

Pervaporation and Solute Separation Through Semi-Interpenetrating and Interpenetrating Polymer Network Membranes Prepared from Poly(4-vinylpyridine) and Poly(glycidyl Methacrylate)

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ABSTRACT: Semi-interpenetrating (SPN) and interpenetrating polymer network (IPN) membranes were prepared from a mixture system of poly(4-vinylpyridine) (P4VP) and poly(glycidyl methacrylate) (PGMA) by quaternizing crosslinking of P4VP with 1,4-dibromobutane (DBB) and by simultaneous crosslinking of P4VP with DBB and PGMA with tetraethylenepentamine (TEPA), respectively. The difference between SPN and IPN was demonstrated by IR, tensile strength, and dimension stability. The membrane performance in pervaporation (PV) for ethanol–water mixtures and reverse osmosis (RO) was investigated. The polymer mixture of 1 : 1 on a monomer base with 30 mol % DBB on the 4VP unit and 5.6–7.5 mol % (8–10 wt %) TEPA on the GMA unit gave an optimum membrane performance. Those crosslinked membranes were stronger than was the cellulose acetate membrane, mostly owing to the PGMA chains, and exhibited a high separation factor for the azeotropic feed in PV. IPN membranes generally showed a performance higher than that of the SPN ones. An attempt to improve the product rate was made by the addition of a water-soluble polymer to the membrane on casting. The separation factor for solubility in the membrane at the feed side dominated the overall separation factor, particularly for feeds of higher ethanol concentrations. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1953–1963, 1998

INTRODUCTION

Interpenetrating polymer networks (IPNs) have attracted many researchers since the appearance of IPNs in the 1960s, because the preparation of IPNs may be regarded as one of effective techniques to yield a sort of polymer alloy or a variety of polymer composites from immiscible polymer components.^{1,2} Recent studies are still focusing on wide branches of synthesis and the physical, mechanical, and structural properties of IPNs.^{2–10} The application of IPNs to separation membranes

has also been attempted to date. Most of the studies were directed toward pervaporation (PV) membranes composed of networks of different characters, such as hydrophilic and hydrophobic components,¹¹ cationic and anionic polymers,¹² and soft and hard segments,¹³ or of networks of analogous characters in order to strengthen water affinity^{14,15} or ethanol affinity.^{16,17}

We studied the synthesis of separation membrane materials containing pyridine moieties and their performance in reverse osmosis (RO),^{18,19} PV,^{20,21} and gas separation.²² Poly(4-vinylpyridine) (P4VP) and most of the 4-vinylpyridine (4VP)-rich copolymers are hydrophilic and water-permeable materials,²³ but they gave rather soft and mechanically weak membranes and required

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reinforcement such as crosslinking²⁴ or support.²⁵ To our knowledge, however, IPNs composed of 4VP or its analogs has not been applied to separation membranes. In this work, we made an attempt to prepare IPN membranes containing the P4VP network quaternized with a bifunctional alkyl halide: 1,4-dibromobutane.

Quaternization-crosslinked P4VP still had a strong tendency to swell with water²³ even after crosslinking owing to increased hydrophilicity, and, hence, poly(glycidyl methacrylate) (PGMA), a multifunctional polymer containing epoxy groups, was used as another network that may work for suppressing the swelling and for giving a tough membrane. Studies of IPNs based on epoxy groups have already appeared in several cases,³⁻⁶ where epoxy groups underwent the reaction by the catalyzing action of bases like amines. PGMA gave a strong and rather hydrophobic film and was found to form crosslinks by the action of P4VP. Therefore, P4VP was able to act not only as a network by itself but also as a catalyst for the opening of epoxy rings of PGMA, yielding another network.

In this study, we dealt with the properties and separation characteristics of those IPN membranes in PV for an ethanol-water mixture or in RO for saline water and the dependence of those characteristics on the composition of the polymer components, the kind of additive employed for membrane preparation, and feed composition.

EXPERIMENTAL

Materials

P4VP was prepared from freshly vacuum-distilled 4VP by emulsion polymerization with a redox initiator, potassium persulfate, and sodium hydrogen sulfite.²⁶ The yield was 87.7%. The molecular weight (M) calculated according to the equation²⁷ $[\eta] = 25.0 \times 10^{-5} M^{0.68}$ was 1.25×10^6 ($[\eta] = 3.50$ in ethanol at 25°C). PGMA was obtained by polymerizing the distilled monomer in a benzene solution with an AIBN initiator (0.09 mol % based on GMA) at 60°C for 4 h. The polymer solution was poured into methanol, and the polymer was reprecipitated from an acetone solution into methanol. The yield was 54.8% and $[\eta]$ was 1.27 in DMF at 25°C. 1,4-Dibromobutane (DBB) and ethylenediamine (EDA) were purchased from Junsei Co. (Japan); diethylenetetramine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA),

poly(ethylene glycol) (PEG, $M = 200$), and poly(vinyl alcohol) (PVA, $M = 66,000$), from Wako Junyaku Co. (Japan); and polyvinylpyrrolidone (PVP, $M = 360,000$), from Tokyo Kasei Co (Japan). They were used as received.

Membrane Preparation

A determined amount of P4VP and PGMA was separately dissolved in *N,N*-dimethylformamide (DMF) so that the total concentration of the two polymers became 3.2 wt % after mixing. When a water-soluble polymer additive was used, it was dissolved in the PGMA solution. In the case of PVA, dimethyl sulfoxide (DMSO) was used because PVA was soluble in DMSO but not in DMF. DBB was dissolved in the P4VP solution just before the mixing of the two-polymer solution.

On a clean glass plate, a metal ring frame of about a 8-cm diameter and a 3-cm height was put, and its outside periphery was fixed on the plate with an adhesive to prevent the casting solution from leaking. The prepared casting solution was placed into the frame after mixing well and heated with a glass cover at 50°C for 2 h and then without a cover for 2 h. The membrane thus obtained was denoted with the code SPN. For the control membrane of PGMA and PEG without P4VP, the same procedure was used with a 5.7 wt % solution of PGMA containing a given amount of PEG.

