

Preparation of Polydimethylsiloxane/Polystyrene Interpenetrating Polymer Network Membranes and Permeation of Aqueous Ethanol Solutions Through the Membranes by Pervaporation

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SYNOPSIS

Polydimethylsiloxane (PDMS)/polystyrene (PSt) interpenetrating polymer network (IPN) membranes were prepared by the bulk copolymerization of styrene and divinylbenzene in the PDMS networks. The interpenetration of PDMS and PSt resulted in the improvement of mechanical properties of PDMS. Transmission electron microscope (TEM) observation demonstrated that the PDMS/PSt IPN membranes have microphase-separated structures consisting of a continuous PDMS phase and a discontinuous PSt phase. When an aqueous ethanol solution was permeated through the PDMS/PSt IPN membranes by pervaporation, the PDMS/PSt IPN membranes exhibited ethanol permselectivity, regardless of the PDMS content. The effects of their microphase-separated structures on the permeability and selectivity for aqueous ethanol solutions are discussed experimentally and theoretically. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Many studies on developments of polymer membranes have been undertaken for the separation and concentration of aqueous ethanol solutions by pervaporation.¹ In pervaporation, the permeability and selectivity of membranes depend on both the solubility and diffusivity of the permeants in them. The solubility of the permeants into the membranes is governed mainly by the affinity of the membranes for the permeants, which results from their chemical structures. The diffusivity of the permeants in the membranes is influenced mainly by the physical structures of the membranes. Therefore, the physical and chemical structures must be precisely designed for the development of high-performance membranes.

As ethanol-permselective membranes for the concentration of aqueous ethanol solutions, the polydimethylsiloxane (PDMS) membrane, the

poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane, and their derivatives are well known.²⁻¹⁷ The ethanol permselectivities of their membranes are attributed to their stronger affinity for ethanol and to the relatively high diffusivity of the ethanol in the membranes. Therefore, the ethanol permselectivity of the membranes can be enhanced by improving their affinity for ethanol and the diffusivity of ethanol in the membranes on the basis of the design of their physical and chemical structures.

There are some studies on the permeation and separation of aqueous ethanol solutions through the PDMS membrane by pervaporation. The PDMS membrane is ethanol permselective, since it has a stronger affinity for ethanol than for water. The high diffusivity of ethanol in the PDMS membrane, which results from free rotation of Si—O bonds, also causes excellent ethanol permselectivity. Although the PDMS membrane has many advantages such as low surface free energy, high gas permeability, and good biocompatibility,¹⁸⁻²² its mechanical properties are rather poor. Therefore, the PDMS membrane is often reinforced by using an inorganic filler like silica and introducing a rigid polymer.²³

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To remove the disadvantages of the PDMS membrane, a variety of graft and block copolymers containing dimethylsiloxane were also synthesized as membrane materials.

Polymer blending is a promising technique for the improvement of physical and chemical properties of materials.²⁴ However, blending of general polymers is difficult because there are few combinations of miscible polymers. Since phase separation generally takes place in the blending of immiscible polymers, improvement of physical and chemical properties of materials is rarely achieved.

One of the methods to blend various polymers is the formation of an interpenetrating polymer network (IPN), which is defined as a combination of two polymers in network form.²⁵⁻³¹ IPN attracts our attention, since improvement of the material properties is expected. Therefore, IPNs containing PDMS as a component were synthesized and their properties have been extensively investigated.³²⁻³⁸ He et al.³⁸ obtained polydimethylsiloxane (PDMS)/poly(methyl methacrylate) (PMMA) IPNs by an *in situ* sequential synthesis and examined some properties of the resulting IPNs. They revealed that interpenetrating the PMMA networks in the PDMS networks can improve the poor mechanical properties of the PDMS networks. The PDMS/PMMA IPNs have such a structure in the PDMS component, which is the first-formed network, and constitutes the continuous phase. As such morphology of the membrane significantly affects the membrane performance, the morphology must be controlled by the volume fraction of each component, preparation conditions, etc.

