expected for membranes prepared from these materials because of their high density in polar sulfonyl groups, which may significantly increase membrane affinity to water and water vapor. However, most of them are soluble even in very common solvents such as methanol.[11] No matter how superior they are as membrane materials for air or natural gas separation, they exhibit limitation in the gas or vapor separation that involves mixtures containing organic compounds, given that the latter compounds may act as solvents when condensed.

The main objective of this work is to develop polyimide capillary membranes with integrally skinned asymmetric structure to be used for the treatment of wood drying or vacuum pyrolysis emissions. A membrane that is highly resistant to organic solvents is sought for, along with good mechanical and ideal vapor separation properties. At the same time, the effect of molecular structures of membrane material on membrane separation properties is investigated. Aqueous solutions of acetic acid (AA) were chosen as a model mixture for this study because acetic acid is one of the main components in wood drying and pyrolysis emissions. For comparison, aqueous solutions of 1-propanol (1-PrOH) with different concentrations were also used for membrane separation tests.

## EXPERIMENTAL

### Materials and Membrane Preparation

The molecular structures of monomer dianhydrides and diamines used in this study are shown in Figure 1. All the monomers used were obtained from Chriskev Co. (Leawood, KS). The dianhydrides [pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), and 3,3′,4,4′-diphenylsulfone tetracarboxylic dianhydride (DSDA)] were recrystallized from acetic anhydride, dried at 220–250°C in $N_2$ for 3–5 h, and stored in a desiccator over silica gel before use. The diamines [4,4′-oxydianiline (ODA), 4,4′-diaminodiphenylsulfone (DDS), and 1,3-bis(4-aminophenoxy)-
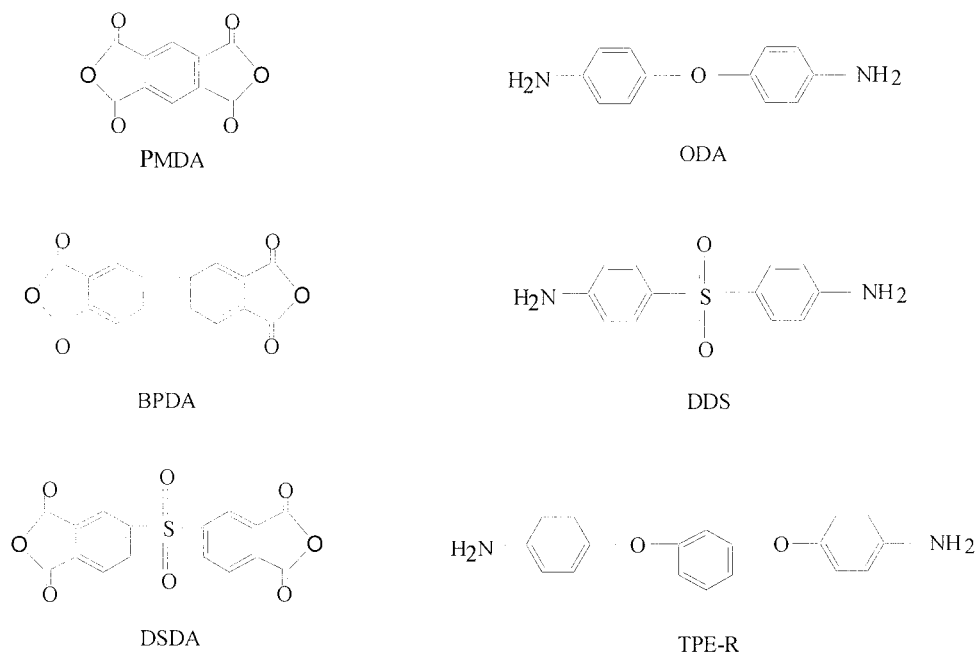
**Figure 1**   Molecular structure of monomers.

benzene (TPE-R)] were recrystallized from ethanol and vacuum dried. *N*-Methyl-2-pyrrolidone (NMP) was dehydrated with $CaSO_4$ and phosphorus pentoxide, respectively, then vacuum distilled before use.

Poly(amic acid) (PAA) precursors were prepared by solution condensation of an aromatic dianhydride with a stoichiometric amount of one or two aromatic diamines in NMP. The casting solutions for preparing the hollow-fiber membranes were made by slowly adding glycerol into the PAA precursors to a glycerol concentration of 14–17 wt % and a PAA concentration of 15–20 wt % in the casting solution was finally obtained. The asymmetric capillary membranes were prepared by the dry/wet phase-inversion method. Water was injected as bore liquid to the center of a polymer solution while the polymer solution was extruded through the annular space of a spinneret. The flow rate of the polymer solution was controlled by $N_2$ pressure applied to the polymer solution reservoir. The air gap was maintained at 200 mm for most of the membrane preparations. There were 3–4 s of residence time for the nascent fiber in air before it entered into the coagulation bath (water). The nascent fibers were left in the coagulation bath and rinsed by water for several hours, after which they were taken out and dried in air at room temperature. The PAA capillary fibers were thermally imidized by plac-

ing the fibers in a nitrogen atmosphere and annealing them at 100°C for 1 h, at 200°C for 1–2 h, and at 300°C for 1 h. For the PMDA-based membranes, the highest curing temperature of 370°C was used. The resulting polyimide capillary membrane had an outside diameter of about 1.75 mm, and a wall thickness of about 200 $\mu$m.

## Measurements

The inherent viscosity of PAA solution was measured with a Ubbelohde viscometer at the concentration of 0.5 g/dL in NMP at 30°C.

The stability of the membranes in an organic environment was characterized by immersing membrane samples in a strong solvent such as NMP and by keeping them in the solvent for several days, to observe whether the samples were dissolved, partially dissolved, or swollen.

A scanning electron microscope (SEM) JSM-840A (Jeol Instruments, Japan) was used to investigate the morphology of asymmetric capillary membranes and to evaluate the external and the internal diameters as well as their skin thickness. Samples were immersed and broken in liquid nitrogen before being coated with gold.

The separation performance of the membranes was tested by using a laboratory-scale separation unit,[3,12] whereby the separation of model vaporous mixtures of 1-propanol (1-PrOH)/$H_2O$ and

acetic acid (AA)/$H_2O$ was attempted. Mixtures with 10–90 wt % of organic components were used as vaporous feeds. The capillary membranes were potted together at both ends with epoxy glue to form bundles with an effective surface area of approximately 80 cm$^2$. Membrane bundles were tested at 85–135°C with feed vapor supplied to the bore side of the capillary fibers. Feed and permeate pressures were controlled at 20–66 and 4–5 kPa, respectively. The retentate and the permeate vapors were condensed in condensers cooled by ice-cold water. After the membranes were equilibrated for 6–8 h in a feed vaporous mixture, the permeate sample was collected, assuming steady-state conditions were reached. The compositions of the feed mixture, the retentate, and the permeate were determined by total carbon analysis using a Beckman Model 915A TOC analyzer (Beckman Instruments, Palo Alto, CA).

