Diamine Modification of P84 Polyimide Membranes for Pervaporation Dehydration of Isopropanol

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The effectiveness of chemical crosslinking modification of P84 copolyimide membranes using diamine compounds for pervaporation dehydration has been investigated and the scheme to enhance separation performance of asymmetric polyimide membranes has been developed. Two diamine crosslinking agents, p-xylenediamine and ethylenediamine (EDA), were used in this study for both dense and asymmetric P84 membranes. Experimental results suggest that the crosslinking reaction induced by EDA is much faster than that by p-xylenediamine because the former has a smaller and linear structure than that of the latter. However, membranes crosslinked by p-xylenediamine are thermally more stable than those by EDA. Membranes modified by p-xylenediamine or EDA have increased hydrophilicity. An increase in the degree of crosslinking reaction initially results in an increase in separation factor with the compensation of lower flux for pervaporation dehydration of isopropanol (IPA). However, a further increase in the degree of crosslinking reaction may swell up the polymeric chains because of the hydrophilic nature of these diamine compounds, thus resulting in low separation performance. It is found that post treatment after crosslinking reaction can significantly enhance as well as tailor membrane performance because of the formation of charge transfer complexes (CTCs) and the enhanced degree of crosslinking reaction. A low-temperature heat treatment may develop pervaporation membranes with high flux and medium separation factor, whereas a high-temperature heat treatment may produce membranes with high separation factor with medium flux. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3462–3472, 2006

Keywords: P84 copolyimide membranes, crosslinking, pervaporation, dehydration, isopropanol

Introduction

An azeotrope of isopropanol (IPA) and water mixture can be effectively and economically separated by pervaporation. To develop high-performance pervaporation membranes for the dehydration of IPA, superior selectivity, permeability, and stability of the membrane are the most important criteria. According to the solution-diffusion mechanism in pervaporation,[1,2] high selectivity and permeability can be achieved if one component has more affinity to the membrane and can diffuse faster in the membrane than the others. As for pervaporation dehydration membranes, water is the component that is preferentially absorbed and transported through the membrane. Therefore, in the earlier stage of developing pervaporation dehydration membranes, significant attention has been given to highly hydrophilic materials that have superior water sorption. However, membranes made from highly hydrophilic materials such as polyacrylic acid (PAA), polyvinyl alcohol (PVA), agarose, alginate, and chitosan exhibited excessive swelling in water and showed poor stability. Through modifications such

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as crosslinking or blending, the stability and the resistance to swelling of these membranes were significantly enhanced.[3-8] The successful commercialization of Sulzer membranes made of a crosslinked PVA-selective layer that can withstand water and many solvents is one example.

With easy processability, thermal stability, chemical resistance, and mechanical strength,[9] polyimide has emerged as an important membrane material for various membrane applications. In pervaporation, polyimide exhibits high selectivity to water but relatively low flux, which may be attributed to its poor hydrophilicity or compact chain packing.[10] Attempts have been made to modify polyimide membranes for better performance. Blending is a simple and economic way to combine the favorable properties of two polymers. Su et al.[11] blended polyimide with doped polyaniline and found considerable improvement of selectivity for water/acetic acid. Recently Chung and coworkers[12] successfully enhanced the hydrophilicity of Matrimid® by blending Matrimid® with a highly hydrophilic polymer: polybenzimidazole (PBI). The performance of the blended Matrimid®/PBI membranes for the dehydration of *tert*-butanol was improved with the addition of a small amount of PBI. Plasma treatment is another way to modify the properties of polyimide. Kaba et al.[13] found that the wettability of polyetherimide (PEI) dense films and the selectivity of the membrane can be significantly improved by the anallylamine–plasma polymerized layer for the dehydration of ethanol. Crosslinking modification of polyimide has been extensively studied in the preparation of gas separation membranes; however, the crosslinking modification of polyimide is seldom used for pervaporation dehydration. Sullivan et al.[14] applied an alternating polyelectrolyte deposition method on top of a porous alumina support and used the reaction between poly(amide acids) containing diaminobenzoic acid (DABA) and poly(allylamine) under heat treatment at 250°C to form a thin layer of polyimide film with amide crosslinks. The amide crosslinks enhanced the selectivity of water/alcohol with relatively high flux. Compared to other modification methods, crosslinking is of great interest because of its applicability and effectiveness to improve both the stability and the performance of polyimide membranes.

Hayes at Du Pont may be the pioneer conducting novel modification methods based on chemicals containing amine groups to modify polyimide gas separation membranes.[15] Heat treatment at $>70°C$ was recommended to complete the crosslinking reaction. Liu et al.[16] discovered a diamine compound—*p*-xylenediamine—that can effectively crosslink 6FDA-durene and 6FDA-durene/mPDA dense films at room temperature. The resultant membranes have improved selectivity for certain gas pairs with reduced permeability. Cao et al.[17] extended the study by using both *p*-xylenediamine and *m*-xylenediamine to crosslink 6FDA-2,6 DAT hollow-fiber membranes for natural gas separation. Tin et al.[18] investigated the applicability of *p*-xylenediamine to commercially available Matrimid® polyimide. Later Shao et al.[19] explored an aliphatic crosslinking agent, ethylenediamine (EDA), which exhibits unique crosslinking characteristics for fluoro-polyimides after thermal treatment. All of the above studies found that the CO_2 plasticization can be effectively suppressed after crosslinking. Besides, the effects of crosslinking modifications on membrane permeability and selectivity appear to be strongly dependent on polymeric composition, structure, and crosslinking agents.

During the crosslinking, the hydrophilic diamines are introduced to the polyimide backbone, forming amide groups and establishing intermolecular bonds. Therefore this type of crosslinking modification has the potential to enhance the pervaporation performance of a polyimide membrane. However, to our best knowledge, the effects of crosslinking modification of polyimide membranes with diamine compounds on pervaporation performance have not been well studied. P84 copolyimide was chosen for this study because it is a promising material for pervaporation.[10,20,21] In addition, detailed studies on the crosslinking modification of P84 copolyimide membranes with diamine compounds are still lacking. The difficulties of crosslinking P84 probably arise from its superior chemical resistance. The small free volume of P84 dense films compared with those membranes made from polyimides containing fluorine groups such as 6FDA-polyimide or bulky side groups such as Matrimid® 5218[22] also creates difficulties for crosslinking reactions to take place.

The aim of this study was to investigate the effects of crosslinking with diamine compounds on the pervaporation performance of P84 membranes for the dehydration of IPA. Two crosslinking agents, *p*-xylenediamine and EDA, were selected and their effects on both dense and asymmetric P84 membranes were compared. The chemical structure and physical properties of these two crosslinking agents are shown in Table 1. The effect of heat treatment on the crosslinked P84 membranes was also studied. The simple crosslinking method may have significant potential for developing pervaporation membranes in real industrial applications.

Experimental

Materials

The P84 copolyimide (BTDA-TDI/MDI, copolyimide of 3,3′4,4′-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine) was purchased from HP Polymer GmbH (Lenzing, Austria). The polymer was dried overnight at 120°C under vacuum before use. *p*-Xylenediamine and EDA were purchased from Sigma-Aldrich. The chemicals were used as received and their chemical structure and properties are listed in Table 1.