When TEPA was used, a given amount of TEPA was dissolved in 10 wt % PGMA solution and heated at 50°C for 10 min before mixing with the P4VP solution containing DBB. The total concentration of P4VP plus PGMA was 6.9 wt %. The solution was then cast onto a clean glass plate with an applicator with a 450- μm thickness and evaporated at 50°C for 2 h. These membranes obtained were denoted with the code IPN.

All the membranes prepared were immersed in water for more than 24 h before use, and the thickness was measured with a Sanko electromagnetic meter SL-110-SP. The thickness ranged from 40 to 60 μm , mostly around 50 μm .

Permeation

PV was carried out in the same apparatus as reported,²¹ which was of a batch type with a 300-mL cell capacity and 18.1-cm² effective membrane area and controlled at 25°C by circulating water in the cell jacket. An aqueous ethanol solution of a determined concentration was supplied in an increasing order of the concentration. The pres-

sure of the permeate side was 0.5 Torr. The flux J_1 was determined by the weight increase of the trap cooled in liquid nitrogen for a given time, and the overall permeability was expressed in $J_1 \times (\text{membrane thickness } \Delta x) (= P) [\text{g cm}^{-1} \text{ h}^{-1}]$. The permeate concentration was determined with a Shimadzu TOC-500 total organic carbon analyzer. The separation factor for water α was obtained by the following equation:

$$\alpha = (Y_w/Y_e)/(X_w/X_e),$$

where X and Y are weight fractions of the feed and permeate, respectively, and the subscripts w and e denote water and ethanol, respectively.

RO was conducted in the same manner as reported previously^{18,21} with a batch-type apparatus similar to that used in the PV. The feed concentration was 0.06M and the pressure applied was 7.85 MPa (80 kg/cm²). The permeate concentration was measured conductometrically. The solute rejection R and hydraulic permeability K_1 were determined according to the following expressions:

$$R = 100(c - c')/c$$

$$J_1 = K_1(\Delta P - \Delta\pi)/\Delta x$$

where c and c' are the feed and product concentration, respectively. J_1 is the volumetric flux; ΔP , the pressure difference; $\Delta\pi$, the osmotic pressure difference; and Δx , the membrane thickness.

Measurements

Crosslinking Rate

This rate was expressed as the time taken for the solution to flow down a given length of a glass tube. A DMF solution (0.265M based on the monomer unit) of PGMA (3.6 wt %) or P4VP (2.7 wt %) was placed in a 50-mL two-necked flask, which was heated at $50 \pm 0.2^\circ\text{C}$ in an oil bath. A determined amount of aliphatic amine (7.5 mol % based on the monomer unit of PGMA, 10 wt % for TEPA) or DBB was added to PGMA or to P4VP, respectively, and well mixed. A glass tube of an inner diameter of 3.4 mm was vertically put into the solution from the top inlet of the flask, the solution was lifted up into the tube by suction, and the time needed to flow down between the two marks 5 cm apart was measured at an adequate interval of time until the measurement became impossible due to too high viscosity.

Composition of the Aqueous Ethanol Solution Sorbed into the Membrane

A sample membrane was immersed in a feed of a given concentration at room temperature for 48 h. The membrane was blotted and placed in a flask that was connected to a cold trap. Before placing the trap in liquid nitrogen, the air of the system was pumped out for a couple of seconds in order to evacuate air moisture. The ethanol and water sorbed and penetrated into the membrane was collected in the trap in a vacuum. After completion, the trap was sealed with stopcocks and warmed to room temperature to avoid condensing air moisture. The composition of the collected liquid was subjected to TOC analysis.

Tensile Strength, Water Content, Swelling Degree, and Infrared Spectra

The tensile strength of a wet sample membrane (about $1 \times 3\text{--}4$ cm) was measured several times with a Shinkoh TOM-5 tensiometer. The water content was represented as the weight percent of water in a blotted wet membrane which was immersed in water at room temperature for more than 24 h.

The swelling degree was defined in this case as weight percent of the absorbed feed liquid against the dry membrane. Changes in length were measured with a couple of membrane pieces of 10 mm width and 40 mm length. Sample pieces were simultaneously immersed in four feed liquids of a different concentration at room temperature for 48 h before measuring.

Infrared spectra were recorded for thin-film samples with a Hitachi 270-30 infrared spectrophotometer. Absorbances at 1260, 910, and 850 cm^{-1} that are characteristic of the epoxy ring²⁸ were obtained relative to the absorbance of the carbonyl stretching vibration at 1735 cm^{-1} by the baseline method.

RESULTS AND DISCUSSION

Influence of the Composition of the Membrane on Membrane Performance

A clear, transparent, and tough film was formed from a DMF solution of a mixture of P4VP and PGMA in all compositions. It was observed that the multi-functional polymer PGMA formed a crosslinked structure by the action of P4VP. Therefore, we investigated, first, the effect of the

polymer composition on the performance of those crosslinked membranes in RO. Figures 1 and 2 illustrate the results. For the membranes without DBB, R and K_1 in Figure 1(b) increase with increasing content of P4VP, but R shows a maximum plateau beyond 20 mol %. Their relative strength in Figure 1(a) tends to decrease gradually with increase in P4VP and suddenly at 100% P4VP. The PGMA membrane ($[P4VP] = 0$) is apparently less hydrophilic in view of its low values of K_1 , water content, and R , although its strength is higher. With the addition of DBB which readily formed a crosslinked structure with P4VP, R shows a tendency to decrease with increase in P4VP [Fig. 1(b)] and so does the strength [Fig. 1(a)], while an increased content of P4VP increases K_1 steeply and water content to some extent. This fact indicates that the membrane strength is supported primarily by PGMA rather than by the DBB-crosslinked P4VP but the latter enhances water permeability.