The performance of the prepared capillary membranes was characterized by permeance ($P/\delta$), defined as

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i}{\Delta p_i \, A t} \qquad (1)$$

where $Q_i$ is the molar quantity of the $i$th component permeating through the membrane area $A$ (m$^2$), during a certain time $t$ (s) at a steady-state condition; and $\Delta p_i$ is the difference in partial pressure across the membrane of species $i$, which is given by

$$\Delta p_i = p_{\text{bore}} X_{\text{ave},i} - p_{\text{perm}} X_{\text{perm},i} \qquad (2)$$

where $p_{\text{bore}}$ and $p_{\text{perm}}$ (Pa) are total pressures on the bore side and the permeate side of the capillary membrane, respectively; $X_{\text{ave},i}$ is the average of mole fraction of species $i$ in the feed and the retentate; and $X_{\text{perm},i}$ is the mole fraction of component $i$ in the permeate.

The ability of a membrane to separate two vapor components $i$ and $j$ is characterized by the membrane selectivity ($\alpha$), which can be determined by the ratio of their permeabilities:

$$\alpha_j^i = \frac{P_i}{P_j} = \frac{\left(\frac{P}{\delta}\right)_i}{\left(\frac{P}{\delta}\right)_j} \qquad (3)$$

For the binary separation system of 1-PrOH/$H_2O$ and AA/$H_2O$, water is designated as $i$ and 1-PrOH and AA are both represented by $j$.

## RESULTS AND DISCUSSION

### Effect of Chemical Structure on Membrane Properties

The inherent viscosity of poly(amic acid)s (PAAs) and some physical properties of their corresponding membranes prepared are given in Table I. The difference between the copolyimides BPDA–50DDS/50ODA of PHF-012, PHF-016, PHF-026-1, PHF-026-2, and PHF-027 in Table I is in the casting solution composition, that is, PHF-012 (PAA, 20 wt %; NMP, 63.5 wt %; glycerol, 16.5 wt %); PHF-016 (PAA, 18 wt %; NMP, 67.5 wt %; glycerol, 14.5 wt %); and PHF-026-1, PHF-026-2, and PHF-027 (PAA, 18 wt %; NMP, 67 wt %; glycerol, 15 wt %). Similarly, for the copolyimides PMDA–50DDS/50ODA the compositions are: for PHF-024-2 (PAA, 16 wt %; NMP, 67 wt %; glycerol, 17%) and for PHF-025-1 and PHF-025-2 (PAA, 18 wt %; NMP, 66 wt %; glycerol, 16 wt %).

It is seen from Table I that the PAAs had inherent viscosities in the range of 0.46–1.98 dL/g. The molecular structure of the diamines strongly influenced the inherent viscosity of the polymer precursors and, consequently, the properties of membranes prepared from the precursors. PAAs prepared from diamines containing sulfonyl (–$SO_2$–) connector groups (e.g., the precursors of PMDA–DDS and BPDA–DDS) exhibited much lower viscosities than those of other PAAs. This may be attributable to the electron-withdrawing property of the sulfonyl group in the diamine moiety, which reduces the nucleophilicity of amino groups in the para positions and decreases the reactivity of the diamine and eventually lowers the molecular weight of PAAs.[13] However, the electron-withdrawing sulfonyl groups in DSDA seem to have little effect on the reactivity of the anhydride group, as reported in the literature.[14] The reaction rate of the dianhydride-containing sulfonyl bridging group (–$SO_2$–), that is, DSDA–ODA and DSDA–TPE–R, is almost the same as that of PMDA–TPE–R and BPDA–ODA, judging from the viscosity buildup observed after about 3 h. However, for PMDA–DDS and BPDA–DDS, the viscosity did not become high enough, even after stirring for 10 h at ambient temperature under $N_2$ stream. Among the mem-

**Table I   Inherent Viscosity of PAAs and Physical Properties of Membranes**

| Code | Sample | $\eta_{inh}$ of PAA[a] (dL/g) | Skin Thickness[b] ($\mu$m) | Solubility in NMP | Brittleness |
|------|--------|------|------|------|------|
| PHF-002 | PMDA–TPE–R | 0.68 | 1.84 | Solvent-resistant | Flexible |
| PHF-003 | PMDA–DDS | 0.52 | — | Solvent-resistant | Very brittle |
| PHF-024-2 | PMDA–50DDS/50ODA | 0.85 | — | Solvent-resistant | Strong |
| PHF-025-1 | PMDA–50DDS/50ODA | 0.84 | — | Solvent-resistant | Strong |
| PHF-025-2 | PMDA–50DDS/50ODA | 0.84 | — | Solvent-resistant | Strong |
| PHF-006 | BPDA–ODA | 1.98 | 0.35 | Solvent-resistant | Flexible |
| PHF-007 | BPDA–DDS | 0.46 | 1.59 | Solvent-resistant | Very brittle |
| PHF-011 | BPDA–80DDS/20ODA | 0.66 | 0.50 | Solvent-resistant | Brittle |
| PHF-012 | BPDA–50DDS/50ODA | 0.82 | 0.65 | Solvent-resistant | Good |
| PHF-016 | BPDA–50DDS/50ODA | 0.71 | — | Solvent-resistant | Good |
| PHF-026-1 | BPDA–50DDS/50ODA | 0.75 | — | Solvent-resistant | Good |
| PHF-026-2 | BPDA–50DDS/50ODA | 0.75 | — | Solvent-resistant | Good |
| PHF-027 | BPDA–50DDS/50ODA | 0.78 | — | Solvent-resistant | Good |
| PHF-018 | BPDA–20DDS/80ODA | 0.88 | — | Solvent-resistant | Good |
| PHF-009 | DSDA–ODA | 0.97 | — | Soluble | Brittle |
| PHF-010 | DSDA–TPE–R | 0.87 | 0.96 | Partially dissolved | Flexible |

[a] Measured in NMP at a concentration of 0.5 g/dL at 30°C.
[b] Measured by SEM observation of the skin layers of the capillary membranes.

branes prepared, PMDA- and BPDA-based membranes showed good solvent resistance, whereas DSDA-based membranes were dissolved or partially dissolved in the solvent NMP (e.g., the membranes of DSDA–ODA and DSDA–TPE–R). It is likely that $-SO_2-$ connector groups in the

**Table II   Water Vapor Separation Properties of Polyimide Capillary Membranes[a]**

| Code | Sample | 1-Propanol/$H_2O$ (50/50 by mass in feed) Water Purity in Permeate (wt %) | Water Permeance $\times 10^{-7}$ (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) | Selectivity $\alpha_{\text{1-prop}}^{H_2O}$ | Acetic Acid (AA)/$H_2O$ (10/90 by mass in feed) Water Purity in Permeate (wt %) | Water Permeance $\times 10^{-7}$ (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) | Selectivity $\alpha_{AA}^{H_2O}$ |
|------|--------|------|------|------|------|------|------|
| PHF-002 | PMDA–TPE–R | 97.81 | 2.06 | 40 | 98.49 | 2.52 | 9.1 |
| PHF-025-1 | PMDA–50DDS/50ODA | 99.88 | 5.44 | 1662 | 99.83 | 5.32 | 110 |
| PHF-025-2 | | 99.83 | 7.10 | 1124 | 99.78 | 6.67 | 90 |
| PHF-024-2 | | 99.89 | 10.0 | 1952 | 99.80 | 8.36 | 98 |
| PHF-007 | BPDA–DDS[b] | 99.95 | 2.88 | 2942 | 98.57 | 2.06 | 126 |
| PHF-006 | BPDA–ODA[b] | 99.70 | 2.98 | 1224 | 98.53 | 2.32 | 120 |
| PHF-018 | BPDA–20DDS/80ODA | 99.89 | 3.63 | 1648 | 99.84 | 4.00 | 106 |
| PHF-016 | BPDA–50DDS/50ODA | 99.90 | 3.65 | 1745 | 99.81 | 3.30 | 85 |
| PHF-012 | | 99.90 | 2.31 | 1437 | 99.89 | 1.98 | 108 |
| PHF-027 | | 99.93 | 3.34 | 2609 | 99.89 | 3.32 | 165 |
| PHF-026-1 | | 99.97 | 3.16 | 4167 | 99.88 | 3.19 | 128 |
| PHF-026-2 | | 99.94 | 2.62 | 2626 | 99.92 | 2.71 | 187 |
| PHF-009 | DSDA–ODA | 94.20 | 3.43 | 31 | — | — | — |
| PHF-010 | DSDA–TPE–R[b] | 96.54 | 1.21 | 38 | 97.50 | 1.08 | 47 |