Most multicomponent membranes have microphase-separated structures which result from a very small entropy of mixing and positive heat of mixing. Since the microphase-separated structures directly influence properties and performance of the membranes, it is important to control the morphology of the microphase separation. However, there are few studies on the relationship between the microphase-separated structures and membrane performance in spite of their importance. Previously, we prepared graft copolymer membranes with pendant oligodimethylsiloxane by the copolymerization of dimethylsiloxane (DMS) macromonomer with methyl methacrylate (MMA) and studied the relationship between their microphase-separated structures and permeation characteristics for aqueous ethanol solutions through their membranes by pervaporation.³⁹ The permeability and selectivity of the graft copolymer membranes were directly correlated with their microphase-separated structures. This led us to the

conclusion that the morphology of microphase separation of the membranes must be designed and controlled for the development of high-performance membranes.

This article describes the relationship between microphase-separated structures of PDMS/poly-styrene (PSt) IPN membranes and the characteristics of permeation and separation for aqueous ethanol solutions through these membranes by pervaporation. The PDMS/PSt IPN membranes were obtained by the *in situ* sequential synthesis process for the improvement of mechanical properties of the PDMS membrane. Permeability and selectivity for aqueous ethanol solutions through their membranes are discussed on the basis of the Flory-Huggins equation and Maxwell's model.

EXPERIMENTAL

Materials

The hydroxyl-terminated PDMS base polymer, whose weight-average molecular weight was 20,000, was supplied by Toray Dow Corning Silicone Co., Ltd. Tetraethyl orthosilicate (TEOS) and stannous dibutyldiacetate were used as a crosslinker and a catalyst in the polycondensation reaction of the PDMS base polymer, respectively. Benzoyl peroxide (BPO) as an initiator in the bulk-polymerization of styrene was purified by reprecipitation from a chloroform solution into a methanol solution. Then, divinylbenzene was used as a crosslinker in the bulk-polymerization of styrene. As the other solvents and reagents, analytical-grade reagents from commercial sources were used without further purification.

Preparation of PDMS/PSt IPN Membranes

The PDMS/PSt IPN membranes were prepared by the polycondensation of the PDMS base polymer and the bulk-polymerization of St as follows: A mixture of PDMS base polymer, TEOS (excess to the PDMS base polymer), and stannous dibutyldiacetate (1.0 wt % relative to the PDMS base polymer) for the formation of the PDMS network was mixed with a mixture of the styrene (St) monomer, divinylbenzene (1.0 wt % relative to the St monomer), and BPO (1.0 wt % relative to the St monomer) for the formation of the PSt network. Two glass plates with polytetrafluoroethylene sheets were separated by 100 μm of spacer to form a mold. The resulting mixture was transferred into the mold. At first, the PDMS network was formed at 25°C for 8 h. Then, the tem-

perature was increased to 80°C and the St monomer was bulk-polymerized for 8 h under a nitrogen atmosphere *in situ*. The resulting IPN membranes were immersed in benzene and methanol to remove the monomer, St homopolymer, and other reagents and dried sufficiently *in vacuo*. Since the PDMS/PSt IPN membranes were sufficiently washed in benzene, unreacted monomer and polymer which were not interpenetrating were completely removed. The compositions of the PDMS/PSt IPN membranes were determined by elemental analysis.

Determination of Surface Free Energy of PDMS/PSt IPN Membranes

Contact angles θ of water and methylene iodide on the surface of the PDMS/PSt IPN membranes were measured with a contact angle meter (Erma Model G-I) at 25°C. The surface free energy was calculated from the contact angle θ by eqs. (1) and (2), according to Owens's method^{40,41}:

$$\frac{(1 + \cos \theta) \cdot \gamma_l}{2} = (\gamma_s^d \cdot \gamma_l^d)^{1/2} + (\gamma_s^p \cdot \gamma_l^p)^{1/2} \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

where γ_s and γ_l are the surface free energy of the solid and the liquid, respectively, and γ_s^d , γ_s^p , γ_l^d , and γ_l^p are the dispersion force components and polar force components of the surface free energy of solid and liquid, respectively.