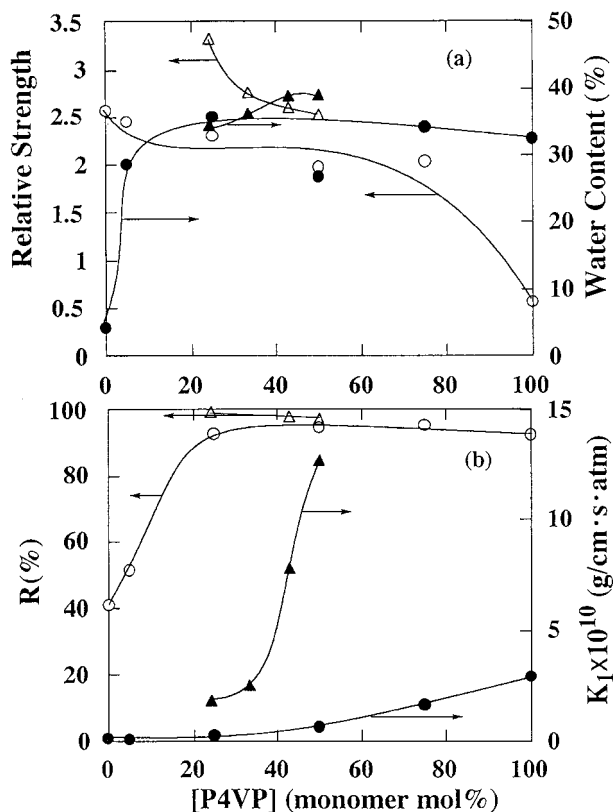


Figure 1 Performance of P4VP-PGMA membranes in RO against P4VP content in monomer unit: (○, ●) without DBB; (△, ▲) with addition of 30 mol % DBB based on 4VP (SPN). Relative strength: based on cellulose acetate (11.6 MPa) prepared by Manjikian's method.²⁹

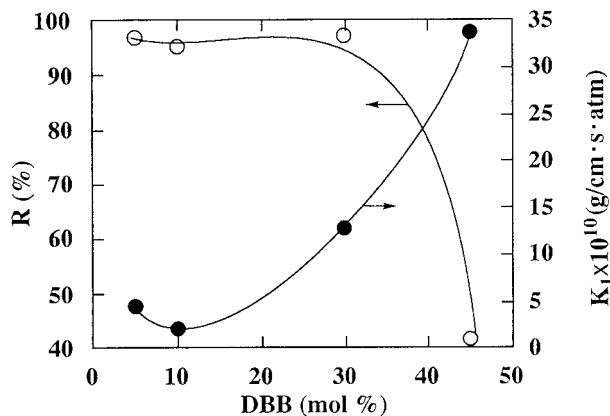


Figure 2 Dependence of R and K_1 on DBB content (based on 4VP) in RO for SPN50 membranes composed of 50% P4VP and 50% PGMA on a molar base.

As for the addition ratio of DBB, Figure 2 shows the results, where 30 mol % DBB is the optimum without the reduction of R . Moreover, in the case of PV as shown in Figure 3, the membrane containing 30 mol % DBB showed an optimum performance as well for all feed compositions, although the absence of DBB showed a higher α at the cost of permeability. Figure 3 also exhibits the usefulness of the membrane for the PV separation with a 96 wt % azeotropic mixture feed.

In view of those facts and of the similarity between RO and PV to each other with respect to liquid penetration into the membrane matrix except for final evaporation in PV, we thus chose the membranes of 50 mol % (on the monomer unit) content of each polymer with 30 mol % DBB and further studied the influence of the preparation conditions, additives, and the structure on PV performance for ethanol-water mixtures.

Formation of Semi-interpenetrating and Interpenetrating Polymer Network

A DMF solution of P4VP and DBB formed a gel in a short time during stirring at room temperature. This indicates that a crosslinked structure is readily formed from those reagents. P4VP, a tertiary amine, however, took a long time to convert the PGMA solution into a gel even at an elevated temperature: about 30 h at 50°C and more than 10 h at 80°C. Therefore, since it is favorable for IPN membrane formation that two independent crosslinking reactions proceed with a comparable rate, it was checked whether an aliphatic primary amine could facilitate the crosslinking of PGMA at a rate comparable with that of P4VP and DBB.

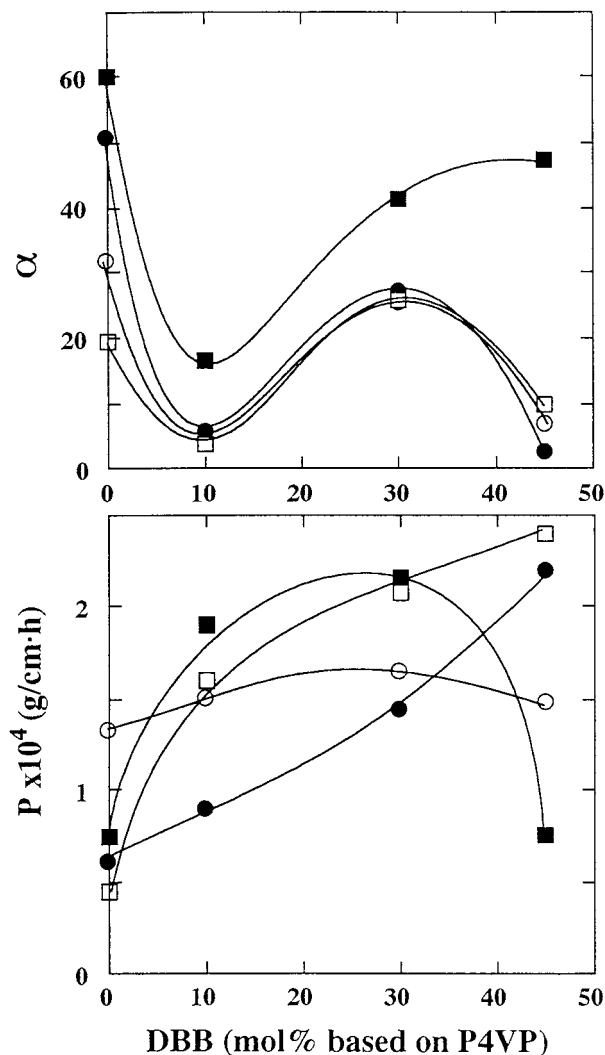


Figure 3 Dependence of α and P on DBB content (based on 4VP) and feed concentration in PV for SPN50 membranes: (○) 20 wt % EtOH; (●) 40 wt % EtOH; (□) 70 wt % EtOH; (■) 96 wt % EtOH.