Fabrication of dense and asymmetric membranes

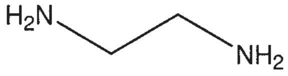
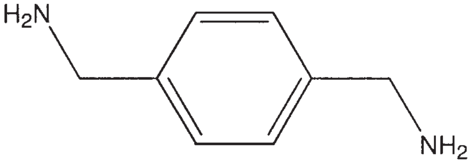
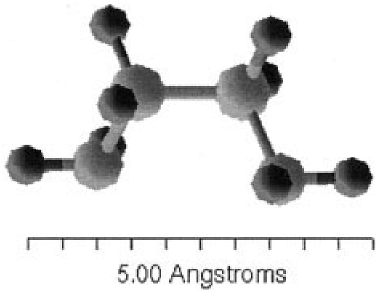
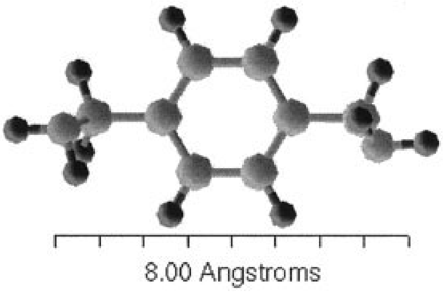
Both dense and asymmetric flat membranes were prepared according to the methods described elsewhere.[10]

Chemical and thermal modification of membranes

A 2.5% (w/v) crosslinking solution was prepared by dissolving *p*-xylenediamine or EDA in methanol. The dense or asymmetric membranes were immersed into the crosslinking solution for a certain time. After that, membranes were taken out from the solution and then washed with fresh methanol to remove the residual crosslinking agents. The membranes were finally dried in air at room temperature.

Heat treatment of membranes was conducted in a Centurion™ Neytech Qex vacuum furnace, by increasing temperature at a rate of 0.6°C/min to a certain temperature, and then held there for 6 h under vacuum.

Table 1. The Chemical and Physical Properties of the Selected Crosslinking Agents

Property	Ethylenediamine (EDA)	*p*-Xylenediamine
Chemical structure		
Molecular weight	60	136
Molecular dimension*		
Boling point (°C)	117	230
Melting point (°C)	8.5	61

*Simulated by Cerius2 software.

Pervaporation experiments

Pervaporation tests were carried out using a lab-scale Sulzer pervaporation unit[23] according to detailed experimental procedures reported elsewhere.[10] Alcohol/water mixtures (85/15 in weight ratio) were used as the feed. Flux and separation factor (SF) were calculated by the following equations:

$$J = \frac{Q}{At} \tag{1}$$

$$SF = \frac{y_2/y_1}{x_2/x_1} \tag{2}$$

where J is the flux; Q is the total mass transferred over time t; A is the membrane area; x_2 and y_2 are the mole fractions of water in the feed and permeate, respectively; and x_1 and y_1 are the mole fractions of alcohol in the feed and permeate, respectively. The feed composition and permeate side pressure were kept constant to focus on the effects of crosslinking. Two to three samples were tested and the data were averaged.

If the dependency of permeation flux on temperature follows the Arrhenius-type relation

$$J = J_0 \exp(-E_J/RT) \tag{3}$$

where E_J is the apparent activation energy of permeation and J_0 is the preexponential factor, then E_J can be obtained from the plot of ln J vs. $1/T$.

Based on the solution-diffusion mechanism, the basic transport equation for pervaporation can be written as follows[24]:

$$J_i = \frac{P_i}{l}\,(x_i \gamma_i p_i^s - y_i p^p) \tag{4}$$

where P_i is the membrane permeability, which is a product of solubility and diffusivity; superscripts s and p correspond to the saturated state and permeate, respectively; l is the membrane dense layer thickness; p_i denotes the partial vapor pressure, whereas P_i/l is the permeance; γ is the activity coefficient. The permeance and selectivity (the permeance ratio) can be calculated from the flux and separation factor following the approach described elsewhere.[23-25] In this article, both flux/separation factor and permeance/selectivity were included for the reader's information. The activation energy based on permeance (E_p) is evaluated based on the Arrhenius-type relation between permeance and temperature.

Membrane characterizations

An attenuated total reflection (ATR) FT-IR (Perkin-Elmer FT-IR spectrometer, Norwalk, CT) was used to examine the degree of chemical crosslinking with a scan number of 16. The X-ray photoelectron spectroscopy (XPS) measurements were carried out by an AXIS His spectrometer (Kratos Analytical Ltd., Manchester, UK) using the monochromatized Al–K$_\alpha$ X-ray source (1486.6 eV photons) at a constant swell time of 10 ms and a pass energy of 40 eV. The reflection UV spectra were obtained in the range of 200–800 nm with a UV-3101 PC (Shimadzu, Kyoto, Japan).

Wide-angle X-ray diffraction (XRD) measurements of the membranes were carried out by a Bruker X-ray diffractometer (Bruker D8 advanced diffractometer, Bruker AXS GmbH, Karlsruhe, Germany) at room temperature using the Cu–K$_\alpha$ radiation wavelength (λ = 1.54 Å) at 40 kV and 30 mA. The average intersegmental distance of polymer chains was reflected by the broad peak center on each X-ray pattern. The *d*-space was calculated by the Bragg's equation

$$n\lambda = 2d \sin\theta \tag{5}$$

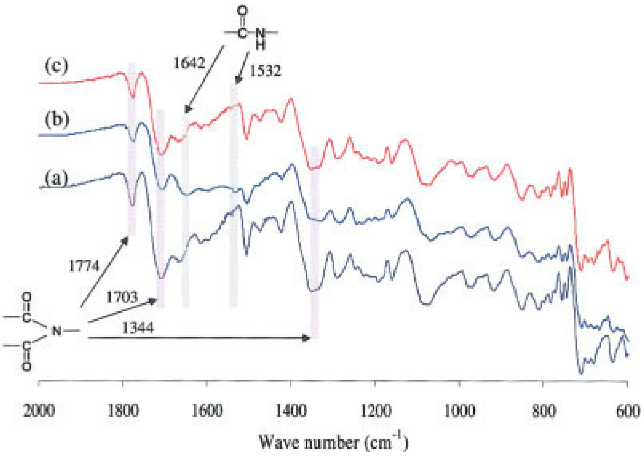


Figure 1. ATR-FTIR spectra of unmodified and modified P84 dense membranes.

(a) P84 original dense film; (b) P84 dense film crosslinked by EDA for 4d; (c) P84 dense film crosslinked by p-Xylenediamine for 4d. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

where θ is the X-ray diffraction angle of the peak.

The densities of dense films were measured by a Mettler-Toledo balance (Columbus, OH) coupled with a density kit based on the Archimedes' principle. The weights of samples in air (w_{air}) and in a known density liquid, that is, HPLC ethanol ($w_{ethanol}$) at room temperature, were used to calculate the density as follows:

$$\rho_{\text{membrane}} = \frac{w_{\text{air}}}{w_{\text{air}} - w_{\text{ethanol}}} \rho_{\text{ethanol}} \tag{6}$$

At least three samples were tested and the data were averaged.

The morphology of asymmetric membranes was observed by using a JSM-6700F field emission scanning electron microscope (FESEM). Samples were prepared by fracturing membranes in liquid nitrogen then coated with platinum. Nanoindentation tests were conducted by an ASI Ultra Micro Indentation System (Canberra, Australia).

The contact angle measurements were performed by a Ramé-Hart contact angle goniometer (model 100-22, Mountain Lakes, NJ) at room temperature. Deionized water droplets were introduced by a Gilmont microsyringe onto the membrane surface. About 4 mm in diameter of liquid droplets formed on the sample surface and the contact angle was measured. At least ten droplets were introduced and the average contact angle data was taken for each membrane.