[a] All results are obtained at 85°C.
[b] Tested with feed mixture AA/$H_2O$ (50/50 by mass).
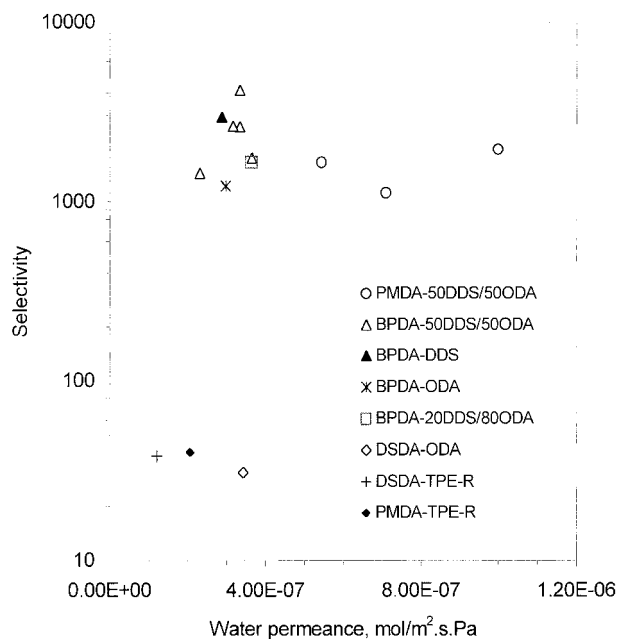
**Figure 2**   $H_2O$/1-PrOH selectivity versus permeance of water vapor: $T$, 85°C; feed, 1-PrOH/$H_2O$ (50/50 by mass) mixture.

dianhydride have a greater influence on the solubility of membranes prepared. Poor solvent resistance of membrane DSDA–ODA was also evi-
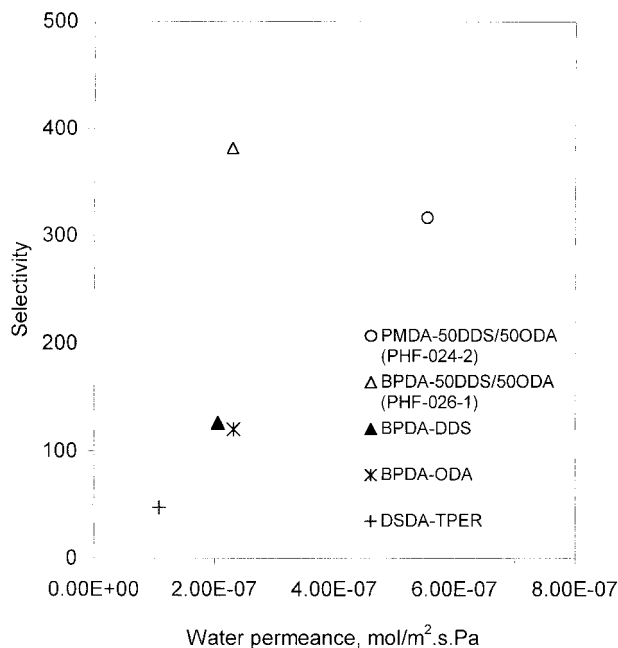


**Figure 3**   $H_2O$/AA selectivity versus permeance of water vapor: $T$, 85°C; feed, AA/$H_2O$ (50/50 by mass) mixture.

**Table III   Physical Properties of Vapor Components[a]**

| Component | Boiling Point (°C) | Critical Molar Volume ($V_c$) (cm³/mol) |
|---|---|---|
| $H_2O$ | 100 | 55.3 |
| 1-Propanol | 97 | 218.5 |
| Acetic acid | 118 | 171.0 |

[a] See Atkins (1998),[19] Van Krevelen (1990),[20] and Reid and Sherwood (1958).[21]

denced by two separation tests with an AA/$H_2O$ mixture. Each time, the membrane was broken within 2 h after allowing the vaporous mixture of AA/$H_2O$ into the membrane module. This, however, did not happen with the 1-PrOH/$H_2O$ mixture. Accordingly, it is considered that DSDA–ODA displays poor solvent resistance, at least in the AA/$H_2O$ environment.

Performance data for the membranes are listed in Table II. It can be seen from Table I and Table II that homopolyimide BPDA–DDS and BPDA–ODA membranes are solvent resistant and exhibit excellent separation properties for water/organic vapor mixtures. However, the BPDA–DDS capillary membrane was very brittle and the copolymer BPDA–DDS/ODA membranes exhibited superior mechanical strength. The enhancement of mechanical strength of the copolyimide
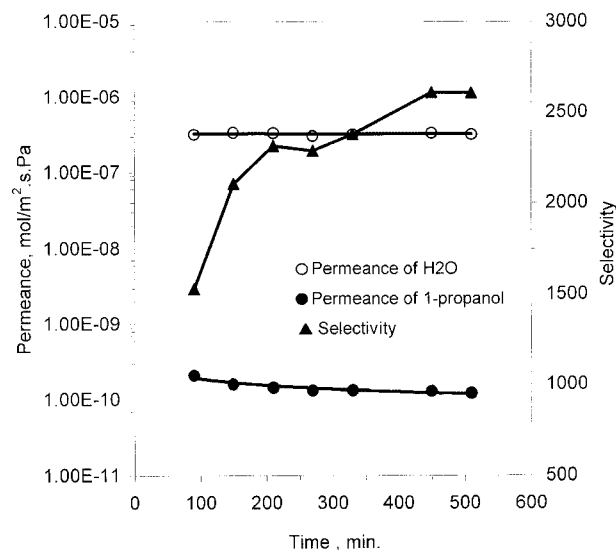