Glass Transition Temperature (T_g) Measurement

Glass transition temperatures (T_g 's) of the PDMS/PSt IPN membranes were determined by differential scanning calorimetry (DSC) (Rigaku; TAS-200). The specimens were heated from about -160 to 180°C with a heating rate of 20°C/min.

Transmission Electron Micrograph (TEM)

Complete PDMS/PSt IPN membranes were embedded in epoxy resin, and their cross sections were cut into thin films (thickness: about 60 nm) with a cryomicrotome (Leica; Reichert Ultracut FC-4E) under the following operation conditions: knife temperature, -130°C, and specimen temperature, -140°C. The morphological features were observed with a transmission electron microscope (TEM) (JEOL JEM-1210) at an accelerating voltage of 120 kV. Since the specimens were not stained, the image contrast in transmission electron microscopy re-

sults from the difference in the electron density of atoms between silicon and carbon.

Permeation Measurement

Pervaporation was carried out using the apparatus reported in an earlier article³⁹ under the following conditions: permeation temperature, 40°C, and pressure of permeation side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm². An aqueous solution of 10 wt % ethanol was used as a feed solution. The ethanol concentrations in the feed and permeate were determined by gas chromatography (Shimadzu GC-9A) equipped with flame ionization detector (FID) and column (Shimadzu Co. Ltd.; Shimalite F) heated at 200°C. The permeation rate in pervaporation was determined from the weight of the permeate collected in a cold trap, permeation time, and effective membrane area.

Tensile Measurement

The tensile strength of the PDMS/PSt IPN membranes was measured by an Instron tester (Shimadzu: AGS-100A) at room temperature at a cross-head speed of 10 mm/min using dumbbell-shaped specimens according to ASTM D 1708-79.

RESULTS AND DISCUSSION

Structures of PDMS/PSt Membrane

Table I shows the composition of the resulting PDMS/PSt IPN membranes determined by elemental analysis and the glass transition temperatures (T_g 's) of the membranes by DSC. The PDMS content in the membrane was higher than that in

Table I Compositions and Glass Transition Temperatures (T_g 's) of the PDMS/PSt IPN Membranes

PDMS/PSt IPN Membrane		T_g (°C)	
PDMS Content in Feed (mol %)	PDMS Content in Membrane (mol %)	High	Low
0	0	106.8	—
30	46.5	109.5	-115.8
50	66.8	110.1	-112.1
70	81.6	110.6	-116.9
90	96.6	96.8	-113.4
100	100	—	-114.1