Results and Discussion

Characterization of P84 membranes crosslinked with p-xylenediamine

Figure 1 shows the ATR-FTIR spectra of the original and 4-day crosslinked P84 dense films. One can observe that the imide characterization peaks at 1774 cm^{-1} (C═O asymmetric stretch), 1703 cm^{-1} (C═O symmetric stretch), and 1344 cm^{-1} (C—N stretch)[19] are almost unchanged after crosslinking. Probably as a result of the superior chemical resistance, small free volume of P84 dense films, and the large molecular size of *p*-xylenediamine, the crosslinking agent penetrates into the dense film with difficulty. Therefore, the crosslinking reaction can take place only at the surface. The density of the 4-day *p*-xylenediamine crosslinked P84 films is slightly lower than that of the original P84 dense films (Table 2). Because the crosslinking is a combined process that includes swelling by methanol and incorporating of crosslinking molecules,[16] the decreased density can be regarded as the combination effects of the swelling of P84 films in methanol and the slow crosslinking rate with *p*-xylenediamine.

Table 2. The Density of the Original and Crosslinked Dense Films

Membrane	Density (g/cm^3)
P84 dense film	1.355
4d *p*-Xylenediamine crosslinked P84 dense film	1.337
4d EDA crosslinked P84 dense film	1.346

However, when we compare ATR-FTIR spectra of the original and crosslinked P84 asymmetric membranes, as shown in Figure 2, the difference is more distinct than that in crosslinked dense films. Because of the porous structure and thin skin layer of asymmetric membranes, the crosslinking agent can easily attack the macromolecules and the reaction takes place much faster than that in dense films. Figure 2 illustrates the ATR-FTIR spectra of P84 asymmetric membranes immersed in a 2.5% (w/v) *p*-xylenediamine methanol solution at varied time intervals. With increased immersion time, the characteristic peaks for imide at around 1774, 1703, and 1344 cm^{-1} gradually disappear, whereas the characteristic peaks for amide groups, that is, 1642 cm^{-1} (C═O stretching) and 1532 cm^{-1} (C—N stretching of the C—N—H group)[19] increase progressively.

XPS results also suggest the growth of nitrogen content on the surface of the asymmetric membranes. Because the crosslinking modification should neither introduce oxygen nor destroy the oxygen from the polymer backbone, the oxygen

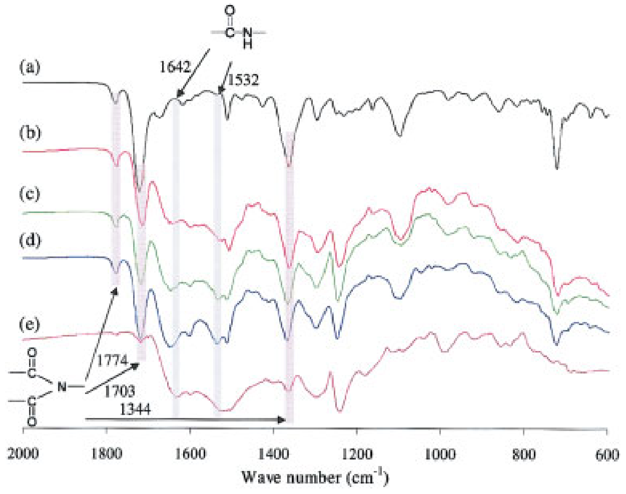


Figure 2. ATR-FTIR spectra of original and modified P84 asymmetric membranes.

(a) P84-original; (b) P84-ckp-1hr; (c) P84-ckp-4hr; (d) P84-ckp-6hr; (e) P84-ckeda-4hr (see Table 3 for membrane ID definition). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Table 3. XPS Analysis of the Original and Modified P84 Asymmetric Membrane Surface

Membrane	Membrane ID	Atomic (%) O_{1s}	Atomic (%) N_{1s}	N_{1s}/O_{1s}
—	P84-original (calculated)	14.60	5.84	0.40
P84 original asymmetric membranes	P84-original (experimental)	14.17	5.7	0.40
2-h *p*-Xylenediamine crosslinked asymmetric membranes	P84-ckp-2hr	13.85	8.11	0.58
4-h *p*-Xylenediamine crosslinked asymmetric membranes	P84-ckp-4hr	13.13	8.15	0.62
6-h *p*-Xylenediamine crosslinked asymmetric membranes	P84-ckp-6hr	12.37	9.5	0.77
4-h EDA crosslinked asymmetric membranes	P84-ckeda-4hr	14.74	11.38	0.77
6-h EDA crosslinked asymmetric membranes	P84-ckeda-6hr	13.44	11.91	0.89
2-h *p*-Xylenediamine crosslinked and 100°C heat-treated asymmetric membranes	P84-ckp-2hr-100°C	15.63	9.01	0.58
2-h *p*-Xylenediamine crosslinked and 200°C heat-treated asymmetric membranes	P84-ckp-2hr-200°C	16.50	8.44	0.51

content can be used as a reference. The ratio of N_{1s} to O_{1s} can thus be considered as an indication of the crosslinking degree. As shown in Table 3, the ratio of N_{1s} to O_{1s} increases with crosslinking time. Additionally, the apparent N_{1s} peak (Figure 3) is broadened and shifted from a higher binding energy (attributed to N—C═O groups, about 400 eV) to a lower binding energy (attributed to C—N groups, about 399 eV), which implies the formation of amide.[13] On the basis of FTIR and XPS results, a reaction mechanism is proposed in Figure 4, which is similar to the crosslinking of 6FDA-polyimde[17] and Matrimid®.[18]

XRD spectra as shown in Figure 5 reveal that the peaks gradually shift to the right after crosslinking, indicating the *d*-space decreases significantly. This may be the result of both hole-filling and networking effect of *p*-xylenediamine molecules in between the polymer chains.

Table 4 shows that the contact angle decreases with an increase in crosslinking time. As we have hypothesized, as more amide groups form on the membrane surface, the hydrophilicity of the membrane increases.

Morphology and mechanical property changes of the modified membranes were examined by FESEM and nanoindentation tests. Clearly in Figure 6, the cross section of the selective skin layer apparently becomes densified after crosslinking. Correspondingly, there are appreciable enhancements in both hardness and modulus of elasticity (Table 5). In addition, the different surface morphologies of crosslinked membranes are probably due to the clusters formed by crosslinking agents (Figure 6), which results from the attached crosslinking molecules. The modulus of elasticity is an indication of the interatomic bonding forces, manifesting the intra-/interpolymer chain bonding formed and the increase of dense layer thickness. The formation of amide linkage reduces the interstitial space between polymer chains and restricts the free rotation of polymer chains, thus increasing rigidity of the polymer chain. Besides, the greater modulus indicates that the membrane is much stiffer after modification.