**Figure 4**   Separation behavior of a copolyimide membrane BPDA–50DDS/50ODA (PHF-027) for the separation of 1-PrOH/$H_2O$: $T$, 85°C; feed, 1-PrOH/$H_2O$ (50/50 by mass) mixture.
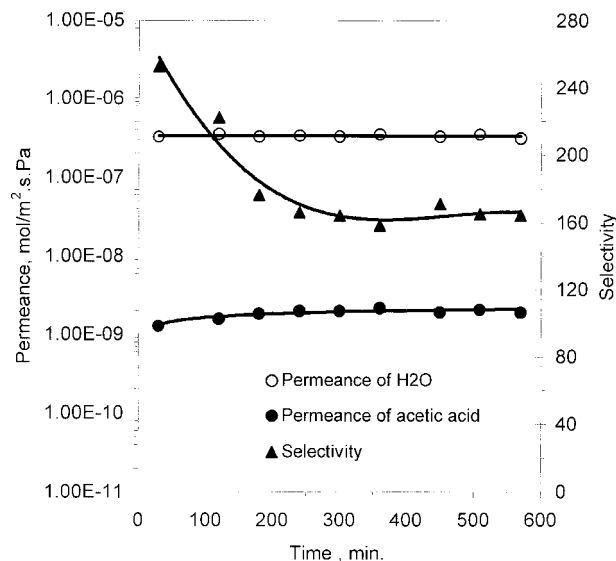
**Figure 5**  Separation behavior of a copolyimide membrane BPDA–50DDS/50ODA (PHF-027) for the separation of AA/$H_2O$: $T$, 85°C; feed, AA/$H_2O$ (10/90 by mass) mixture.

BPDA–DDS/ODA may be ascribed to the introduction of the flexible ether group (–O–) linkages into the backbone of polyimide by adding ODA, which can render the polymer molecular chain more flexible. The reactivity is also enhanced by adding ODA, leading to an increase in molecular weight, as evidenced by an increase in the inherent viscosity from 0.46 dL/g of BPDA–DDS (PHF-007) to 0.75 dL/g (PHF-026-1) and 0.82 dL/g (PHF-012) of BPDA–50DDS/50ODA. Both favor the improvement of mechanical strength of the membrane prepared.

Assuming that the skin layer of the asymmetric capillary membranes was defect free and the selectivity data given in Table II can represent permeation properties of the polyimides, it is evident from Table II that polyimides prepared from dianhydride and diamine monomers, both containing either an aromatic ring or two aromatic rings connected by a rigid sulfonyl backbone, exhibit higher water vapor selectivities. On the other hand, polyimides prepared from a diamine



(a)



( b )



(c)
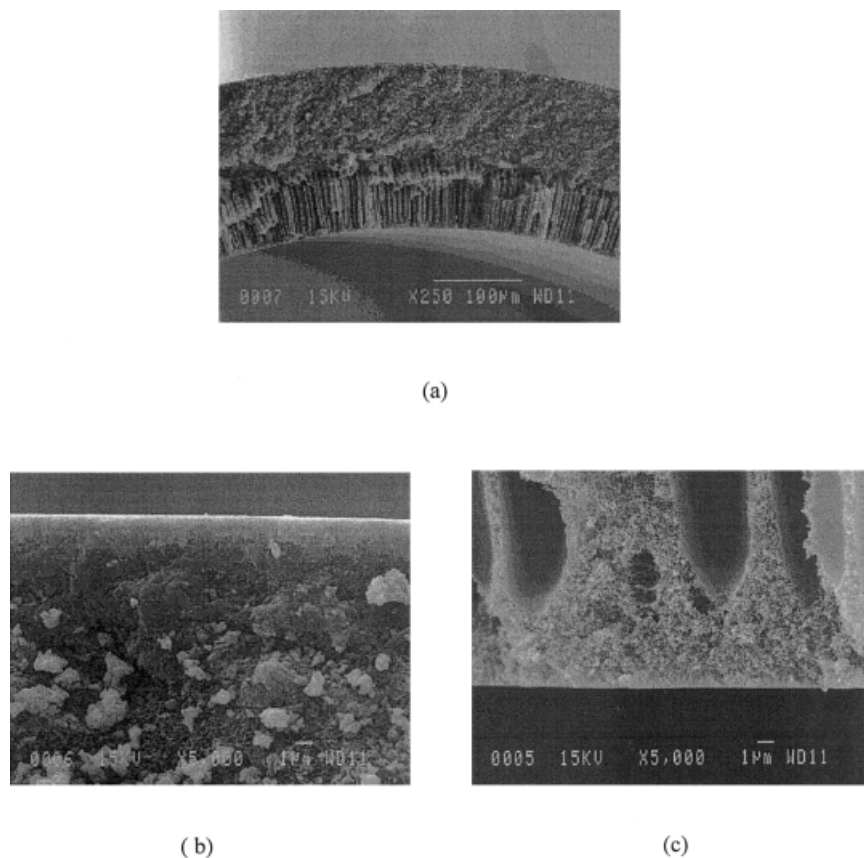
**Figure 6**  SEM photographs of membrane cross section (BPDA–DDS): (a) cross section; (b) outside; (c) inside.
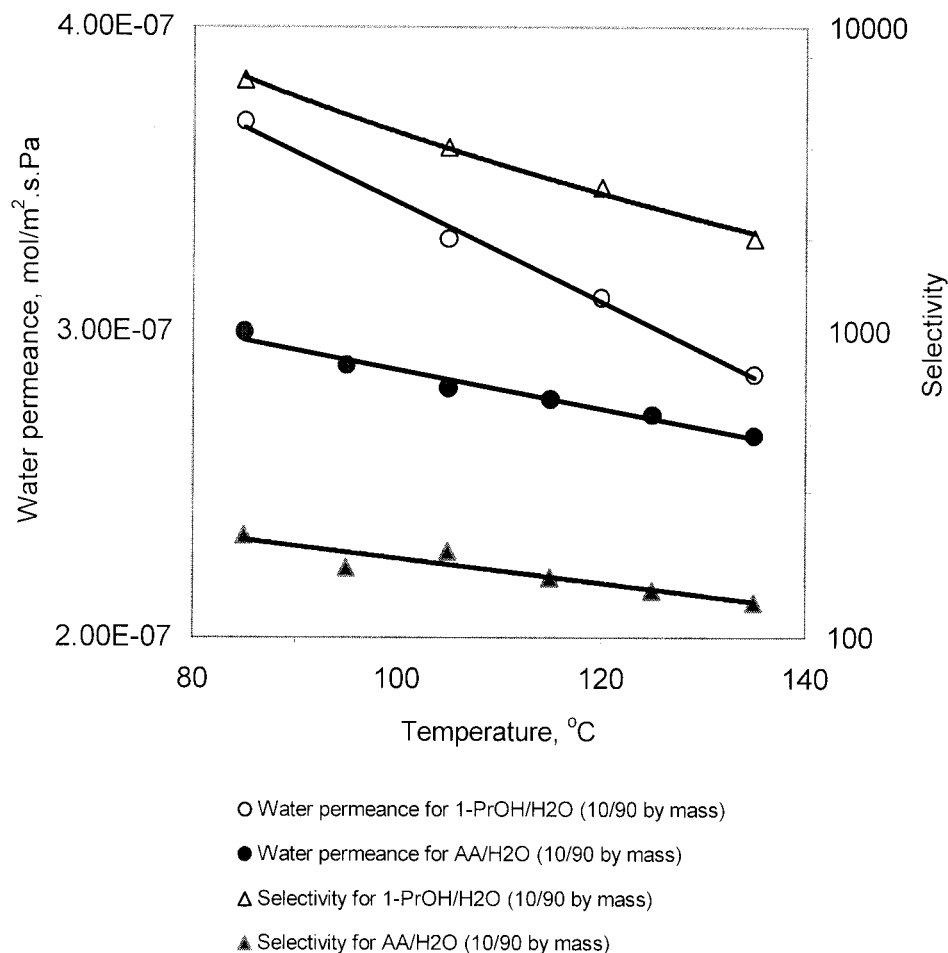
**Figure 7**   Effect of temperature on water permeance and selectivity for the copolyimide BPDA–50DDS/50ODA membrane (PHF-026-1).

