

# Solute Rejection by Poly(ethylene-co-vinyl alcohol) Membrane Prepared by Thermally Induced Phase Separation

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**ABSTRACT:** Porous poly(ethylene-co-vinyl alcohol) (EVOH) membranes were prepared by polymer crystallization by the thermally induced phase separation (TIPS) process. The permeability of these membranes was examined with respect to solutes of various sizes. Higher solute rejection and lower water permeance were obtained by increasing the polymer concentration in the membrane preparation process and by increasing the cooling rate in the TIPS process. These results were discussed based on the crystalline particle sizes formed in the membranes. The membrane performances were influenced by the kinds of diluents used in the TIPS process. The membranes prepared in the EVOH/propanediol system showed a higher rejection coefficient than did those in the EVOH/butanediol system. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2456–2463, 2001

**Key words:** poly(ethylene-co-vinyl alcohol) membrane; thermally induced phase separation; solute rejection; crystallization; porous membrane

## INTRODUCTION

Poly(ethylene-co-vinyl alcohol) (EVOH) has hydrophilic (vinyl alcohol) and hydrophobic (ethylene) segments in a single molecules. EVOH is a unique polymer that is insoluble in water and has good blood compatibility. Hollow-fiber EVOH membranes have been used for blood purification devices including hemodialyzers and plasmapheresis.<sup>1</sup>

Yamashita et al. prepared porous EVOH membranes and investigated membrane properties for hemodialysis.<sup>2</sup> The system of dimethyl sulfoxide (solvent) and water (precipitant) was the most favorable for making hemodialysis membranes. The membrane properties were greatly influenced by the coagulation temperature and polymer concentration. The effect of the EVOH molecular weight on the membrane properties was investigated by Matsumoto et al.<sup>3</sup> The water flux of the membrane depended on the molecular weight rather than on the composition of the copolymer. They showed that membranes prepared from high molecular weight EVOH had small pores and exhibited low water fluxes. Recently, Young

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et al. studied the formation of the EVOH membrane.<sup>4–9</sup> The calculated phase diagram and concentration profiles during the membrane-formation process illustrated reasonably the obtained structures such as an asymmetric cellular morphology and a skinless particulate morphology. Furthermore, solute rejection by the EVOH membrane with asymmetric and particulate morphologies was examined.<sup>10</sup> Asymmetric membranes rejected large dextran molecules and let through small molecules. The particulate membranes exhibited an unusual filtration behavior, that is, there exists a maximum rejection at an intermediate dextran molecular weight. They suggested that small molecules tend to be trapped inside the nanopores within the EVOH particles, whereas large molecules permeate through the tortuous channels outside the particles.

All the above-mentioned membranes were prepared by the traditional immersion precipitation method. In this process, a homogeneous polymer solution was dispersed uniformly on a plate, then precipitated in a nonsolvent bath to form a porous structure. An alternative way to produce the porous structure is a thermally induced phase separation (TIPS) process.<sup>11–17</sup> In the TIPS process, a homogeneous solution is formed by melt-blending the polymer with a high boiling diluent at high temperature; the solution is then cast into the desired shape, the cast solution is cooled to induce phase separation and solidification of the polymer, and, finally, the diluent is removed typically by solvent extraction to produce a microporous structure. The TIPS method has the advantage that it is applicable to a wide range of polymers, including polymers that could not be formed into membranes via the traditional immersion precipitation method due to poor solubil-

ity. In addition, because the phase separation is thermally induced rather than nonsolvent exchange-induced, there are fewer variables that need to be controlled.

In our previous work, porous EVOH membranes were prepared by the TIPS process.<sup>18</sup> The porous structures were formed by solid–liquid phase separation (polymer crystallization) rather than by liquid–liquid phase separation. The sizes of crystalline particles increased with an increasing polymer concentration and a decreasing cooling rate. Solute rejections by the EVOH membrane prepared by the TIPS process are reported in this work.

## EXPERIMENTAL

### Materials

The membrane material studied in this work is an EVOH polymer having an ethylene content of 32 mol % and a degree of polymerization of 1500. This polymer was supplied by the Kuraray Co. (Tokyo, Japan). The diluents were 1,3-propanediol and 1,3-butanediol. These diluents were purchased from the Nacalai Tesque Co. (Kyoto, Japan). All materials were used as received.