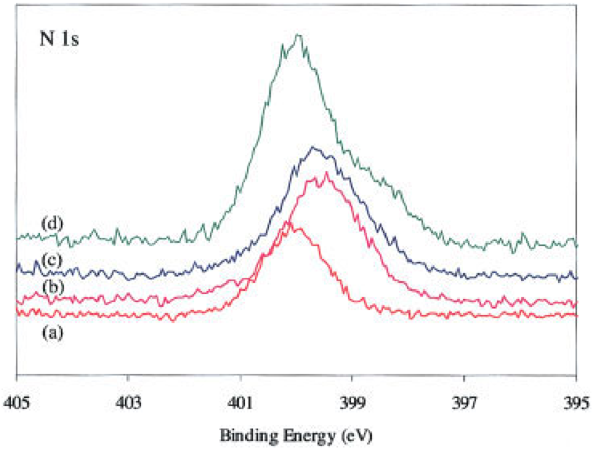


Figure 3. N_{1s} **XPS spectra of original and *p*-xylenediamine modified asymmetric P84 membranes.**

(a) P84-original; (b) P84-ckp-2hr; (c) P84-ckp-2hr-100°C; (d) P84-ckp-2hr-200°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Pervaporation performance of P84 asymmetric membranes crosslinked with p-xylenediamine

The pervaporation performance of membranes crosslinked with *p*-xylenediamine at different time intervals is shown in Table 6. The flux decreases initially then increases after a 6-h immersion. The separation factor is significantly improved and reaches the highest value after a 4-h crosslinking reaction, and then decreases with a prolonged immersion time. The reduced interstitial space as shown in Figure 5, densification of the skin layer, and the increased hydrophilicity as shown in Table 4 may be the major causes leading to the enhanced selectivity and reduced flux. However, after a prolonged immersion time, the higher crosslinking degree increases the transport resistance of the subsupport layer. In addition, as immersion time increases, chain branching may also occur. With more and more hydrophilic groups introducing onto the membrane, the resultant membrane can be easily swelled, which deteriorates performance of the membrane.

Characterization and pervaporation performance of P84 membranes crosslinked with ethylenediamine (EDA)

Compared to *p*-xylenediamine, the molecular size of EDA is much smaller. As a consequence, it can more easily penetrate into the membrane. Figure 1 also compares the ATR-FTIR spectra of the original and 4-day EDA crosslinked P84 dense films. Amide peaks can be easily found in 4-day EDA crosslinked films. Although the density of EDA crosslinked dense films is less than that of the original dense film (Table 2), it is slightly higher than that of the *p*-xylenediamine crosslinked films. The higher density can be attributed to the faster crosslinking rate of EDA.

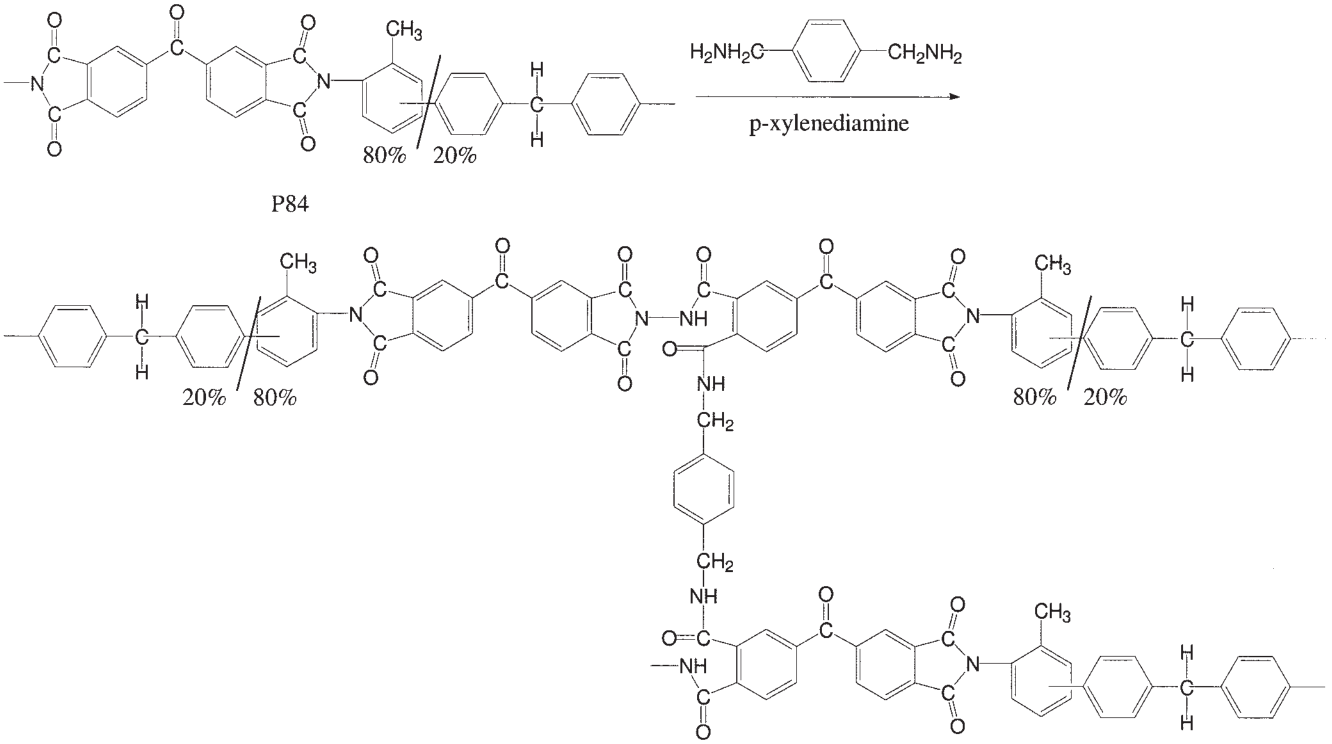


Figure 4. Proposed crosslinking mechanism for P84 copolyimide with *p*-xylenediamine.

ATR-FTIR in Figure 2 compares the 4-h crosslinked asymmetric membranes with EDA and *p*-xylenediamine. The intensity of the amide peaks after 4-h EDA crosslinking is apparently greater than that of a 4-h *p*-xylenediamine crosslinked membrane. As shown in Table 3, the N_{1s}/O_{1s} ratio of a 4-h EDA crosslinked membrane is greater than that of a 4-h *p*-xylenediamine crosslinked membrane. This again confirms that the crosslinking reaction with EDA as a crosslinking agent is faster than that with *p*-xylenediamine.

Compared to *p*-xylenediamine crosslinked membranes, a thicker densified skin layer of the cross section and a much rougher surface of the 4-h EDA crosslinked membranes can be observed by FESEM as shown in Figure 6. In addition, Table 5 indicates that the 4-h EDA crosslinked membrane has a

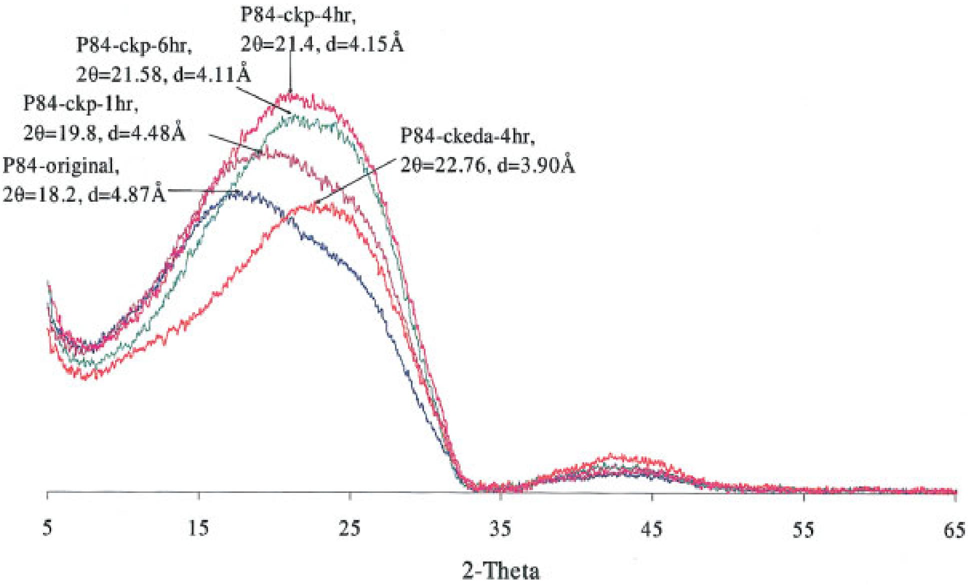


Figure 5. XRD spectra of the original and modified asymmetric P84 membranes.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Table 4. Contact Angles of the Original and Modified P84 Asymmetric Membranes