TPE–R, whose amine-substituted aromatic rings are connected by a long flexible chain with two –O– linkages (e.g., PMDA–TPE–R and DSDA–TPE–R), show low water vapor separation properties, which is in good agreement with the relationships found in dense gas separation membranes.[15,16]

It is known that to improve the selectivity and permeability of polyimide membranes, the following factors must be considered:

- The backbone chains must be stiffened by inhibiting their intrarotational mobility so as to improve the selectivity.
- At the same time, intersegmental packing of the polymer chains must be simultaneously prevented so as to have a good permeability.

The sulfonyl ($-SO_2-$) group is more bulky and rigid than the ether linkage group (–O–). Accord-

ingly, molecular chains of polyimide containing sulfonyl groups will be much stiffer than those of polyimide containing ether group linkages; thus, both selectivity and permeability of polyimide-containing sulfonyl groups will be higher than those of polyimide-containing ether linkages. This outcome is evidenced by the experiment results of BPDA–DDS and BPDA–ODA, that is, the former shows both higher permeability and selectivity than that of the latter in separations of both 1-PrOH/$H_2O$ and AA/$H_2O$ mixtures. Moreover, BPDA–DDS is more brittle than BPDA–ODA.

Generally, copolymerization is one of the most useful methods of preparing membrane materials for the separation of organic compounds, given that the ratio of the "hard" and "soft" segments can easily be adjusted, through which some unexpected membrane materials with ideal mechanical properties along with good gas permeability and selectivity properties may be obtained. For
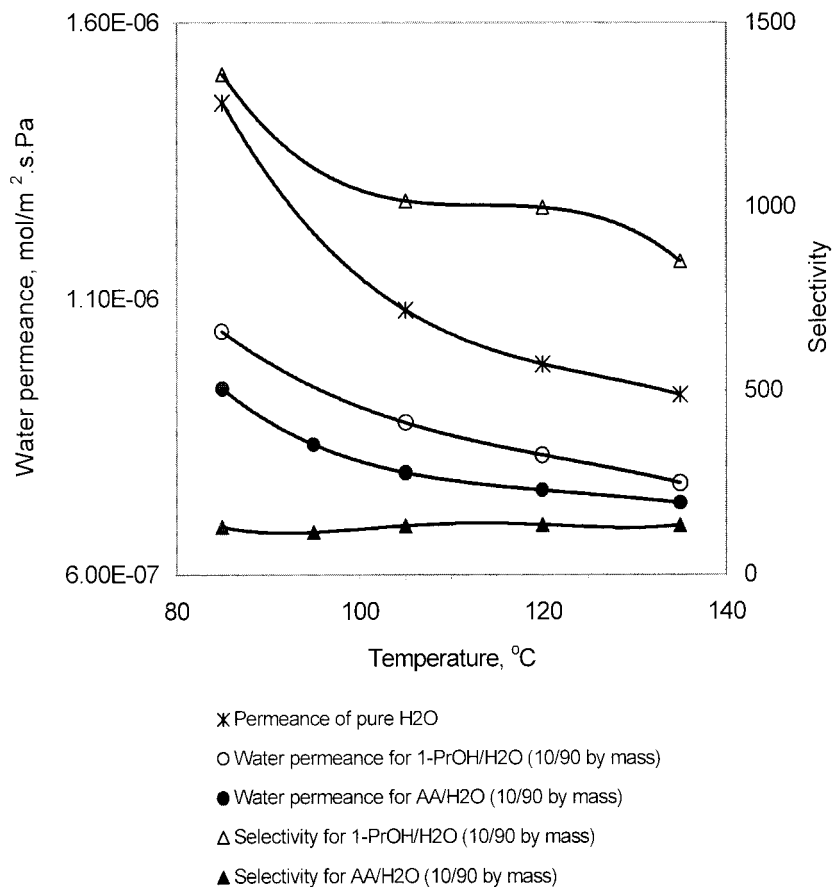
**Figure 8**  Effect of temperature on water permeance and selectivity for the copolyimide PMDA–50DDS/50ODA membrane (PHF-024-2).

example, Friesen et al.[17] used the copolymer of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA)/PMDA–ODA as a membrane material to prepare composite hollow-fiber membranes with high stability in organic solvents for the dehydration of organics. Similarly, asymmetric capillary membranes were prepared in this work from copolyimides that are based on either PMDA or BPDA dianhydride and mixtures of DDS/ODA diamines. In Figure 2 membrane selectivity was plotted versus water permeance for the separation of 1-PrOH/$H_2O$ (50/50 by mass) for the capillary membranes prepared from PMDA–50DDS/50ODA, BPDA–50DDS/50ODA, and BPDA–20DDS/80ODA copolymers along with the data for the membranes prepared from BPDA–DDS, BPDA–ODA, DSDA–ODA, DSDA–TPE–R, and PMDA–TPE–R homopolymers. From Table I, it is seen that BPDA–DDS and DSDA–ODA are brittle, whereas most of the copolyimide membranes are very strong and solvent resistant. The permeance of water vapor for BPDA–50DDS/50ODA