### Membrane Preparation and Characterization

Homogeneous polymer–diluent samples were prepared by a method previously described.<sup>17,19</sup> A solid sample was chopped into small sheets and placed between a pair of glass plates. For adjusting the membrane thickness, a Teflon film of 200- $\mu\text{m}$  thickness with a square opening in the center was inserted between the glass plates. The

**Table I** Molecular Weight, Stokes Radius, Diffusion Coefficient  $D_\infty$ , and Mass-transfer Coefficient  $k$  of Solute Used in this Work

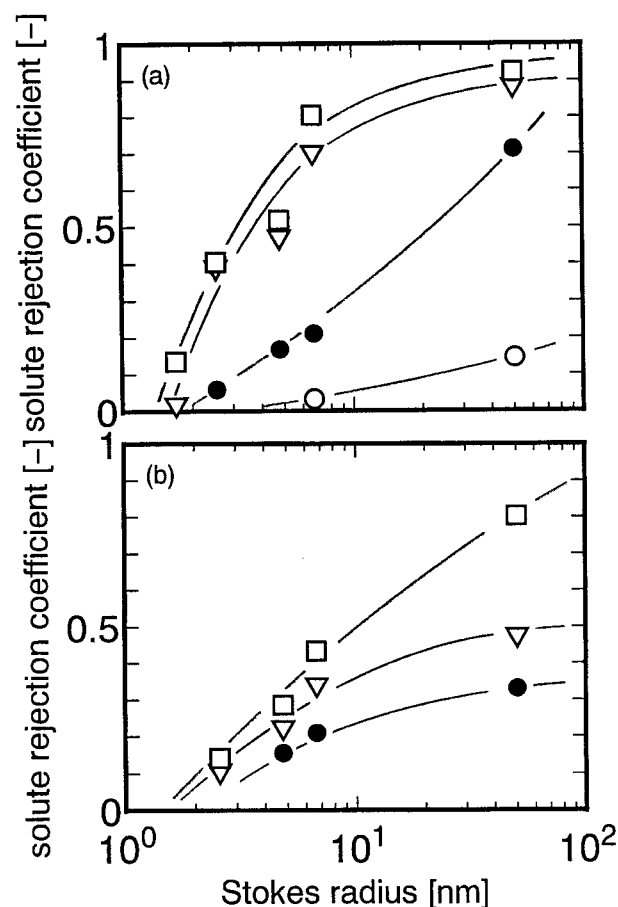
Solute	Molecular Weight	Stokes Radius (nm)	$D_\infty$ (m <sup>2</sup> /s)	$k$ (m/s)
Lysozyme	14,600	1.69 <sup>a</sup>	$1.27 \times 10^{-10}$ <sup>b</sup>	$1.23 \times 10^{-5}$
Ovalbumin	45,000	2.53 <sup>a</sup>	$8.47 \times 10^{-10}$ <sup>b</sup>	$9.35 \times 10^{-6}$
$\gamma$ -Globulin	160,000	4.77 <sup>a</sup>	$4.49 \times 10^{-11}$ <sup>c</sup>	$6.11 \times 10^{-6}$
Ferritin	440,000	6.77 <sup>a</sup>	$3.21 \times 10^{-11}$ <sup>c</sup>	$4.88 \times 10^{-6}$
Latex particle	—	50	$4.29 \times 10^{-12}$ <sup>d</sup>	$1.27 \times 10^{-6}$

<sup>a</sup> Estimated from Stokes–Einstein equation by using  $D_\infty$ .

<sup>b</sup> Ref. 20.

<sup>c</sup> Estimated by the following equation<sup>21</sup>:  $D_\infty$  (m<sup>2</sup>/s) =  $8.34 \times 10^{-12} \{T/(\mu M^{1/3})\}$ , where  $\mu$  is the solution viscosity (cP), and  $M$ , the molecular weight.

<sup>d</sup> Estimated from the Stokes–Einstein equation by using the particle radius.



**Figure 1** Relation between the solute rejection coefficient and the solute Stokes radius. Membranes were prepared by cooling in air at room temperature. (a) EVOH/propanediol system: (○) polymer concentration = 15 wt %, transmembrane pressure = 0.15 atm; (●) 20 wt %, 0.25 atm; (▽) 30 wt %, 0.5 atm; (□) 40 wt %, 3.0 atm. (b) EVOH/butanediol system: (●) polymer concentration = 20 wt %, transmembrane pressure = 0.1 atm; (▽) 30 wt %, 0.25 atm; (□) 40 wt %, 0.5 atm.