Membrane	Contact Angle (°)
P84-original	67.0
P84-ckp-2hr	65.9
P84-ckp-4hr	64.8
P84-ckp-6hr	61.4
P84-ckeda-4hr	60.8
P84-ckp-2hr-100°C	68.2
P84-ckp-2hr-200°C	75.8

Table 5. Nanoindentation Results of the Original and Modified P84 Asymmetric Membranes

Membrane	Hardness (GPa)	Modulus (GPa)
P84-original	0.08	0.62
P84-ckp-4hr	1.28	4.43
P84-ckeda-4hr	1.26	6.89
P84-ckp-2hr	0.63	3.13
P84-ckp-2hr-100°C	0.94	4.60
P84-ckp-2hr-200°C	3.10	6.69

similar hardness but a higher modulus than that of the 4-h *p*-xylenediamine crosslinked membrane, which is attributed to the thicker dense layer and higher degree of crosslinking modification. The lower contact angle of the 4-h EDA crosslinked membranes (Table 4) than that of 4-h *p*-xylenediamine crosslinked membranes shows that the former is more hydrophilic than the latter.

Table 7 summarizes the pervaporation performance of EDA crosslinked P84 asymmetric membranes. The flux decline of EDA crosslinked membranes is much more drastic than *p*-xylenediamine crosslinked membranes because of their thicker and more densified skin layer. After 1-h crosslinking with EDA, the flux drops 60% of the value of the original membranes, whereas the flux drop of 1-h *p*-xylenediamine crosslinked membranes is only 38%. However, the increase of separation factor by 1 h EDA crosslinking is more prominent than that with 1-h *p*-xylenediamine crosslinking. Similar to *p*-xylenediamine crosslinked membranes, the flux decreases and reaches the lowest point after 2-h crosslinking with EDA, then increases. On the other hand, the separation factor reaches a maximum with 2-h EDA crosslinking, then decreases. As mentioned earlier, this phenomenon may result from the increased hydrophilicity, which induces severe swelling. Therefore, to modify and enhance polyimide materials for pervapo-

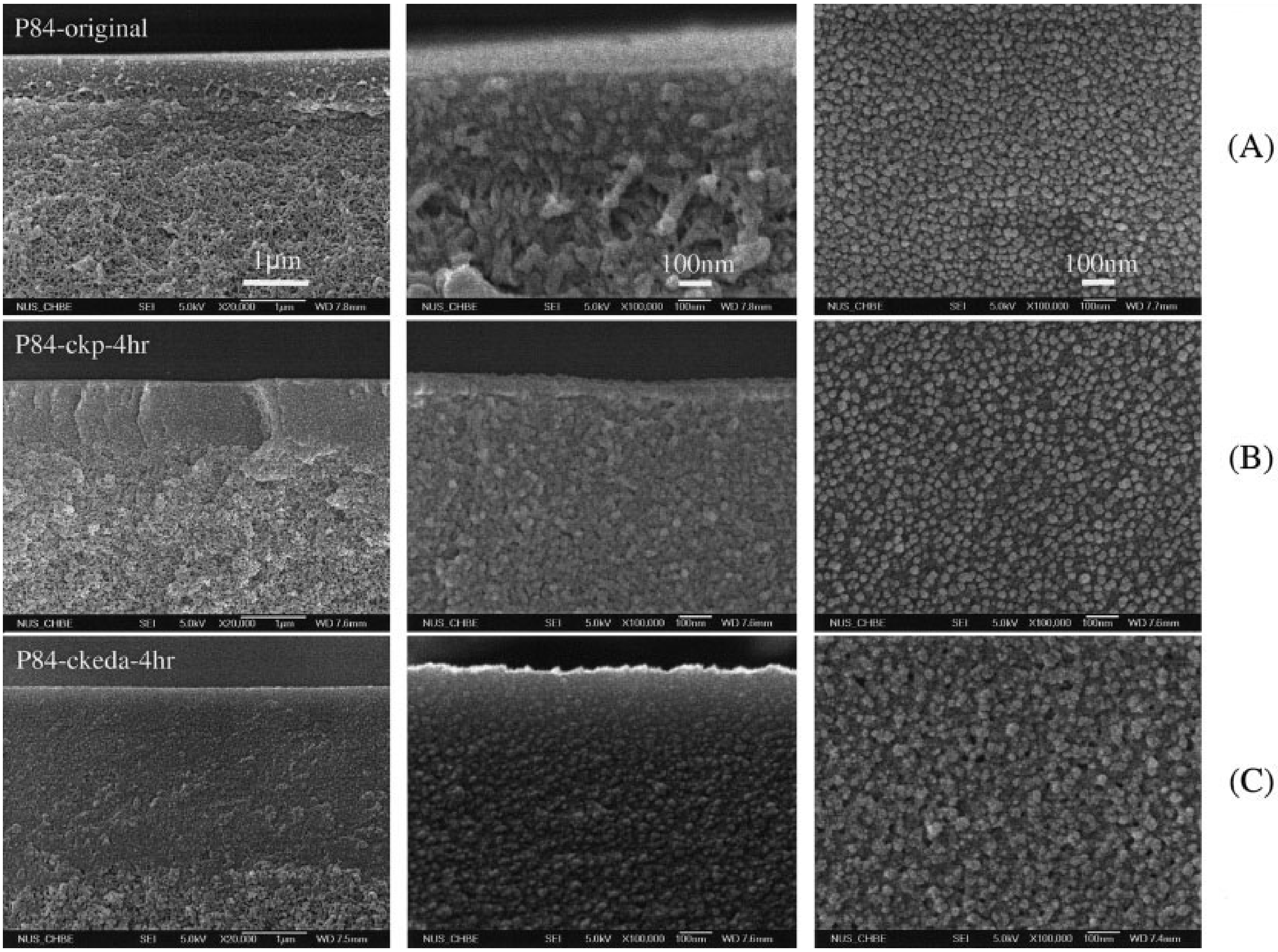


Figure 6. Morphology of the cross section, top-skin layer (middle), and surface (right) of (A) original asymmetric membrane; (B) *p*-xylenediamine crosslinked 4 h; and (C) EDA crosslinked 4 h.