membrane is in the range of 2.31–3.65 × $10^{-7}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$, similar to that of BPDA–DDS and BPDA–ODA membranes, and the selectivity is above 1000 without exception. The highest value for the selectivity is more than 4000, corresponding to 99.97% purity of permeate water. The membranes prepared from PMDA–50DDS/50ODA copolymer also show selectivities above 1000 without exception. Moreover, they display water permeance almost two- or threefold as high as that of BPDA-based membranes. This result can be explained by the higher diffusion coefficient of water in the PMDA-based membranes, as observed in PMDA–ODA dense films.[18] Further study of water vapor sorption in the related polyimide dense membranes revealed that both water uptake and diffusion coefficient of water vapor in PMDA-based membrane are much higher than those of BPDA-based membranes. Accordingly, the permeability of water vapor in PMDA-based membrane would be higher than that of the BPDA-based membrane.
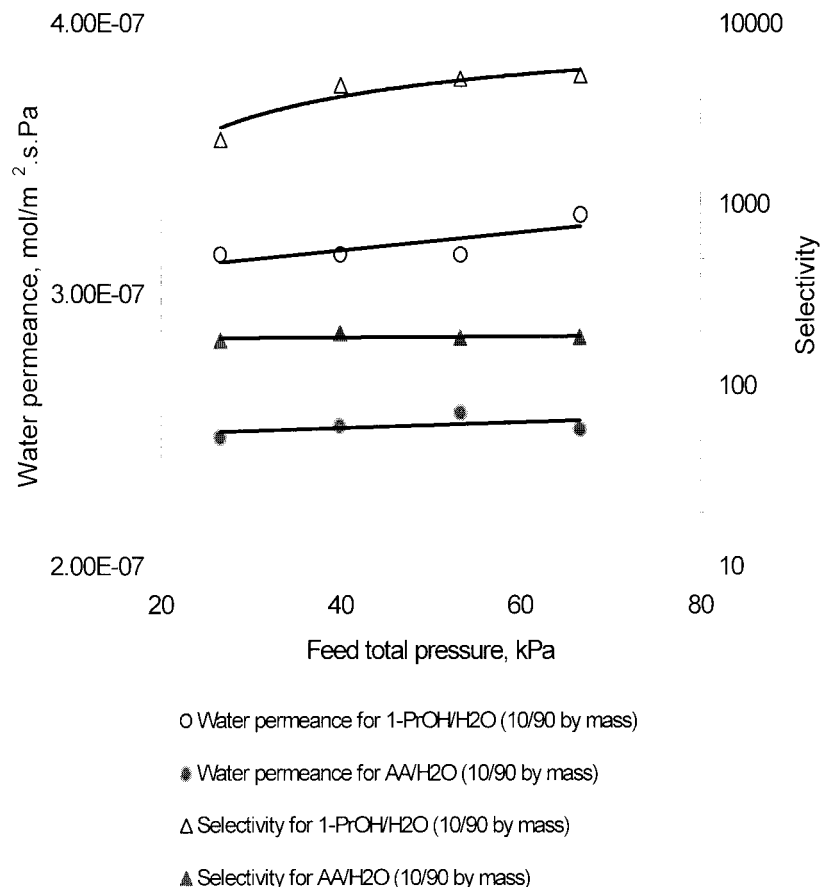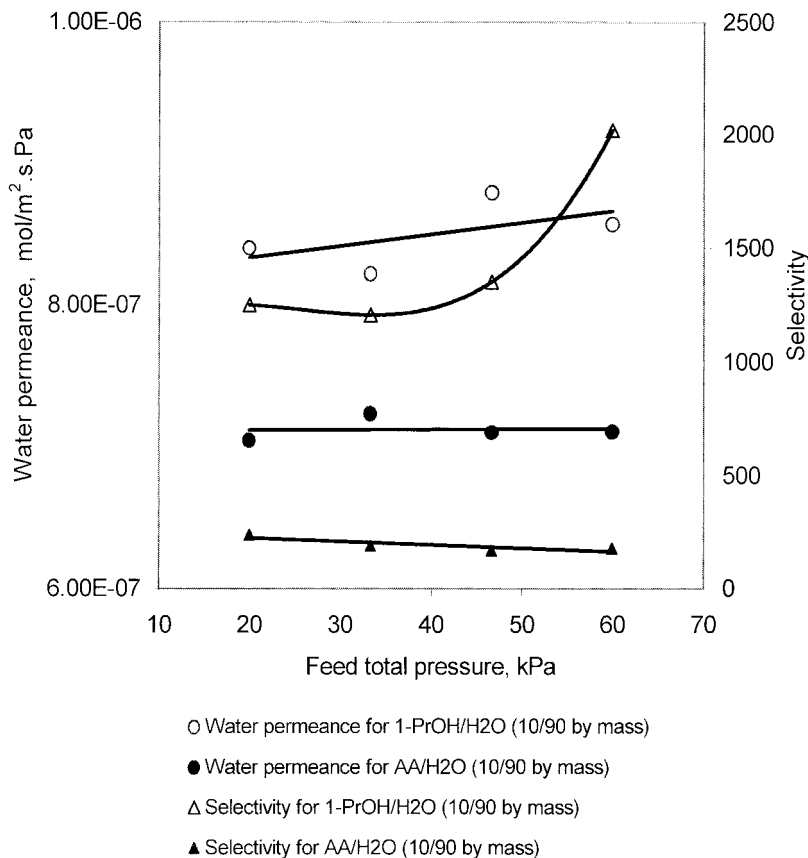
**Figure 9** Effect of upstream pressure on water permeance and selectivity for the copolyimide BPDA–50DDS/50ODA membrane (PHF-026-1): $T$, 105°C.

Similar vapor permeation characteristics are given in Figure 3 for AA/H$_2$O (50/50 by mass) separation by copolyimide membranes BPDA–50DDS/50ODA (PHF-026-1) and PMDA–50DDS/50ODA (PHF-024-2), and by the homopolymeric membranes BPDA–DDS, BPDA–ODA, and DSDA–TPE–R. It is seen that almost the same tendency exists for the membranes between the separation of 1-PrOH/H$_2$O (50/50 by mass) and AA/H$_2$O (50/50 by mass). The water permeance for BPDA–50DDS/50ODA membrane is $2.30 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, similar to that of BP-DA–DDS ($2.06 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) and BPDA–ODA ($2.32 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) membranes, and the selectivity is above 300. PMDA–50DDS/50ODA also shows selectivity above 300 for the separation of AA/H$_2$O, and the permeance for water vapor ($5.54 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) is almost 2.5-fold as high as that of BPDA-based membranes. DSDA–TPE–R showed poorer performance than did either BPDA–DDS or BPDA–ODA for the separation of AA/H$_2$O be-

cause of the long flexible chains of aromatic rings with a repeat unit containing two ether (–O–) linkages. Comparing separations of AA/H$_2$O and 1-PrOH/H$_2$O mixtures, water permeance is slightly lower and selectivity is much lower in AA/H$_2$O separation than that in 1-PrOH/H$_2$O separation. This is natural, given that AA has a smaller molecular size, as represented by the critical molar volumes shown in Table III, and a higher boiling point than that of 1-PrOH, which implies that AA may have both a higher diffusion coefficient and a higher sorption, and hence is more permeable in the membrane.

In short, the asymmetric membranes made from PMDA–50DDS/50ODA and BPDA–50DDS/50ODA are thus considered to be of practical usefulness for applications in the removal of the water from water/organic mixtures because of their excellent chemical stability and separation and permeation characteristics.

Figures 4 and 5 show the typical behavior of the polyimide membranes during the initial few

O Water permeance for 1-PrOH/H2O (10/90 by mass)

● Water permeance for AA/H2O (10/90 by mass)

△ Selectivity for 1-PrOH/H2O (10/90 by mass)

▲ Selectivity for AA/H2O (10/90 by mass)

**Figure 10**  Effect of upstream pressure on water permeance and selectivity for the copolyimide PMDA–50DDS/50ODA membrane (PHF-024-2): $T$, 105°C.

hours of operation period for the separation of 1-PrOH/$H_2O$ and AA/$H_2O$, respectively. A BPDA–50DDS/50ODA membrane coded as PHF-027 was used for this experiment. It can be seen from the figures that the permeances of water for 1-PrOH/$H_2O$ and AA/$H_2O$ mixtures are almost the same and both remain at $3.3 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ throughout the experiments. On the other hand, the selectivity for the separation of 1-PrOH/$H_2O$ mixture increases with time. After about 6 h, when the steady state is reached, the highest selectivity is achieved. This is the reflection of a decrease in 1-PrOH permeance from 2.09 to 1.22 $\times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. An opposite trend is observed for AA/$H_2O$ separation. The permeance of AA increases form 1.27 to $2.1 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$.