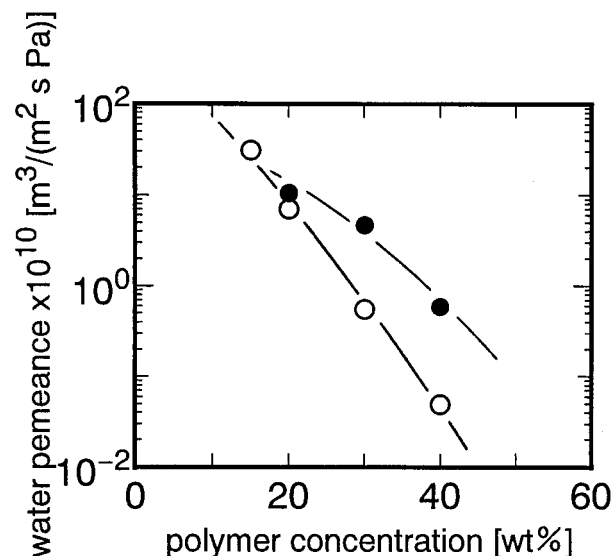
glass plates including the sample were heated at 423.2 K in an oven for 20 min to cause melt-blending. Then, the glass plates were cooled mainly in air at room temperature. Quenching in ice water was also done to study the effect of the cooling rate on the membrane structure and performance. In this experiment, a pair of stainless-steel plates was used instead of the glass plates. After cooling, the sample was peeled from the plates and stored in water.

The porosity of the membrane was estimated from the ideal porosity,  $P_{\text{ideal}}$ , calculated from the initial polymer concentration and the measured contraction ratio in the membrane volume at immersion in water after the preparation,  $f$ . The

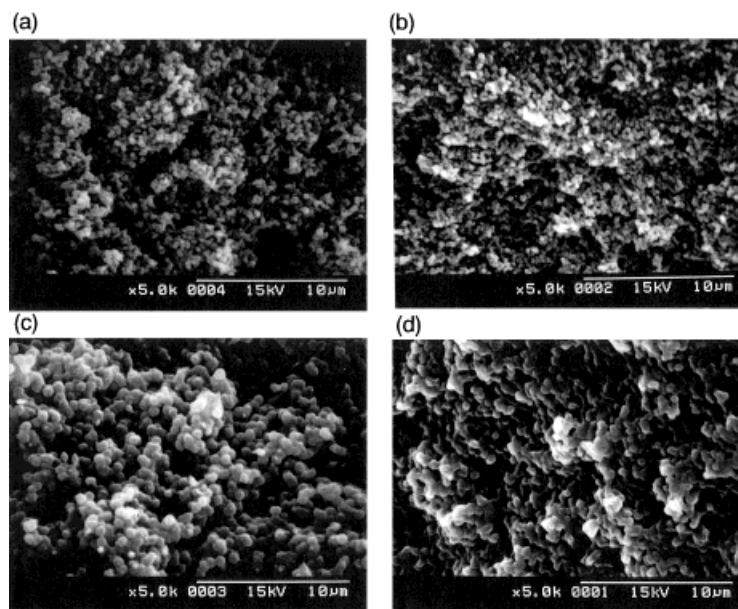
membrane porosity was calculated as  $(f - 1.0 + P_{\text{ideal}})/f$ . For SEM observation, the membrane was immersed in *t*-butyl alcohol and freeze-dried. The resulting microporous structure was fractured in liquid nitrogen and mounted vertically on a sample holder. The surface of the sample was sputtered with Au/Pd in a vacuum. An SEM (Hitachi Co., S-2150) with an accelerating voltage of 15 kV was used to examine the membrane cross sections.