Table 6. Pervaporation Performance of the Original and *p*-Xylenediamine Crosslinked P84 Asymmetric Membranes

Membrane	Operating T (°C)	Feed Water (wt %)	Permeate Water (wt %)	Flux (g m^{-2} h^{-1})	SF	Permeance (g m^{-2} h^{-1} kPa^{-1}) Water	Permeance (g m^{-2} h^{-1} kPa^{-1}) IPA	Selectivity
P84-original	60	15	73.38	2578	16	127.4	23.87	5
P84-ckp-1hr	60	15	96.85	1599	174	104.3	1.75	59
P84-ckp-2hr	60	15	97.09	1398	189	91.38	1.42	65
P84-ckp-4hr	60	15	98.88	1015	505	67.6	0.40	170
P84-ckp-6hr	60	15	97.66	1143	236	75.2	0.93	81

ration dehydration applications, the hydrophilic and hydrophobic groups in the modified membrane material must be well balanced.[26]

Effect of heat treatment on p-xylenediamine crosslinked membrane

The thermal stability of modified asymmetric membranes was investigated by TGA before conducting heat treatment. As shown in Figure 7, the original P84 membrane is thermally stable up to 400°C. The first decomposition peak at <100°C is attributed to the release of absorbed water. The decomposition peak at around 300°C for the 2- and 4-h *p*-xylenediamine crosslinked membranes suggests that most weight loss of *p*-xylenediamine occurred at this temperature. The decomposition peak of the 4-h EDA crosslinked membrane is at about 250°C. Because of the energy needed to break the formed

Table 7. Pervaporation Performance of the Original and EDA Crosslinked P84 Asymmetric Membranes

Membrane	Operating T (°C)	Feed Water (wt %)	Permeate Water (wt %)	Flux (g m^{-2} h^{-1})	SF	Permeance (g m^{-2} h^{-1} kPa^{-1}) Water	Permeance (g m^{-2} h^{-1} kPa^{-1}) IPA	Selectivity
P84-original	60	15	73.38	2578	16	127.4	23.87	5
P84-ckeda-1hr	60	15	98.86	1012	490	67.4	0.40	167
P84-ckeda-2hr	60	15	99.07	534	604	35.7	0.17	206
P84-ckeda-3hr	60	15	98.58	911	392	60.5	0.45	134
P84-ckeda-4hr	60	15	97.72	1104	242	72.6	0.88	83

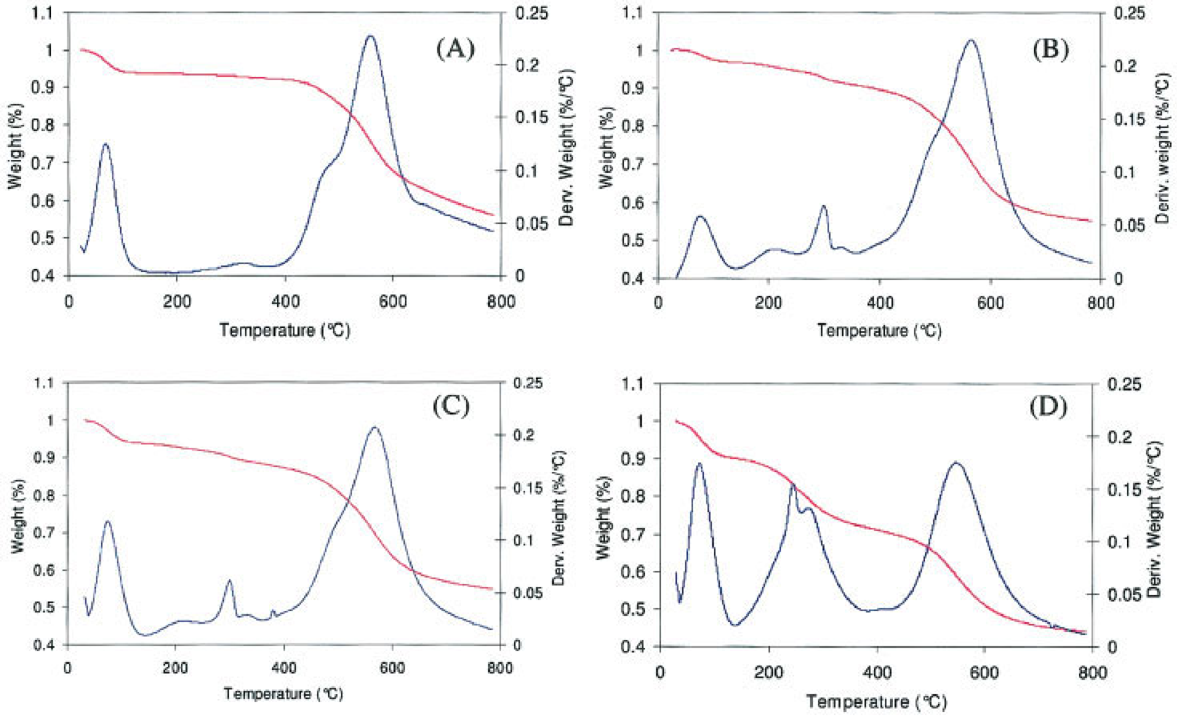


Figure 7. TGA of the original and modified asymmetric membranes.

(A) The original; (B) *p*-xylenediamine crosslinked 2 h; (C) *p*-xylenediamine crosslinked 4 h; (D) EDA crosslinked 4 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

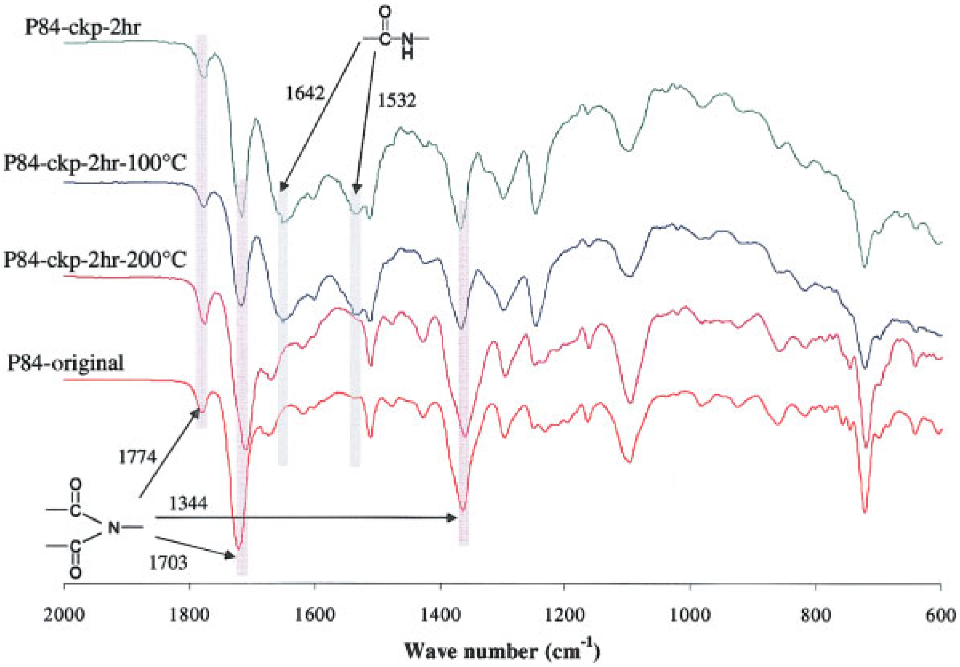


Figure 8. ATR-FTIR spectra of the original, 2-h *p*-xylenediamine crosslinked membranes with/without heat treatment.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

chemical bonds, the decomposition peaks corresponding with the loss of crosslinking agents are much higher than the boiling points of *p*-xylenediamine and EDA (Table 1). The original and crosslinked membranes all have a degradation peak at around 580°C, which is attributed to decomposition of the polymer main chain. TGA results suggest that *p*-xylenediamine crosslinked membranes are thermally more stable than EDA crosslinked membranes. The higher the degree of crosslinking modification, the more weight loss can be observed at 300°C when we compared TGA curves of 2- and 4-h *p*-xylenediamine crosslinked membranes. As a result, moderate heat treatment temperatures, that is, 100 and 200°C, were chosen for further heat treatment study for the 2-h *p*-xylenediamine crosslinked membranes.