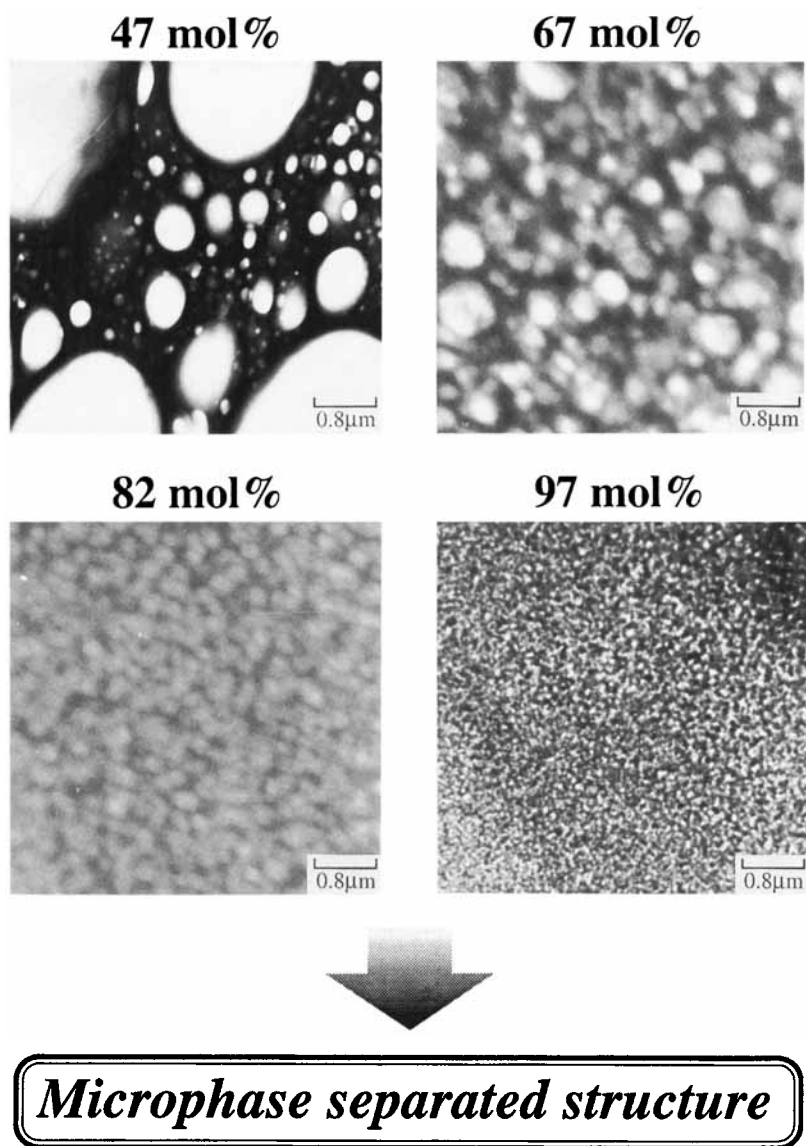


Figure 1 Transmission electron micrographs of the cross section of PDMS/PSt IPN membranes.

the feed. This is because all of the St monomer was not polymerized and some PSt chains were not interpenetrating in the PDMS networks. The fact that PSt in the PDMS/PSt IPN membrane was not dissolved in benzene suggests that the PSt chains in the membranes were interpenetrating in the PDMS networks. Furthermore, it was found that every PDMS/PSt IPN membrane has two T_g 's at about -115 and 110°C . T_g 's of the PDMS and PSt homopolymer membranes were -114.1 and 106.8°C , respectively. Therefore, the lower T_g results from the PDMS component, and the higher T_g , from the PSt component. Both the higher T_g and lower T_g were independent of the composition of the PDMS/

PSt IPN membranes. The presence of two constant T_g 's means that the PDMS/PSt IPN membranes have heterogeneous structures consisting of a PDMS phase and a PSt phase.

Figure 1 shows transmission electron micrographs (TEM) for the cross section of the PDMS/PSt IPN membranes with various compositions. Since image contrast results from the difference in electron density between silicon and carbon, the dark part in Figure 1 is assigned to the PDMS phase containing silicon whose electron density is higher than that of carbon. The TEM observations demonstrated that the PDMS/PSt IPN membranes have microphase-separated structures. With increasing PDMS con-

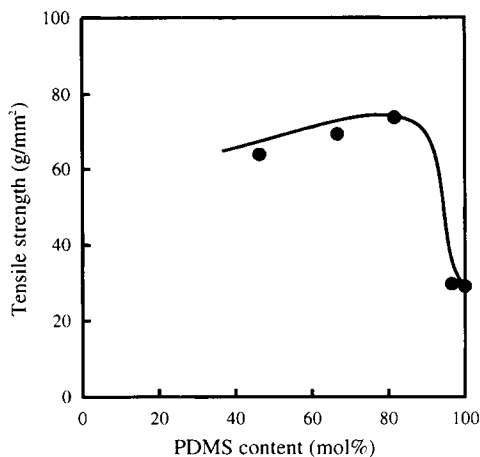


Figure 2 Stress-strain curve of PDMS/PSt IPN membranes.