These phenomena can be explained by the combined effects of membrane plasticization by organic vapors, on one hand, and the formation of clusters of vapor molecules, on the other. Plasticization occurs when the sorption of vapor reaches such a high level that the mobility of

polymer segments increases, resulting in an increase in diffusion coefficient. Cluster formation lowers the diffusion coefficient, in that the size of a diffusion unit becomes larger than that of individual molecules.[11] However, plasticization seems to affect the permeation more in the polyimide membranes studied. As confirmed in our further study of water vapor sorption in the related dense membranes at 30°C, Zimm–Lundberg analysis of the isotherms of water vapor sorption in these membranes indicated the absence of water clustering.

**SEM Observation**

The membrane morphology was characterized by SEM for BPDA–50DDS/50ODA, BPDA–80DDS/20ODA, BPDA–DDS, BPDA–ODA, PMDA–TPE–R, and DSDA–TPE–R membranes. As an example, Figure 6 (a), (b), and (c) show, respectively, the cross section of a BPDA–DDS membrane, the cross sections near the external skin, and the internal skin surface of the membrane. It
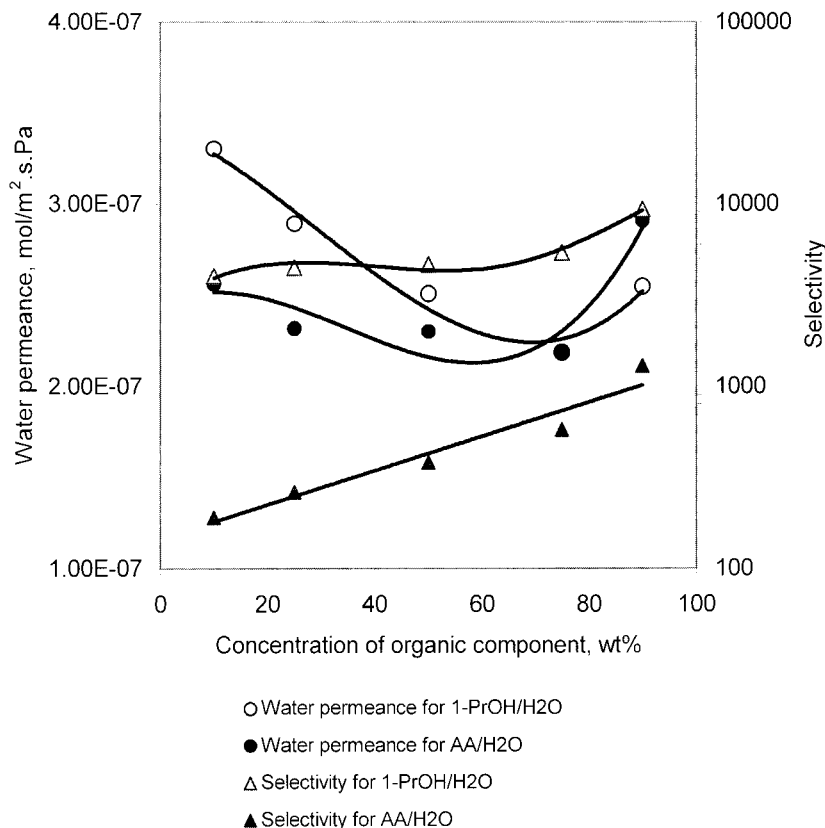
**Figure 11**  Effect of feed concentration on the separation performance for the copolyimide BPDA–50DDS/50ODA membrane (PHF-026-1): $T$, 105°C; feed total pressure, 40 kPa.

can be seen clearly that the presence of macrovoids, also called *fingerlike cavities,* extends from the internal skin surface up to about a half of the cross section of the membrane, before being connected through a spongelike body to the external skin surface. Dense skin layers both on the internal and on the external surfaces of the capillary membrane can be seen [see Fig. 6(b) and (c)], the external skin being much thicker than the internal skin. The external skin thickness is about 1.5 $\mu$m and the internal skin thickness is about 0.1 $\mu$m. Similarly, the dense skin layer thickness of the other membranes could also be approximately evaluated (see Table I).

### Effect of Test Conditions on Membrane Performance

#### Effect of Temperature

Normally, gas permeability through polymeric membranes increases with temperature. However, for condensable gases or vapors, the perme-

ation behavior may have a more complicated temperature dependency.[22,23] The permeation of small molecules through dense or nonporous membranes usually occurs by the solution–diffusion mechanism with two key steps: sorption of the penetrant molecules in the membrane and diffusion of the sorbed molecules through the membrane. Hence, the permeability $P$ can be formulated by diffusivity $D$ and solubility $S$[24,25]:

$$P = DS \tag{4}$$

Figures 7 and 8 illustrate the effect of temperature on membrane performance for the copolyimide BPDA–50DDS/50ODA (PHF-026-1) and PMDA–50DDS/50ODA (PHF-024-2) membranes, respectively. In both figures, the experimental results for the separation of water vapor from 1-PrOH/$H_2O$ (10/90 by mass) and AA/$H_2O$ (10/90 by mass) are shown. It can be seen that both water permeance and selectivity decrease with an increase in temperature. The effect of tempera-
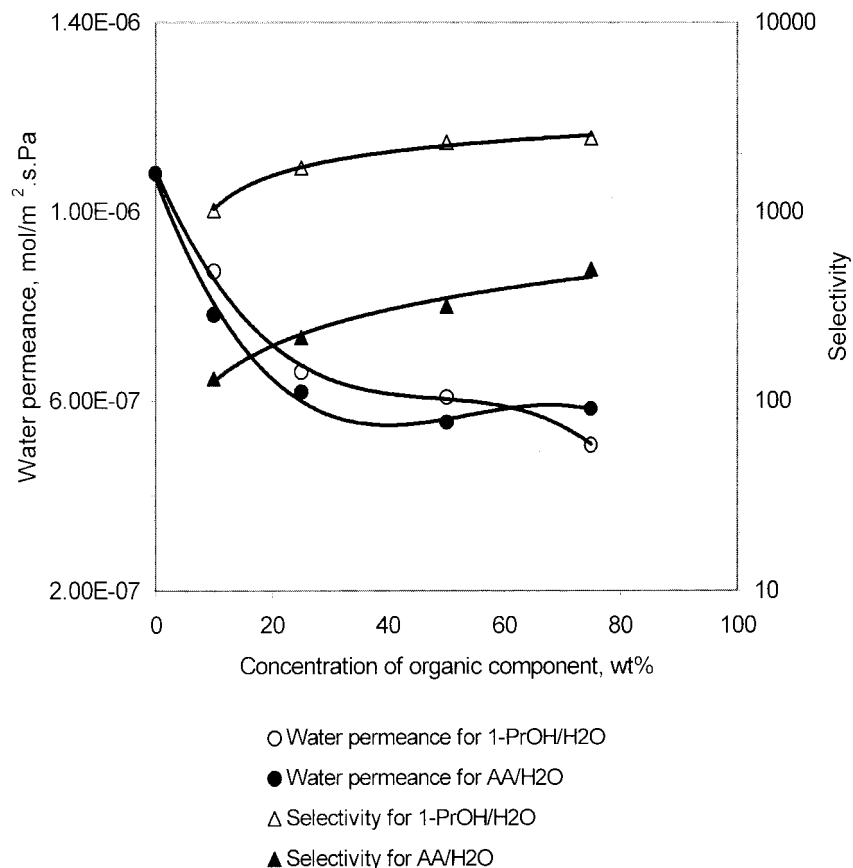
**Figure 12**   Effect of feed concentration on the separation performance for the copoly-imide PMDA–50DDS/50ODA membrane (PHF-024-2): $T$, 105°C; feed total pressure, 40 kPa.

ture on selectivity is greater for 1-PrOH/$H_2O$ than for AA/$H_2O$. Comparing the BPDA–50DDS/50ODA membrane with the PMDA–50DDS/50ODA membrane, the selectivity for AA/$H_2O$ decreases slightly for the former membrane, whereas it remains constant for the latter; and the water permeance of the PMDA–50DDS/50ODA membrane is more temperature sensitive than the BPDA–50DDS/50ODA membrane.