The changes of functional groups with heat treatment were analyzed by ATR-FTIR and XPS. As shown in Figure 8, it is interesting that the peaks corresponding to amide groups are slightly intensified after heat treatment at 100°C; however, the peaks of imide groups dominate again after heat treatment at 200°C. XPS results tabulated in Table 3 show the unchanged N_{1s}/O_{1s} ratio after heat treatment at 100°C and the decrease of N_{1s}/O_{1s} ratio after heat treatment at 200°C. In addition, the N_{1s} peak after 100°C heat treatment is almost unchanged, whereas the N_{1s} peak after 200°C heat treatment shifts back to the higher binding energy (Figure 3). This implies that *p*-xylenediamine crosslinked membranes are thermally stable at 100°C and the amidization reaction can be somewhat promoted at low heat treatment temperatures because of further reaction between imide groups and free amine groups. At high temperatures, the amide groups may be reversed to imide groups and diamine compounds are released. These phenomena are consistent with the investigations by Xiao et al.[27] and Shao et al.[19,28] for polyamidoamine (PAMAM), EDA, and 1,3-cyclohexanebis(methylamine) (CHBA) crosslinked 6FDA-durene membranes.

When the crosslinked asymmetric membranes were heat treated, apparent color changes were observed. The color of the crosslinked asymmetric membranes changed from the original pale yellow to yellow (heat treated at 100°C), then to orange yellow (heat treated at 200°C). The UV–vis absorption band as listed in Table 8 can be used to characterize the color changes. The coloration of 200 and 250°C heat-treated asymmetric membranes was included as a reference. One can observe that the color of the membranes changes after heat treatment and the UV shift is greater at a higher heat-treatment temperature. The color changes after thermal treatment are mainly attributed to the formation of charge transfer complexes (CTCs).[29,30] It has been generally accepted that polyimides are likely to form CTCs through their inherent electron donor (the diamine moi-

Table 8. UV Wavelength and Color Changes of Modified P84 Membranes

Membrane	Color	λ (UV) (nm)	Δλ (UV Shift) (nm)
P84-original	Light yellow	464	—
P84-asymmetric-200°C*	Yellow	505	41
P84-asymmetric-250°C*	Yellow	510	46
P84-ckp-2hr	Light yellow	460	—
P84-ckp-2hr-100°C	Yellow	494	30
P84-ckp-2hr-200°C	Orange yellow	590	126

*P84-asymmetric-200°C and P84-asymmetric-250°C are P84 asymmetric membranes heat treated at 200 and 250°C, respectively.

Table 9. Pervaporation Performance of the Original and Crosslinked Membrane after Heat Treatment

Membrane	Operating T (°C)	Feed Water (wt %)	Permeate Water (wt %)	Flux (g m^{-2} h^{-1})	SF	Permeance (g m^{-2} h^{-1} kPa^{-1}) Water	IPA	Selectivity
P84-asymmetric-100°C*	60	15	92.06	1068	66	66.2	2.95	22
P84-ckp-2hr	60	15	97.09	1398	189	91.38	1.42	65
P84-ckp-2hr-100°C	60	15	99.43	1105	980	74.0	0.22	335
P84-ckp-2hr-200°C	60	15	99.67	335	1733	22.5	0.04	592

*P84-asymmetric-100°C are P84 asymmetric membranes heat treated at 100°C.

ety) and electron acceptor (the dianhydride moiety) elements. These CTCs are in a nonequilibrium state and are strongly affected by heat-treatment temperature.[31] The higher the heat treatment temperature, the more CTCs can be formed because of the closer donor and acceptor distance induced by the thermal motion of polymer chains. The intra- and interchain CTCs can restrict the mobility of the macromolecules and have an effect similar to that of crosslinking modification.[31] Moreover, the red shift of UV wavelength of membranes with heat treatment after crosslinking is much higher than that of the membrane with heat treatment alone. The crosslinking reaction opens the rigid imide rings and forms amide structure, which probably makes the polymer chain more flexible, thus significantly enhancing the chances to form CTCs. Additionally, the newly incorporated functional groups may have stronger charge transfer ability.

With an increase in heat-treatment temperature, the contact angle (Table 4) increases because a densified skin layer usually has less hydrophilicity compared to that of a loosely packed skin layer. Nanoindentation test results in Table 5 show the dramatic enhancement of hardness and modulus after heat treatment, especially for the 200°C heat-treated membranes. These indicate the intermolecular forces and networking are strongly boosted after heat treatment.

Pervaporation results of 2-h crosslinked membranes with and without heat treatment are summarized in Table 9. Compared to asymmetric membranes with only crosslinking, the 2-h crosslinked membranes and then heat treated at 100°C have a significantly superior separation factor. When the heat treatment temperature is raised to 200°C, further decreases of flux with a considerable increase of separation factor are achieved. The performance enhancement after low heat-treatment temperatures (that is, 100°C) may be mainly attributed to the higher degree of crosslinking modification and the formation of CTCs. At a higher heat-treatment temperature, the formation of CTCs and the decomposition of those unstable crosslinked bonds compete with each other and determine the final membrane performance. Therefore, for a proper crosslinking membrane, a low-temperature heat treatment may develop pervaporation membranes with high flux and medium separation factor, whereas a high-temperature heat treatment may produce membranes with high separation factor with medium flux.

Effects of operating temperature on crosslinked membranes

The 2-h *p*-xylenediamine crosslinked asymmetric membranes with or without 200°C treatment were tested at various temperatures and the performances are shown in Table 10. The performance of 100°C heat-treated asymmetric membranes was included as a reference. Although flux increases with an increase in operating temperature, the permeance decreases. This is attributed to the decreased sorption at higher temperature, which is consistent with our previous observation.[10] The selectivity varied slightly with temperature, indicating that the thermal expansion of *p*-xylenediamine crosslinked polymer chains is restricted by intra-/intermolecular bonds. Furthermore, the calculated activation energies based on the flux of 2-h crosslinked with or without heat-treatment asymmetric membranes are 37.7 and 36.6 kJ/mol, respectively, which are apparently lower than the activation energies of a 250°C heat-treated P84 asymmetric membrane (40 kJ/mol) (calculated from Qiao et al.[10]), or a PVA/PAN composite membrane PERVAP2510 (45.4 kJ/mol).[25] The lower activation energy of crosslinked P84 membranes suggests less temperature dependency of penetrant transport because of highly restricted thermal motion of polymer chains. The E_p of membranes P84-ckp-2hr-200°C and P84-ckp-2hr are −3.7 kJ/mol and −2.6 kJ/mol, respectively. The negative value of E_p is resulted from the decreasing trend in permeability with temperature.

Conclusions

We have crosslinked P84 membranes with two crosslinking agents, that is, *p*-xylenediamine and EDA for the pervaporation

Table 10. Pervaporation Performance of Crosslinked Membrane at Different Temperatures