The comparison was made by measuring the flow time for the DMF solution to flow down in the 5-cm range of a vertical glass tube. The results are shown in Figure 4. A step increase in the time indicates the crosslinking or gelation to a considerable extent, and the reactions of P4VP with DBB represent the fastest gel formation. With the aliphatic amines used, the efficiency decreased in the order TEPA > TETA > DETA > EDA, corresponding to the decreasing order of the nitrogen atom number in the molecular formula. Because the absence of those amines, that is, the presence of P4VP alone, needed a long crosslinking time as described above, the membranes made under the conditions without those aliphatic amines should

have consisted of a semi-interpenetrating polymer network (SPN) with PGMA almost intact. In contrast, under the conditions in the presence of one of those amines, interpenetrating polymer network (IPN) membranes should have been formed, because a DMF solution of an increased concentration (10 wt %) of PGMA with TEPA [PGMA + TEPA] was heated at 50°C for 10 min prior to mixing with the solution containing P4VP and DBB [P4VP + DBB] and more than 10 min made the solution too viscous to mix with the P4VP solution, although the time difference in the initiation of a steep viscosity increase between [P4VP + DBB] and [PGMA + TEPA] was about 150 min as shown in Figure 4.

Infrared (IR) absorption analysis showed a relative extent of the reaction of the epoxy ring. Table I summarizes the results. In spite of some contribution of TEPA to the absorptions, IPN50-30TEPA10 membranes prepared by evaporation at 50°C show absorbances less than those of SPN50-30, which suggests a greater extent of the epoxy ring opening. When IPN50-30TEPA10 prepared via preheating is compared with the corresponding membrane without preheating, the former shows decreased absorbances, indicating a more extensive network formation in the membrane prepared via preheating.

As for the strength comparison, IPN membranes, as seen in Table II, are stronger than the SPN and become stronger with increase in TEPA.

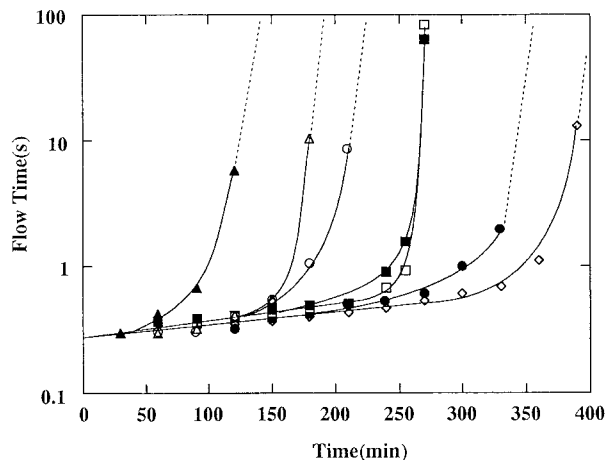


Figure 4 Difference in initiation of gelation in P4VP and PGMA with a crosslinking agent at 50°C: (○) P4VP + 10 mol % DBB; (△) P4VP + 20 mol % DBB; (▲) P4VP + 30 mol % DBB; (◇) PGMA + EDA; (●) PGMA + DETA; (□) PGMA + TETA; (■) PGMA + TEPA. Concentration of P4VP: 2.7 wt %, and of PGMA: 3.6 wt %. Amine added: 7.5 mol % based on GMA.

Table I Relative Absorbances in Infrared Absorptions for the Epoxy Group

Membrane ^a	Relative Absorbance ^b At		
	1260	910	850 cm ⁻¹
SPN50-30	0.683	0.501	0.450
IPN50-30TEPA10 ^c	0.444	0.312	0.270
IPN50-30TEPA10 ^d	0.312	0.247	0.202

^a "50" denotes the mol % based on the monomer unit in the P4VP-PGMA mixture. "30" and the number after TEPA mean the addition of 30 mol % DBB based on the 4VP unit and 10 wt % (7.5 mol %) TEPA based on PGMA to the membrane, respectively.

^b Relative to ν (C=O) at 1735 cm⁻¹; 1260, 910, and 850 cm⁻¹: characteristic for the epoxy ring, 1260 supposed to be due to ν_s , 910 due to ν_{as} or trans material, and 850 due to cis material.²⁸

^c Prepared via no preheating.

^d Prepared via preheating.

The membrane cast after the preheating at 10 wt % TEPA addition is stronger, supporting a network of a greater extent by the preheating. In general, those membranes showed a strength higher than that of the cellulose acetate membrane.

PV Performance of IPN Membranes

As TEPA displayed the fastest crosslinking among the amines employed as seen in Figure 4, TEPA-containing membranes were compared with respect to the effect of preheating on the separation performance. Figure 5 illustrates the results. The membrane prepared via preheating shows a little higher permeabilities for all feed compositions and a rather higher α especially for the feed of higher ethanol concentrations. There-

Table II Tensile Strength and Water Content of SPN and IPN Membranes

Membrane Code ^a	Relative Strength ^b	Water Content
SPN50-30	2.5	39.2
IPN50-30TEPA5	4.5	40.0
IPN50-30TEPA8	5.0	35.4
IPN50-30TEPA10	6.7 (4.6 ^c)	62.7 (36.6 ^c)

^a TEPA5 and 8 mean the addition of 5 and 8 wt % (3.7 and 6.0 mol %) TEPA based on PMGA to the membrane, respectively.