tent, the PDMS phase increased gradually. Regardless of the composition of the PDMS/PSt IPN membranes, however, all membranes had a morphology such as that of some spherical PSt domains that exist in the PDMS matrix. In general, for a polymer blend, even if the two polymer components are well mixed with each other, they are often phase-separated to some extent. Then, the two components tend to form two mutually continuous phases in which the first-formed network is predominant.^{42,43} In a previous article,³⁹ we examined the structures of the methyl methacrylate-dimethylsiloxane graft copolymer (MMA-*g*-DMS) membranes by TEM and observed the microphase-separated structures in the MMA-*g*-DMS membranes. However, the morphology of the PDMS/PSt IPN membranes is quite different from that of the MMA-*g*-DMS membranes. Such a difference in the morphology is attributed to the difference between the blend and the graft copolymer. In contrast to the MMA-*g*-DMS membrane, the PDMS/PSt IPN membrane was prepared by the bulk-polymerization of St in the PDMS networks. Therefore, PSt components are liable to form large domains in the continuous PDMS phase and have difficulty forming the continuous phase. This is the reason why the PDMS/PSt IPN membranes have microphase-separated structures consisting of PSt domains and the continuous PDMS phase, regardless of the PDMS content in the membrane.

It is well known that a PDMS membrane has excellent ethanol permselectivity: Ethanol is preferentially permeated from an aqueous ethanol solution through the membrane by pervaporation. However, the disadvantage of the PDMS membrane is weak mechanical strength. The mechanical strength of the PDMS membrane can be improved

by the introduction of another component that has strong mechanical properties. Since PSt chains interpenetrated the PDMS chains in the PDMS/PSt IPN membrane, improvement of the mechanical strength of such a membrane can be expected. Therefore, we also investigated the mechanical strength of the PDMS/PSt IPN membranes. The relationship between the PDMS content and tensile strength of the PDMS/PSt IPN membranes is shown in Figure 2. The tensile strengths of the PDMS/PSt IPN membranes were twice that of the PDMS membrane. This indicates that the interpenetration of PSt in the PDMS networks can improve mechanical properties of the PDMS membranes. As revealed from TEM observations, however, the PDMS/PSt IPN membranes consist of PSt domains and the continuous PDMS phase. The discontinuity of the PSt component in the PDMS/PSt IPN membrane causes insufficient improvement of their tensile strength.

Characteristics of Permeation and Separation for Aqueous Ethanol Solutions Through the PDMS/PSt IPN Membrane

Figure 3 shows the effect of the PDMS content on ethanol concentration in the permeate and normalized permeation rate through the PDMS/PSt IPN membranes by pervaporation. The ethanol concentration in the permeate through the PSt membrane is much lower than that in the feed. This result agrees with that in a previous article⁴⁴ and means that the PSt membrane is water-permselective in spite of the hydrophobicity of PSt. For the PDMS/

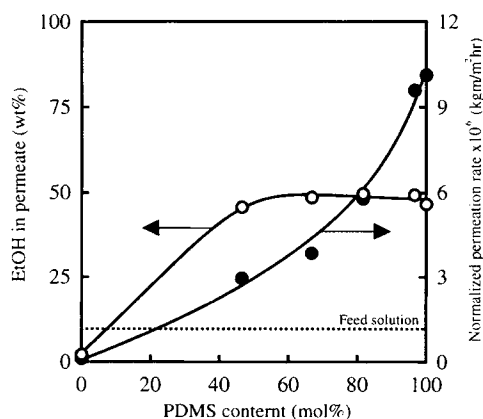


Figure 3 Effect of the PDMS content on (O) the ethanol concentration in the permeate and (●) the normalized permeation rate for an aqueous solution of 10 wt % ethanol through the PDMS/PSt IPN membranes at 40°C by pervaporation. Dashed line is the feed composition.