### Filtration

Solute rejection was measured using a stirred cell (Advantec Co., Tokyo, Japan, UHP-25K) at a stirring speed of 1300 rpm. A nitrogen gas tank connected to the filtration cell was used as the pressure source. The solutes were lysozyme from egg white (Seikagaku Co., Tokyo, Japan, 6× crystallized), ovalbumin (Sigma Chemical Co., St. Louis, MO, Grade V, 98% purity),  $\gamma$ -globulin (Nacalai Tesque Co., Kyoto, Japan), ferritin from horse spleen (Nacalai Tesque Co., Kyoto, Japan), and polystyrene latex particle (Duke Scientific Co., Palo Alto, CA, diameter: 100 nm). The molecular weight and Stokes radius are summarized in Table I. The feed solutions were prepared by dissolving the proteins in a 0.05 mol/dm<sup>3</sup> phosphate-buffered solution (disodium hydrogenphosphate + potassium dihydrogenphosphate, pH 7.0). The protein concentrations were 0.1 g/dm<sup>3</sup> for ly-



**Figure 2** Relation between the pure water permeance and the polymer concentration: (○) EVOH/propanediol system; (●) EVOH/butanediol system.



**Figure 3** SEM photomicrographs of cross sections of membranes in EVOH/propanediol system. Polymer concentration = (a) 15 wt %, (b) 20 wt %, (c) 30 wt %, and (d) 40 wt %.

sozyme,  $0.2 \text{ g/dm}^3$  for ovalbumin,  $0.1 \text{ g/dm}^3$  for  $\gamma$ -globulin, and  $0.002 \text{ g/dm}^3$  for ferritin. The latex particle was dispersed in an aqueous nonionic surfactant (0.01% Triton X-100) at the concentration of  $1.03 \times 10^{11}$  particles/ $\text{dm}^3$ . The solute concentrations in the filtrate were measured using a UV spectrophotometer (Hitachi Co., U-2000) at the wavelengths of 280 nm for lysozyme, ovalbumin, and  $\gamma$ -globulin, 275 nm for ferritin, and 385 nm for latex particle. When the solute concentration in the filtrate reached a stable constant value, it was regarded as the membrane property.

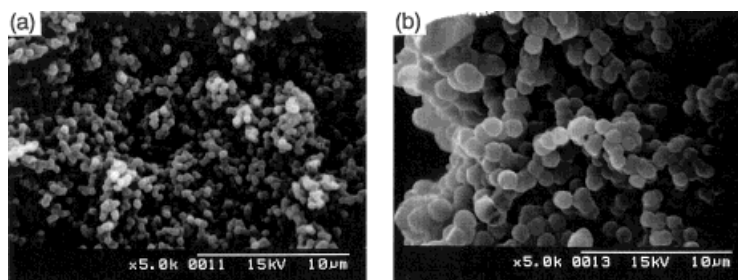
## RESULTS AND DISCUSSION

Figure 1 shows the relations between the solute rejection coefficient and the solute Stokes radius

for the membranes prepared in both the EVOH/propanediol system and the EVOH/butanediol system. The membranes were prepared by cooling in air at room temperature. The solute rejection coefficient  $R$  is defined as

$$R = 1 - C_f/C_0 \quad (1)$$

where  $C_0$  and  $C_f$  are solute concentrations in the feed and the filtrate, respectively. In both systems,  $R$  increased with increasing polymer concentration in the membrane-preparation process. A higher rejection coefficient was obtained in the EVOH/propanediol system than in the EVOH/butanediol system. The membrane prepared from a 40 wt % polymer solution in the EVOH/pro-



**Figure 4** SEM photomicrographs of cross sections of membranes in EVOH/butanediol system. Polymer concentration = (a) 20 wt % and (b) 40 wt %.

**Table II Porosities of Membranes Prepared in Various Conditions**

System	Polymer Concentration	Cooling Condition	Porosity
EVOH/propanediol	15 wt %	Cooled in air	0.84
	20 wt %	Cooled in air	0.80
	30 wt %	Cooled in air	0.65
	40 wt %	Cooled in air	0.52
	15 wt %	Quenched in ice water	0.83
EVOH/butanediol	20 wt %	Quenched in ice water	0.77
	20 wt %	Cooled in air	0.80
	30 wt %	Cooled in air	0.68
	40 wt %	Cooled in air	0.57

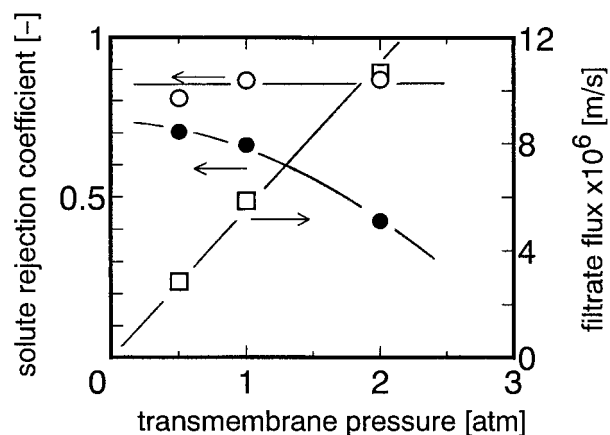
panediol system showed a high rejection coefficient for ferritin with a Stokes radius of 6.77 nm. This means that the EVOH membrane prepared by this TIPS process has an ultrafiltration property.