^b Relative to cellulose acetate membrane prepared by Manjikian's method²⁹ as shown in Figure 1.

^c Prepared via no preheating.

fore, the heating of [PGMA + TEPA] just before casting was effective for producing membranes superior in both separation performance and strength, probably due to the network formation of PGMA to a greater extent. Figure 6 shows the TEPA content dependency, where 5.6 mol % (8 wt %) TEPA showed a maximum α of 1000 in this study, although the permeability was small. As seen from Figures 5 and 6, those IPN membranes seem to be useful for the separation of azeotropic 96 wt % ethanol feed. The increase in TEPA content has a tendency to increase α and decrease P as a whole (Fig. 6), indicating the formation of a denser network of a greater crosslinking degree along with the increasing addition of TEPA. This fact can also be discussed in the swelling ability of the membranes prepared under different conditions, which is shown in Figure 7. In general, the

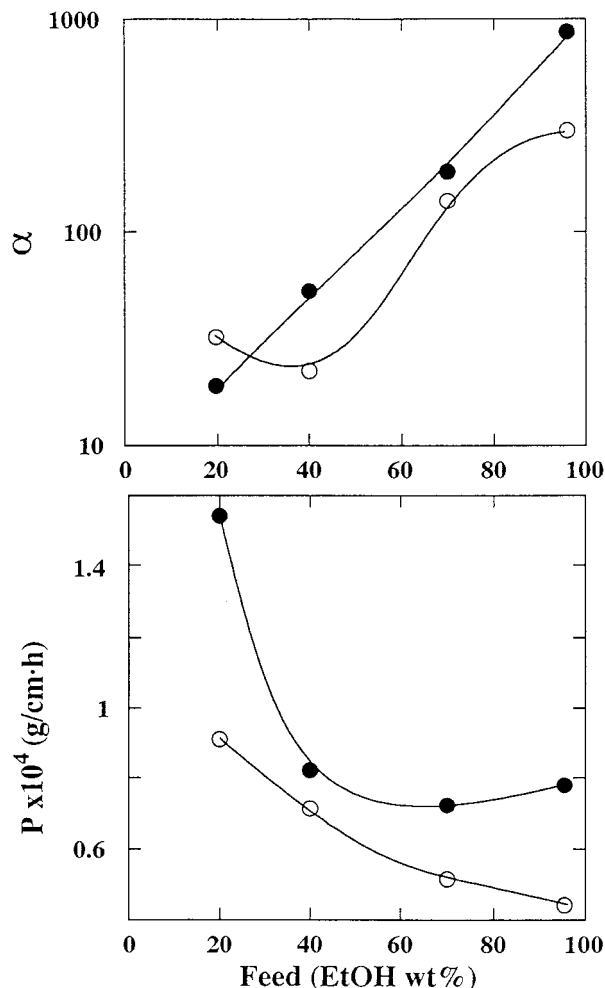


Figure 5 Effect of heat treatment in IPN50-30TEPA10 on PV performance: (●) heated at 50°C prior to casting; (○) not preheated.

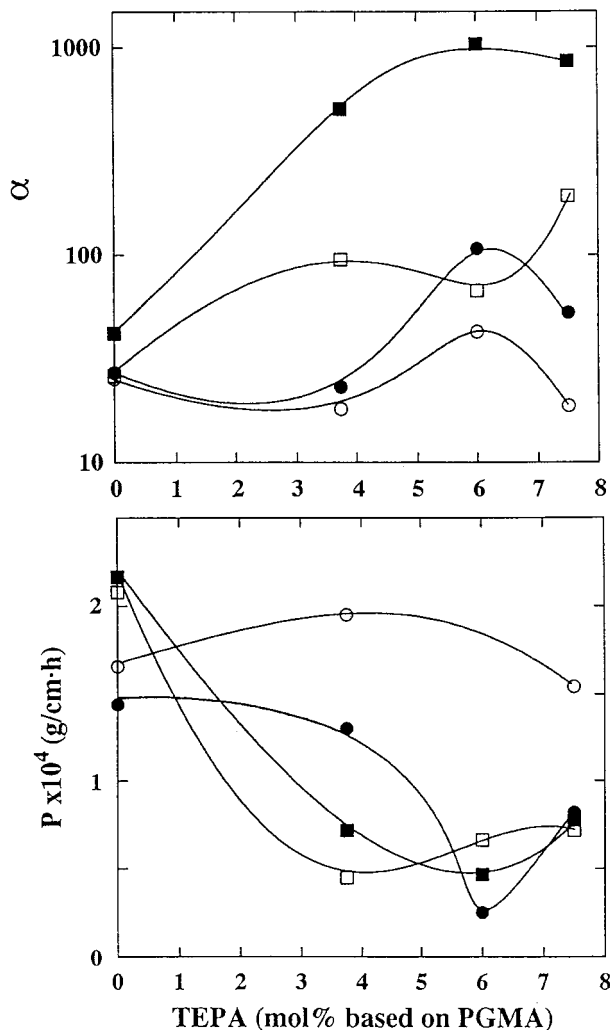


Figure 6 Dependence of α and P on TEPA content and feed concentration in PV for IPN50-30 membranes: (○) 20 wt % EtOH; (●) 40 wt % EtOH; (□) 70 wt % EtOH; (■) 96 wt % EtOH.

strongest affinity of the feed to the membranes is shown at about 70 wt % ethanol feed. The IPN membrane has a better dimension stability, that is, smaller increases in length, representing a denser network of the IPN membrane compared with the SPN50 membranes. On the other hand, IPN50-30TEPA10 prepared via preheating exhibits the largest weight increase. This is probably caused by the great affinity of the incorporated TEPA to both ethanol and water. A lower weight increase of the nonpreheated IPN50-30TEPA10 membrane may imply a less extent of crosslinking, presumably, for example, due to the leaching of some intact TEPA out of the membrane. A greater extent of the network of IPN than of SPN

is also supported by a higher strength of IPN in Table II.