PSt IPN membrane having a PDMS content of more than 40 mol %, on the contrary, the ethanol concentration in the permeate was about 50 wt %. This leads us to the conclusion that the PDMS/PSt IPN membranes have ethanol permselectivity at a similar level to the PDMS membrane. Furthermore, since the PDMS/PSt IPN membrane with a PDMS content of 40 mol % has stronger mechanical properties than those of the PDMS membrane as described in the previous section, the membrane possesses both strong mechanical properties and excellent ethanol permselectivity, namely, IPN formation of PDMS and PSt enabled us to improve the disadvantage of the PDMS membrane while retaining the ethanol permselectivity. On the other hand, the normalized permeation rate increased gradually with increase in the PDMS content. The diffusivity of permeants in the PDMS phase is higher than in the PSt phase because of the lower T_g of PDMS than that of PSt. Therefore, the higher the PDMS content becomes, the larger the normalized permeation rate the PDMS/PSt IPN membranes exhibit.

The permeation and separation of aqueous ethanol solutions through polymer membranes by pervaporation are based on the solution-diffusion mechanism.¹ In this mechanism, the surface characteristics of the membranes are important factors to determine the sorption of the permeants into the membranes. We focused on the surface characteristics of the PDMS/PSt IPN membranes and tried to clarify the reason why the membranes exhibit excellent ethanol permselectivity, regardless of the PDMS content.

Contact angle measurements can elucidate surface characteristics of the membranes. Furthermore, the surface free energy calculated from the contact angles becomes an indicator for the hydrophilicity and the stability of the membrane surface.⁴¹ We measured the contact angles of water and methylene iodide on the PDMS/PSt IPN membranes and calculated their surface free energy to investigate the surface characteristics of the membranes. The results are plotted in Figure 4. The contact angles of water on the PDMS/PSt IPN membranes were more than 90°. Such large contact angles of water demonstrate that the PDMS/PSt IPN membranes have very hydrophobic surfaces. The surface free energy of the PSt membrane was about 35 erg/cm², and the surface free energy of the membrane decreased sharply by interpenetrating PDMS. The surface free energy of the PDMS/PSt IPN membranes was constant at a PDMS content of more than 40 mol %. The surface free energy of the PDMS/PSt IPN membranes was approximately the same as that of

the PDMS membrane. This is because the PDMS component is more dominantly localized at the membrane surface to make the surface more stable, i.e., the measurement of the surface free energy revealed that the surface of the PDMS/PSt IPN membrane is almost covered with the PDMS component. This conclusion is not in conflict with the result of the TEM observation that the PDMS component forms a continuous bulk phase containing PSt domains in the PDMS/PSt IPN membrane as shown in Figure 1. The PDMS phase localized at the membrane surface must have an affect on the solubility of the permeants into the PDMS/PSt IPN membrane.

The solubility of the permeants into the membrane is determined by the relationship among water, ethanol, and the membrane on the basis of the Flory-Huggins equation.^{1,45-47} Especially, the affinity of water and ethanol for the membrane is an important factor to govern the concentration of ethanol incorporated into the membrane. Therefore, we calculated the theoretical ethanol concentration in the PDMS/PSt IPN membrane using the Flory-Huggins equation as follows: At first, the surface composition of the PDMS/PSt IPN membrane was presumed from the surface free energy in Figure 4. Polymer-solvent interaction parameters between the PDMS or PSt membrane and water (χ_{13}) were obtained by eq. (3) from the degree of swelling of the membrane in water. Polymer-solvent interaction parameters between the PDMS or PSt membrane and ethanol (χ_{23}) were also determined in a similar manner:

$$\ln(1 - V_p) + V_p + \chi V_p^2 + \frac{v_1 \cdot \rho}{M_c} \left(V_p^{1/3} - \frac{V_p}{2} \right) = 0 \quad (3)$$

where V_p is the volume fraction of polymer; χ , the polymer-solvent interaction parameter; v_1 , the molar volume of the solvent; ρ , the density of the polymer; and M_c , the molecular weight between two crosslinking points.