Figure 2 shows the relation between a pure water permeance and the polymer concentration in the membrane-preparation process. In both two systems, the water permeance decreased with increase of the polymer concentration. The membrane in the EVOH/butanediol system showed higher water permeance at the same polymer concentration condition.

Figures 3 and 4 show SEM photomicrographs of cross sections of the membranes used in the filtration experiments. Membrane structures in the EVOH/propanediol system are shown in Figure 3 and those in the EVOH/butanediol system are shown in Figure 4. The structure of the cross section near the surface was confirmed to be almost the same as that near the center of the membrane. In all membranes, crystalline EVOH particles were observed. The particle size increased with increasing polymer concentration. The larger particles were obtained in the EVOH/butanediol system at the same polymer concentration condition than in the EVOH/propanediol system. These tendencies are the same as those reported in our previous article.<sup>18</sup> Solute transports through the membrane by way of the interconnected open pores between the EVOH particles. As shown in Table II, increase of the polymer concentration leads to lower porosity of the membrane. This means that a space volume between particles is lower in the membrane prepared from the higher polymer concentration condition. This is the reason that the higher solute rejection coefficient and the lower water permeance were obtained at the high polymer concentration condi-

tion in Figures 1 and 2. When the porosities are compared with the membranes prepared in the two systems, those are similar at the same polymer concentration condition, as shown in Table II. However, the larger crystalline particles were obtained in the EVOH/butanediol system. The larger the particles are, the larger become the channel sizes of open pores between the particles. This leads to the lower solute rejection and the higher water permeance in the EVOH/butanediol system, as shown in Figures 1 and 2.

The effect of transmembrane pressure on the solute rejection coefficient and the filtrate flux is shown in Figure 5. The flux increased linearly with increasing pressure, whereas the rejection coefficient decreased. The decrease in the rejection coefficient can be explained by the concentration polarization phenomena. At the steady state,



**Figure 5** Effect of transmembrane pressure on the solute rejection coefficient and the filtrate flux. EVOH/propanediol system, polymer concentration = 30 wt %. (○) Actual rejection coefficient; (●) apparent rejection coefficient; (□) filtrate flux.

a solute concentration at the membrane–solution interface  $C_i$  is explained as<sup>10,22</sup>

$$\frac{C_i - C_f}{C_0 - C_f} = \exp(J_v/k) \quad (2)$$

where  $J_v$  is the filtrate flux and  $k$  is the mass-transfer coefficient in the boundary layer. The actual solute rejection coefficient  $R_a$  is defined as

$$R_a = 1 - C_i/C_0 \quad (3)$$

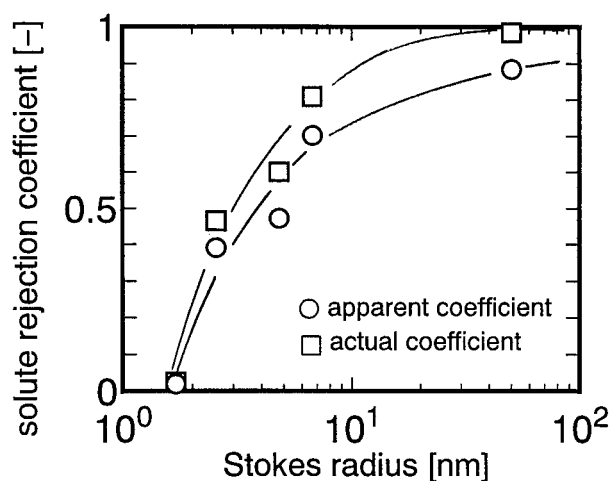
$R_a$  can be related to  $R$  as follows:

$$R_a = \frac{R \exp(J_v/k)}{R \exp(J_v/k) + (1 - R)} \quad (4)$$

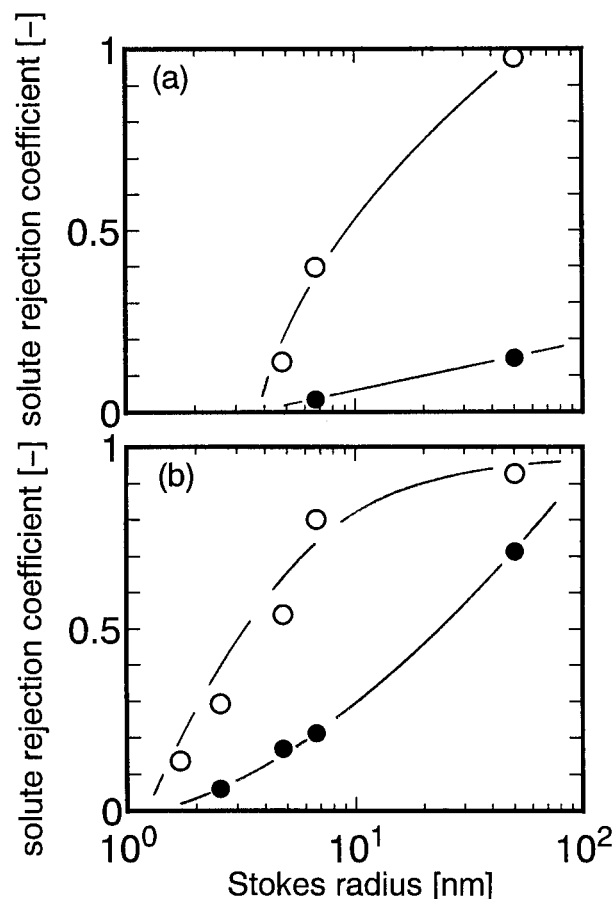
To obtain  $R_a$ ,  $k$  must be determined. The mass-transfer coefficient in a stirred cell can be estimated from the following empirical correlation<sup>10,23</sup>:

$$(kr)/D_\infty = 0.23\text{Re}^{0.567}\text{Sc}^{0.33} \quad (5)$$

where  $r$  is the radius of the stirred cell;  $\text{Re}$ , the Reynolds number;  $\text{Sc}$ , the Schmidt number; and  $D_\infty$ , the solute diffusion coefficient at infinite dilution in water.  $D_\infty$  and  $k$  for each solute are listed in Table I. As can be seen in Figure 5, the actual solute rejection coefficients estimated from eq. (4)



**Figure 6** Relation between the actual rejection coefficient and the apparent rejection coefficient. EVOH/propanediol system, polymer concentration = 30 wt %, transmembrane pressure = 0.5 atm.



**Figure 7** Effect of cooling process on the solute rejection coefficient. EVOH/propanediol system. (a) Polymer concentration = 15 wt %: (○) quenched in ice water, transmembrane pressure = 0.25 atm; (●) cooled in air, transmembrane pressure = 0.15 atm. (b) Polymer concentration = 20 wt %: (○) quenched in ice water, transmembrane pressure = 2.0 atm; (●) cooled in air, transmembrane pressure = 0.25 atm.

are independent of the pressure and nearly constant.

The relation between the actual solute rejection coefficient  $R_a$  and the apparent rejection coefficient  $R$  is shown in Figure 6. The data of the apparent rejection coefficient are the parts of the experimental results shown in Figure 1. Although the difference between two rejection coefficients is not so remarkable in this experimental condition, the difference became larger as the Stokes radius increased. This is because the solute concentration at the membrane–solution interface was larger for the larger solute due to the lower diffusion coefficient. The actual rejection coefficient for the latex particle with the radius of 50 nm reached almost unity.