In comparison between the two SPN membranes in Figure 7, SPN50-30 containing 30 mol % DBB (based on a 4VP unit) shows changes lower than those of SPN50-10 containing 10 mol % DBB. Those lower changes of SPN50-30 correspond to an increased hydrophobicity due to methylene groups of DBB in addition to a greater extent of crosslinking.

The separation performance of IPN50-30TEPA10 prepared via preheating in RO was $R = 95.2\%$ and $K_1 = 0.8 \times 10^{-10}$. The R value is comparable with that of the control membranes without DBB and SPN50 at 50 mol % P4VP in Figure 1(b), and SPN50-30, in Figure 2, but K_1 is smaller than that of the SPNs, probably because of a more extensive network in the IPN membrane. In summary, the

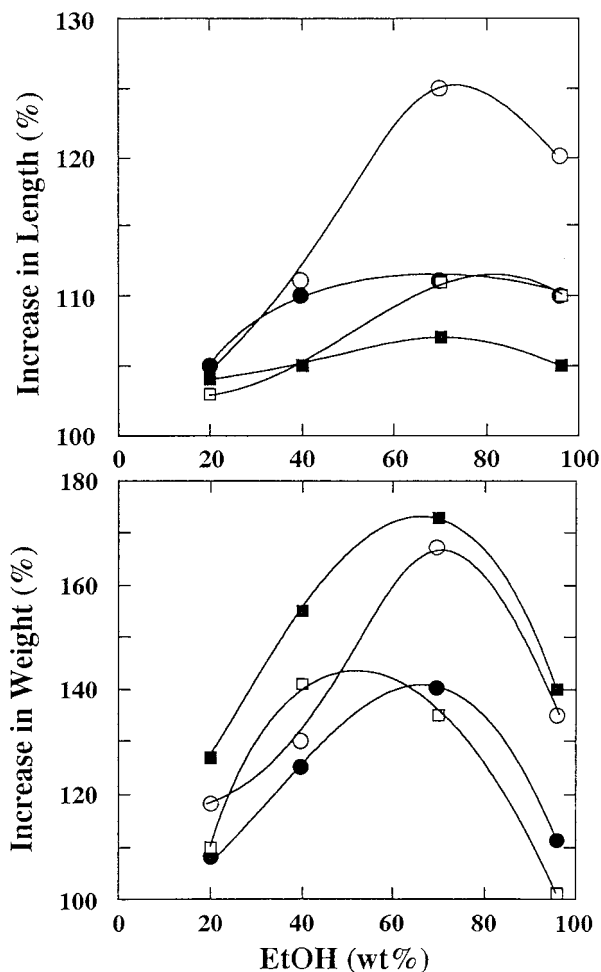


Figure 7 Swelling test of membranes: (○) SPN50-10; (●) SPN50-30; (□) IPN50-30TEPA 10 (not preheated); (■) IPN50-30TEPA 10 (preheated).

difference in performance between the SPN and the IPN (Figs. 3 and 5 and Table II) originates principally from the crosslinking degree, showing characteristics of larger P , smaller α , and smaller strength in the SPN and the opposite tendency in the IPN.

Improvement of Permeability

For separation membranes, it is also important to increase the product rate as well as the separation factor. One of the strategies to improve the permeability is the incorporation of a very hydrophilic polymer to the membrane matrix. A problem then arises if the hydrophilic polymer could be dissolved to give a homogeneous cast solution. Three water-soluble polymers, PEG, PVP, and PVA, were able to be dissolved in DMF or DMSO when a small amount was added. Those polymer-containing membranes were studied for 20 wt % ethanol feed, as summarized in Table III. Because only PEG improved the permeability without reducing α and the addition of a larger amount of PEG was possible, the effect of PEG content on the performance was investigated and is shown in Figure 8. The permeability increases two to nearly four times with increasing content of PEG. However, α tends to decrease beyond 5 mol % addition in a trade-off way with increase in the permeability. Terminal hydroxy groups of PEG can react with the epoxy groups of PGMA, giving another network. The occurrence of such a reaction can be demonstrated by the fact that when 25 mol % PEG (based on the GMA unit) was added ($\Delta x = 38 \mu\text{m}$), the relative strength of 1.62 of PGMA ($\Delta x = 38 \mu\text{m}$) decreased to 1.11 due to the increase in soft ethylene oxide $-\text{CH}_2\text{CH}_2\text{O}-$ segments, but it increased to 1.44 when 50 mol % PEG was added ($\Delta x = 36 \mu\text{m}$) in spite of a further increase in the soft segments, indicating the extensive net-

Table III Pervaporation of SPN50-30 Containing a Water-soluble Polymer

Membrane Code ^a	Δx (μm)	α	$P \times 10^4$ ($\text{g cm}^{-1} \text{h}^{-1}$)
SPN50-30	70	25.3	1.6
SPN50-30PEG	58	24.9	2.7
SPN50-30PVP	67	17.1	0.52
SPN50-30PVA	51	8.3	0.66

Pervaporation was for 20 wt % ethanol feed.

^a The water-soluble polymer was added in 7 wt % based on PGMA.