Membrane	Operating T (°C)	Feed Water (wt %)	Permeate Water (wt %)	Flux (g m^{-2} h^{-1})	SF	Permeance (g m^{-2} h^{-1} kPa^{-1}) Water	IPA	Selectivity	E_J (kJ/mol)
P84-ckp-2hr-200°C	100	15	99.68	1382	1774	19.53	0.03	630	
	80	15	99.72	716	2018	20.94	0.03	707	
	60	15	99.67	335	1733	22.50	0.04	592	36.6
P84-ckp-2hr	100	15	96.46	6008	154	82.13	1.50	55	
	80	15	96.52	3283	157	92.90	1.69	55	
	60	15	97.09	1398	189	91.38	1.42	65	37.7

dehydration of isopropanol. The effects of crosslinking on dense and asymmetric membranes were investigated. With increasing crosslinking time, the imide groups of P84 gradually disappear, whereas the amide groups appear and intensify as confirmed by ATR-FTIR and XPS. EDA crosslinked membranes show a closer chain packing and stronger amide peaks, indicating a faster crosslinking rate compared to that of *p*-xylenediamine. The pervaporation performance of crosslinked membranes with both crosslinking agents shows that flux decreases at a certain degree of crosslinking, then increases with a prolonged crosslinking time. The separation factor shows an opposite trend. This is explained by the fact that membrane hydrophilicity and swelling increase with an increase in the degree of crosslinking reaction. In addition, *p*-xylenediamine crosslinked membranes show a better thermal stability than that of EDA crosslinked ones. The effects of heat treatment after *p*-xylenediamine crosslinking have been studied. It was found that thermal treatment facilitates formation of CTCs for the crosslinked membranes. A low-temperature heat treatment favors a higher degree of crosslinking, whereas a high-temperature heat treatment might reverse the amide groups to imide groups. The separation factor is further improved after heat treatment at the compensation of lower flux. Furthermore, the pervaporation performance of crosslinked membrane appear to be less temperature dependent because of the restricted thermal motion/expansion of polymer chains. In short, through proper control of crosslinking time and heat-treatment temperature, one can easily tailor the membrane performance with high flux and reasonable separation factor or high separation factor with reasonable flux.

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Literature Cited

1. Crespo JG, Böddeker KW, eds. *Membrane Process in Separation and Purification*. Dordrecht, The Netherlands: Kluwer Academic; 1995.
2. Feng X, Huang RYM. Liquid separation by membrane pervaporation: A review. *Ind Eng Chem Res*. 1997;36:1048–1066.
3. Huang RYM, Yeom CK. Pervaporation separation of aqueous mixtures using cross-linked poly(vinyl alcohol) (PVA). II. Permeation of ethanol–water mixtures. *J Membr Sci*. 1990;51:273–292.
4. Yeom CK, Huang RYM. Modelling of the pervaporation separation of ethanol–water mixtures through cross-linked poly(vinyl alcohol) membrane. *J Membr Sci*. 1992;67:39–55.
5. Burshe MC, Sawant SB, Joshi JB, Pangarkar VG. Sorption and permeation of binary water–alcohol systems through PVA membranes cross-linked with multifunctional cross-linking agents. *Sep Purif Technol*. 1997;12:145–156.
6. Lee YM, Nam SY, Woo DJ. Pervaporation of ionically surface cross-linked chitosan composite membranes for water–alcohol mixtures. *J Membr Sci*. 1997;133:103–110.
7. Huang RYM, Pal R, Moon GY. Cross-linked chitosan composite membrane for the pervaporation dehydration of alcohol mixtures and enhancement of structural stability of chitosan/polysulfone composite membranes. *J Membr Sci*. 1999;160:17–30.
8. Chanachai A, Jiraratananon R, Uttapap D, Moon GY, Anderson WA, Huang RYM. Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes. *J Membr Sci*. 2000;166:271–280.
9. Ohya H, Kudryavtsev VV, Semenova SI. *Polyimide Membranes—Applications, Fabrications, and Properties*. New York: Gordon & Breach; 1996.
10. Qiao X, Chung TS, Pramoda KP. Fabrication and characterization of BTDA-TDI/MDI (P84) co-polyimide membranes for the pervaporation dehydration of isopropanol. *J Membr Sci*. 2005;264:176–189.
11. Su TM, Ball IJ, Conklin JA, Huang SC, Larson RK, Nguyen SL, Lew BM, Kaner RB. Polyaniline/polyimide blends for pervaporation and gas separation studies. *Synth Met*. 1997;84:801–802.
12. Chung TS, Guo WF, Liu Y. Enhanced Matrimid membranes for pervaporation by homogeneous blends with polybenzimidazole (PBI). *J Membr Sci*. 2006;271:221-231.
13. Kaba M, Rakloui N, Guimon MF, Mas A. Improvement of the water selectivity of ULTEM poly(ether imide) pervaporation films by an allylamine-plasma-polymerized layer. *J Appl Polym Sci*. 2005;97: 2088–2096.
14. Sullivan DM, Bruening ML. Ultrathin, cross-linked polyimide pervaporation membranes prepared from polyelectrolyte multilayers. *J Membr Sci*. 2005;248:161–170.
15. HayesRA.*Amine-Modified Polyimide Membranes*.U.S. Patent Number 4 981 497; 1991.
16. Liu Y, Wang R, Chung TS. Chemical cross-linking modification of polyimide membranes for gas separation. *J Membr Sci*. 2001;189:231–239.
17. Cao C. Chemical cross-linking modification of 6FDA-2,6-DAT hollow fiber membranes for natural gas separation. *J Membr Sci*. 2003; 216:257–268.
18. Tin PS, Chung TS, Liu Y, Wang R, Liu SL, Pramoda KP. Effects of cross-linking modification on gas separation performance of Matrimid membranes. *J Membr Sci*. 2003;225:77–90.
19. Shao L, Chung TS, Goh SH, Pramoda KP. Polyimide modification by a linear aliphatic diamine to enhance transport performance and plasticization resistance. *J Membr Sci*. 2005;256:46–56.
20. Liu R, Qiao X, Chung TS. The development of high performance P84 co-polyimide hollow fibers for pervaporation dehydration of isopropanol. *Chem Eng Sci*. 2005;60:6674–6686.
21. Qiao X, Chung TS.Fundamental characteristics of sorption, swelling and permeation of P84 co-polyimide membranes for pervaporation dehydration of alcohols. *Ind Eng Chem Res*. 2005;44:8938-8943.
22. Tin PS, Chung TS, Liu Y, Wang R. Separation of CO_2/CH_4 through carbon molecular sieve membranes derived from P84 polyimide. *Carbon* 2004;42:3123–3131.
23. Guo WF, Chung TS, Matsuura T. Pervaporation study on the dehydration of aqueous butanol solutions: A comparison of flux vs. permeance, separation factor vs. selectivity. *J Membr Sci*. 2004;245:199–210.
24. Wijmans JG, Baker RW. A simple predictive treatment of the permeation process in pervaporation. *J Membr Sci*. 1993;79:101–113.
25. Qiao X, Chung TS, Guo WF, Matsuura T, Teoh MM. Dehydration of isopropanol and its comparison with dehydration of butanol isomers from thermodynamic and molecular aspects. *J Membr Sci*. 2005;252: 37–49.
26. Koops GH, Smolders CA. Estimation and evaluation of polymeric materials for pervaporation membranes. In Huang RYM, ed. *Pervaporation Membrane Separation Process*. London, UK: Elsevier Applied Science; 1991.
27. XiaoY, Shao L, Chung TS, Schiraldi DA. Effects of thermal treatments and dendrimers chemical structures on the properties of highly surface crosslinked polyimide films. *Ind Eng Chem Res*. 2005;44:3059–3067.
28. Shao L, Chung TS, Goh SH, Pramoda KP. The effects of 1,3-cyclohexanebis(methylamine) modification on gas transport and plasticization resistance of polyimide membranes. *J Membr Sci*. 2005;267:78–89.
29. Kawakami H, Mikawa M, Nagaoka S. Gas transport properties in thermally cured aromatic polyimide membranes. *J Membr Sci*. 1996; 118:223–230.
30. Barsema JN, Klijnstra SD, Balster JH, Van der Vegt NFA, Koops GH, Wessling M. Intermediate polymer to carbon gas separation membranes based on Matrimid PI. *J Membr Sci*. 2004;238:93–102.
31. Hasegawa M, Horie K. Photophysics, photochemistry, and optical properties of polyimides. *Prog Polym Sci*. 2001;26:259–335.

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