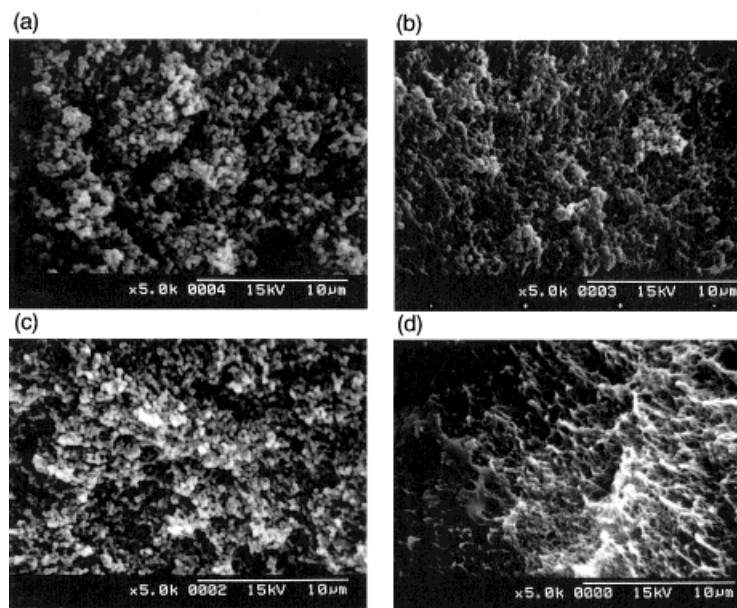
**Table III Water Permeance of Membranes Prepared in Various Conditions: EVOH/Propanediol System**

Polymer Concentration	Cooling Condition	Water Permeance [ $\text{m}^3/(\text{m}^2 \text{ s Pa})$ ]
15 wt %	Cooled in air	$31.3 \times 10^{-10}$
15 wt %	Quenched in ice-water	$2.19 \times 10^{-10}$
20 wt %	Cooled in air	$7.05 \times 10^{-10}$
20 wt %	Quenched in ice-water	$0.18 \times 10^{-10}$

Figure 7 shows the solute rejection coefficient when two cooling processes were used. At the higher cooling rate process, that is, quenching in ice water, the higher rejection coefficients were obtained in both 15 and 20 wt % polymer solution conditions. On the contrary, the water permeance drastically decreased in quenching in ice water, as shown in Table III. In a 20 wt % polymer solution condition, the water permeance in the membrane prepared by quenching in ice water is about 1/40 of that in the membrane prepared by cooling in air. The rejection coefficients of the membrane prepared from a 20 wt % polymer so-

lution by quenching in ice water are comparable to those of the membrane prepared from a 40 wt % polymer solution by cooling in the room temperature air shown in Figure 1. However, it should be noted that the water permeance of the former membrane is about four times higher than that of the latter membrane.

Cross sections of the membranes prepared in two cooling processes are shown in Figure 8. The higher cooling rate brought about the smaller particle sizes in two polymer concentration conditions. This is because the crystallization period from the onset to the cessation of the crystallization is shorter in the higher cooling rate condition.<sup>18</sup> As shown in Table II, the porosities of the membranes prepared at the high cooling rate are lower than those prepared at the lower cooling rate at the same polymer concentration condition. The difference, however, is not so distinguished because the initial polymer concentrations are the same. Therefore, the difference in the membrane performances can not be explained by only the difference in the porosities. In the membrane with the smaller particles prepared at the higher cooling rate, the channel size of the open pores between the particles becomes small. This leads to the higher rejection coefficient shown in Figure 7 and the lower water permeance in Table III.



**Figure 8** SEM photomicrographs of cross sections of membranes in two cooling processes. EVOH/propanediol system: (a) cooled in air, polymer concentration = 15 wt %; (b) quenched in ice water, polymer concentration = 15 wt %; (c) cooled in air, polymer concentration = 20 wt %; (d) quenched in ice water, polymer concentration = 20 wt %.

Thus, in the TIPS process, the membrane performances can be easily controlled by the cooling rate.

## CONCLUSIONS

The solute rejections were investigated with the EVOH membranes prepared by the TIPS process. As the polymer concentrations in the membrane preparation process increased, the resultant membranes showed a higher solute rejection coefficient with the lower water permeance. The membranes prepared in the EVOH/propanediol system had a high rejection coefficient and lower water permeance than had those in the EVOH/butanediol system. This is because the smaller crystalline particles formed in the EVOH/propanediol system led to the smaller channel size of open pores between the particles.

The membrane performances were influenced by the cooling rate. The higher cooling rate brought about the higher rejection coefficient. The membrane performance can be controlled by adjusting the cooling rate in the TIPS process.

The effect of the transmembrane pressure on the solute rejection was investigated. The rejection coefficient decreased with increasing pressure. This was explained by the concentration polarization phenomena. The actual rejection coefficient based on the solute concentration at the membrane-solution interface was independent of the pressure.

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