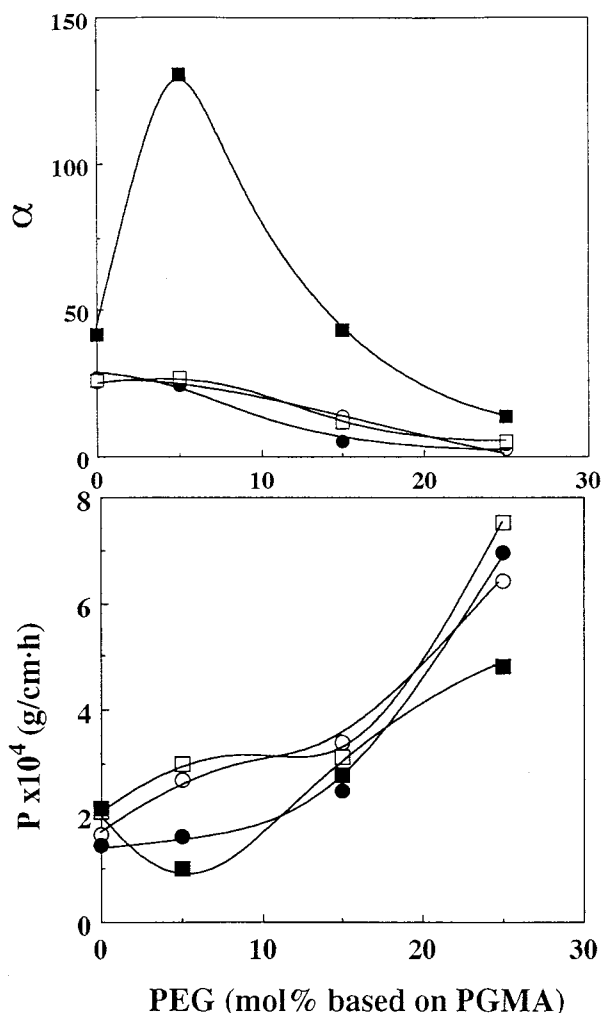


Figure 8 Dependence of α and P on PEG ($M = 200$) content and feed concentration in PV for SPN50-30 membranes: (○) 20 wt % EtOH; (●) 40 wt % EtOH; (□) 70 wt % EtOH; (■) 96 wt % EtOH.

work formation. The addition of not more than 10–15 mol % PEG could improve the permeability without deteriorating α , and the addition of 5 mol % PEG showed a remarkably increasing effect to α for 96 wt % ethanol feed.

The IPN membranes of the present study showed high α values as shown in Figure 6, particularly for the 96 wt % ethanol solution [$\alpha = 900$, $P = 0.8 \text{ g cm}^{-1} \text{h}^{-1}$ at 25°C , tensile strength = 77.7 MPa]. For comparison, some results of other hydrophilic IPN membranes reported by various authors at or near the azeotropic points are listed in Table IV. It can be seen that our membranes have high α values but low or comparable P values compared with others although the conditions are different and the performance of PVA/PAAM

membranes depends on the composition. Relatively lower permeabilities of the present membranes probably stems from a low hydrophilic character of PGMA, which, however, contributes to the membrane strength to a great extent.

Consideration on the Permeation Mechanism

PV generally includes three major steps: preferential sorption of a penetrant into the membrane on the feed side, their phase transition from liquid to vapor, and the diffusion of liquid and vapor through the membrane. Thus, the overall separation factor α should consist of α^S , α^{EV} , and α^D , that is, $\alpha = \alpha^S \alpha^{EV} \alpha^D$, where α^S is the separation factor for the solubility of water in the membrane on the feed side; α^{EV} , for evaporation of water at a certain interface in the membrane; and α^D , for the overall diffusion of water prior to and after the evaporation.³⁰ α^S was evaluated from the composition of the sorbed liquid in equilibrium with the feed of a certain concentration [Figs. 9(a) and 10(a)], and α^{EV} , from the vapor–liquid diagram of the ethanol–water mixture at the composition of the sorbed liquid. From those values and the observed overall α values, α^D was calculated, and they are shown in Figures 9(b) and 10(b). α^{EV} is always less than unity because water is less volatile. α^S is greater than α^D in the whole range of the feed composition studied. This fact indicates that the difference in solubility between water and ethanol at the surface of membrane in contact with the feed plays a very crucial role. This is commonly observed in both cases of SPN and IPN, probably because both types of membranes are similar in chemical quality. With decreasing ethanol concentration, α^D approaches α^S , more re-

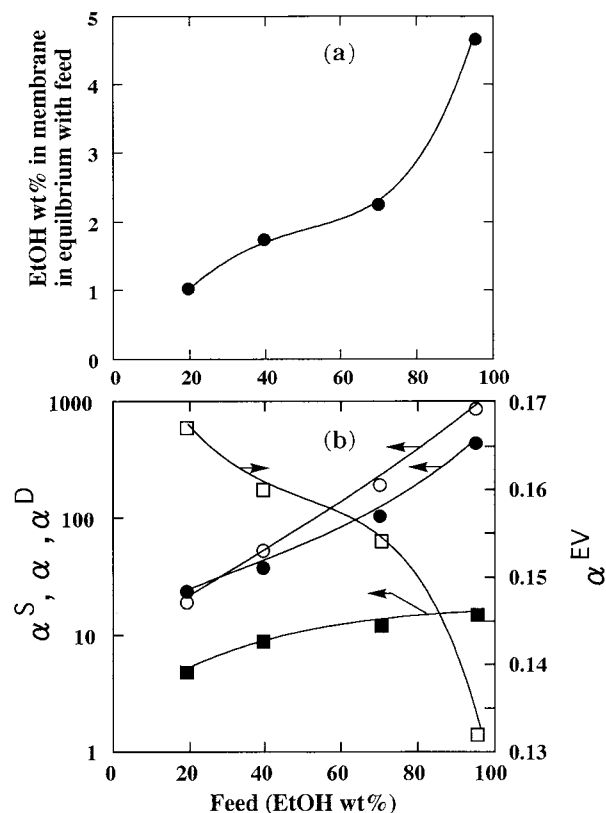


Figure 9 Concentration dependence (a) of sorbed liquid composition in IPN50-30TEPA 10 (preheated) membrane and (b) of separation factors: (○) α ; (●) α^S ; (□) α^{EV} ; (■) α^D .

markably in Figure 10(b), indicating that the diffusion process becomes relatively important with a decrease in ethanol concentration. The tendencies of α^S and α^D in Figure 10(b) are very similar to the results for the sulfonated ion-exchange