*Effect of Feed Pressure*

Figures 9 and 10 illustrate the effect of upstream pressure on the performance of the BPDA–50DDS/50ODA (PHF-026-1) and PMDA–50DDS/50ODA (PHF-024-2) polyimide membranes, respectively, at 105°C. Both water permeance and selectivity increase with increasing feed pressure for the separation of 1-PrOH/$H_2O$ (10/90 by mass) for both membranes, although the extent of increase in selectivity is greater for the PMDA–50DDS/50ODA membrane, particularly when the

feed pressure is high. In the case of AA/$H_2O$ (10/90 by mass), water permeance is independent of feed pressure for both membranes, whereas the selectivity is either independent of feed pressure (BPDA–50DDS/50ODA, Fig. 9) or decreases slightly (PMDA–50DDS/50ODA, Fig. 10) with an increase in pressure. At a constant temperature, the effect of total feed pressure on water permeance is mainly caused by the increase of sorption of water vapor in the membrane with an increase in partial pressure of water.

**Effect of Feed Concentration on Membrane Permeance and Selectivity**

Figures 11 and 12 show the variation of water permeance and selectivity as a function of the feed concentration of the organic components. The BPDA–50DDS/50ODA (PHF-026-1) and PMDA–50DDS/50ODA (PHF-024-2) membranes were used for these experiments at 105°C with a

feed pressure of 40 kPa, and a downstream pressure of 4 kPa, respectively. In general, water permeance decreases and selectivity increases with an increase in organic content in the feed. This may be attributed to the plasticization of the membrane by water at relatively low organic content in the feed.[26,27] However, for the copolyimide BPDA–50DDS/50ODA membrane an increase of water permeance is observed when the feed organic concentration is as high as 75 wt % (see Fig. 11). This could be explained by the plasticization that is contributed mostly by water, when the organic content is relatively low, whereas the organic components start to contribute to plasticization when their concentrations become high. Plasticization of membrane may decrease selectivity because of an increase of polymer segment mobility.

## CONCLUSIONS

The present study showed that the solvent-resistant polyimide capillary membranes with integrally skinned asymmetric structures, without pinholes, can be prepared from PMDA- and BPDA-based membrane materials by the dry/wet phase-inversion method. For the asymmetric polyimide membranes studied, a tendency similar to that of homogeneous dense membrane can be found, that is, membranes prepared from monomers in which both diamine- and dianhydride-containing rigid backbone and aromatic rings display higher permeability and selectivity. Test conditions exhibit influences on membrane separation performance. It was found that decreasing temperature or increasing feed pressure favors the separation of water vapor from organics in the polyimide membranes. Membranes prepared from copolyimide BPDA–50DDS/50ODA and PMDA–50DDS/50ODA exhibited the best mechanical and chemical properties along with excellent water vapor separation performance. These membranes are particularly useful in the removal of water from water/organic mixtures.

## REFERENCES

1. Fagernas, L.; Sipila, K. in Developments in Thermochemical Biomass Conversion; Bridgwater, A. V.; Boocock, D. G. B., Eds.; Chapman & Hall: London, 1997; pp 783–797.
2. Pakdel, H.; Amen-Chen, C.; Roy, C. Can J Chem Eng 1997, 75, 121.
3. Cranford, R. J.; Roy, C.; Matsuura, T. Can J Chem Eng 1997, 75, 471.
4. Paul, D. R.; Yampol'skii, Y. P. Polymeric Gas Separation Membranes; CRC Press: Boca Raton, FL, 1994; pp 100–127.
5. Marek, M., Jr.; Brynda, E.; Pientka, Z.; Brozova, L. Macromol Rapid Commun 1998, 19, 53.
6. Yamamoto, H.; Mi, Y.; Stern, S. A. J Polym Sci Part B: Polym Phys 1990, 28, 2291.
7. Hensema, E. R.; Smolders, C. A. in Gas Separation Technology; Vansant, E. F.; Dewolfs, R., Eds.; Elsevier Science: Amsterdam, 1990; pp 373–388.
8. Matsumoto, K.; Xu, P. J Appl Polym Sci 1993, 47, 1961.
9. Paul, D. R. Macromol Symp 1999, 138, 13.
10. Okamoto, K.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. J Membr Sci 1992, 68, 53.
11. Ozcayir, Y. F.; Goetz, G.; Bikson, B. U.S. Pat. 5,725,633, 1998.
12. Chabot, S.; Roy, C.; Chowdhury, G.; Matsuura, T. J Appl Polym Sci 1997, 65, 1263.
13. Bell, V. L.; Stump, B. L.; Gager, H. J Polym Sci 1976, 14, 2275.
14. Hao, J.; Tanaka, K.; Kita, H.; Okamoto, K. J Polym Sci Part A: Polym Chem 1998, 36, 485.
15. Matsumoto, K.; Xu, P. J Membr Sci 1996, 61, 1615.
16. Mi, Y.; Hirose, T. J Polym Res 1996, 3, 11.
17. Friesen, D. T.; McCray, S. B.; Newbold, D. D.; Ray, R. J. U.S. Pat. 5,753,008, 1998.
18. Han, H.; Seo, J.; Ree, M.; Pyo, S. M.; Gryte, C. C. Polymer 1998, 39, 2963.
19. Atkins, P. W. Physical Chemistry, 6th ed.; Freeman: New York, 1998; p 920.
20. Van Krevelen, D. W. Properties of Polymers, 3rd ed.; Elsevier Science: Amsterdam, 1990; pp 774–789.
21. Reid, R. C.; Sherwood, T. K. Properties of Gases and Liquids (Chemical Engineering Series); McGraw-Hill: New York, 1958; p 30.
22. Yeom, C. K.; Lee, S. H.; Lee, J. M. J Appl Polym Sci 2000, 78, 179.
23. Vieth, W. R. Diffusion in and through Polymers: Principles and Applications; Carl Hanser Verlag: New York, 1991; pp 73–78.
24. Bicerano, J. Prediction of Polymer Properties; Marcel Dekker: New York, 1993; pp 318–331.
25. Stern, S. A. in Industrial Processing with Membranes; Lacey, R. E.; Loeb, S., Eds.; Wiley: New York, 1972; pp 279–299.
26. Vieth, W. R. Diffusion in and through Polymers: Principles and Applications; Carl Hanser Verlag: New York, 1991; p 212.
27. Ray, S. K.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. J Membr Sci 1998, 138, 1.