Table IV Pervaporation Performance of Water-selective IPN Membranes

Membranes (Wt Ratio)	Ethanol in Feed (wt %)	Temperature (°C)	α	$P \times 10^4$ (g cm ⁻¹ h ⁻¹)	References
PU(HMDI-PTEG)/PS (7/3)	95	30	~ 5	8	11
PU(Quaternized)/P(MMA-AA) (1/1)	90	30	~ 4	~ 13	12
PU(HTPB-H ₁₂ MDI)/P4VP (75/25)	90	25	3	~ 7	13
PVA/PAAm (5/1)	95	75	45–4100	0.4–0.24	14
PVA/PAA (1/1)	95	50	50	0.6–0.8	15
PE/PSS (IEC 2.9)	90	25	20	~ 2	30
P4VP/PGMA (1/1 in moles)	90	25	800	0.75	This study
P4VP/PGMA (1/1 in moles)	96	25	900	0.8	This study

PU: polyurethane; HMDI: hexamethylene diisocyanate; PTEG: poly(tetramethylene ether)glycol; PS: polystyrene; MMA: methyl methacrylate; (P)AA: poly(acrylic acid); HTPB: hydroxy-terminated polybutadiene; H₁₂MDI: 4,4'-dicyclohexylmethane diisocyanate; PAAm: polyacrylamide; PE: polyethylene; PSS: polystyrene sulfonate; IEC: ion-exchange capacity (mequiv/g).

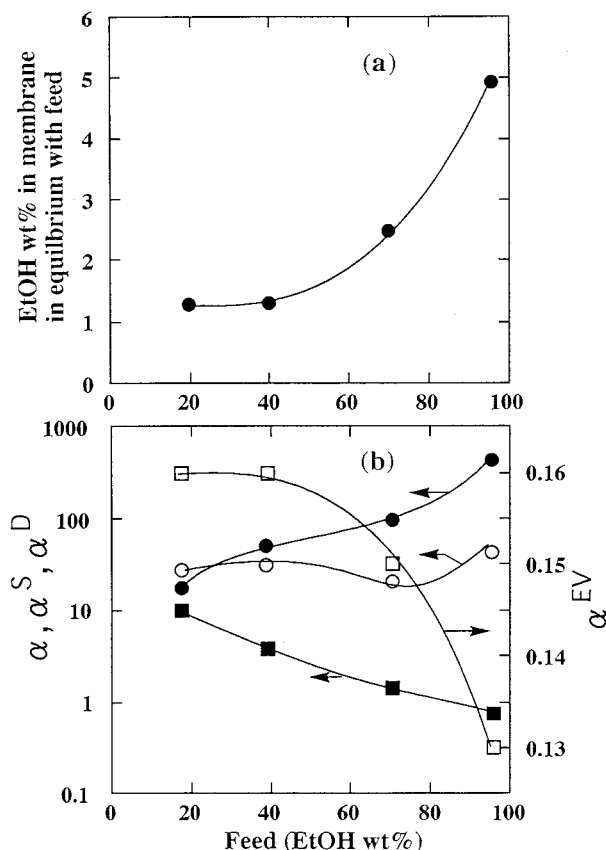


Figure 10 Concentration dependence (a) of sorbed liquid composition in SPN50-30 membrane and (b) of separation factors: (○) α^S ; (●) α^D ; (□) α^{EV} ; (■) α^D .

membrane of the polyethylene/poly(styrene-co-DVB) interpolymer (PESS)³⁰ whose structure is essentially of SPN type, although the values of α^S in this study are about 3–25 times higher than those in the latter. However, the variation of α^D for the IPN membrane shown in Figure 9(b) is just opposite to that for the SPN membrane shown in Figure 10(b). This is very likely to be caused by the highly crosslinked structure of the IPN membrane, which will enable water to permeate more readily because of the molecular size difference even for the feeds of higher ethanol (lower water) concentration. SPN membranes, to the contrary, have a less degree of crosslinking, containing more movable segments, and will allow ethanol molecules to penetrate together with water, leading to lower α^D with increasing ethanol concentration.

The crosslinked PGMA domains of hydrophobic character in the membrane matrix may alter somewhat the relative contribution of the diffusion process to the overall separation with varying

ethanol concentration of the feed, in view of the fact that the α^D of the polyamide-6 membrane that is more hydrophobic than that of the PESS membrane exceeded the α^S for the feeds of low ethanol concentration below 10 mol % (22.1 wt %) in addition to the tendency of α^S and α^D similar to that in Figure 10(b).³⁰

CONCLUSIONS

The following conclusions can be drawn from the discussion described above:

1. A mixture of P4VP and PGMA could give a transparent and tough film from all their compositions. By the addition of DBB alone to the mixture, SPN membranes were formed with a fast quaternizing crosslinking of P4VP with DBB. By the addition of both DBB and an aliphatic primary amine, particularly TEPA, IPN membranes were formed with epoxy ring-opening crosslinking in a rate comparable with the quaternization by heating [PGMA + TEPA] prior to casting.
2. The membranes of an optimum performance were prepared from a 50 mol % mixture of each polymer based on the monomer unit by the addition of 30 mol % DBB based on 4VP.
3. Those membranes exhibited a high rejection in RO and a high value of α in PV. Particularly for the azeotropic feed, α amounted to about 1000 when 6.0 mol % (8 wt %) TEPA based on PGMA was added. Generally, the IPN membrane displayed a performance superior to that of the SPN membrane.
4. The improvement of permeability was attained to some extent by the addition of the water-soluble polymer PEG which also could form another network with PGMA.
5. All the SPN and IPN membranes showed a tensile strength 2.5–6.5 times higher than that of cellulose acetate, probably by the principal contribution of PGMA and its network. IPN membranes were more than twice stronger than were SPN membranes. Also, the dimension stability of IPN was higher than that of SPN, despite a higher swelling degree by weight in the former.
6. Because α^S was higher than α^D , the predominant dissolution of water over ethanol into the present hydrophilic membranes at the feed side determines the overall separation factor. The variation of α^D with the feed of

different ethanol concentrations is attributable to the degree of crosslinking in the membrane matrix.

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