Furthermore, as an interaction parameter between water and ethanol (χ_{12}), we used the values calculated by eq. (4)⁴⁸:

$$\chi_{12} = \frac{1}{x_1 u_2} \left(x_1 \ln \frac{x_1}{u_1} + x_2 \ln \frac{x_2}{u_2} + \frac{\Delta G^E}{RT} \right) \quad (4)$$

where x_i is the weight fraction of components i ; u_i , the volume fraction of component i in a binary liquid mixture; and ΔG^E , the excess free energy of mixing data.

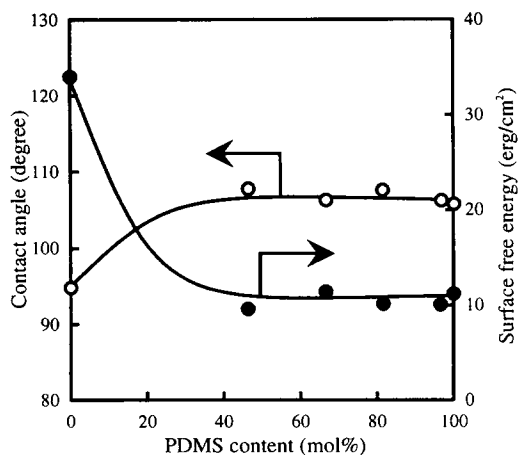


Figure 4 Effect of the PDMS content on the contact angle of water (O) on the PDMS/PSt IPN membranes and (●) their surface free energies.

Finally, the resulting interaction parameters were substituted in eq. (5)⁴⁵⁻⁴⁷ and the volume fractions of water and ethanol in the PDMS/PSt IPN membrane, ϕ_1 , ϕ_2 , were obtained from the volume fractions of water and ethanol in the feed solution, V_1 , V_2 :

$$\ln\left(\frac{\phi_1}{\phi_2}\right) - \ln\left(\frac{V_1}{V_2}\right) = (m-1)\ln\left(\frac{\phi_1}{V_2}\right) - \chi_{12}(\phi_2 - \phi_1) - \chi_{12}(V_2 - V_1) - \phi_3(\chi_{13} - m\chi_{23}) \quad (5)$$

The results are shown in Figure 5. The dotted line indicates a theoretical ethanol concentration in the PDMS/PSt IPN membrane on the assumption that the membrane has a homogeneous surface consisting of both the PDMS phase and the PSt phase. Since the PDMS/PSt IPN membrane has a heterogeneous surface at which the PDMS component is predominantly localized, the theoretical ethanol concentration in the membrane was higher than that in the case of a homogeneous surface. An aqueous solution of 10 wt % ethanol was theoretically concentrated to about 82 wt % ethanol using the PDMS/PSt IPN membrane. The hydrophobicity of the PDMS and PSt components causes preferential incorporation of ethanol from an aqueous ethanol solution. The preferential incorporation of ethanol results in the ethanol permselectivity of the PDMS/PSt IPN membranes in pervaporation. At a PDMS content of more than 40 mol %, furthermore, the ethanol concentration in the membrane was kept constant at 82 wt %. This is attributed to the fact that the surfaces of the PDMS/PSt IPN membranes at more than 40 mol % are almost completely cov-

ered with the PDMS component. The constant and high ethanol concentration in the PDMS/PSt IPN membranes can be the reason why the PDMS/PSt IPN membranes with PDMS content of more than 40 mol % exhibit excellent ethanol permselectivity at a similar level to the PDMS membrane.

Relationship Between Microphase-separated Structures and Characteristics of Permeation and Separation for Aqueous Ethanol Solutions

In a previous article,³⁹ we investigated the relationship between the microphase-separated structures of the MMA-*g*-DMS membranes and the characteristics of permeation and separation for aqueous ethanol solutions through the membranes. It was found that the microphase-separated structure of the membrane directly affects the characteristics of permeation and separation for aqueous ethanol solutions. Therefore, it is important to study the ethanol permselectivity of the PDMS/PSt IPN membranes from the standpoint of their microphase-separated structures.

Maxwell's equation is applied to the permeation of gas through a membrane that has a microphase-separated model structure consisting of a continuous

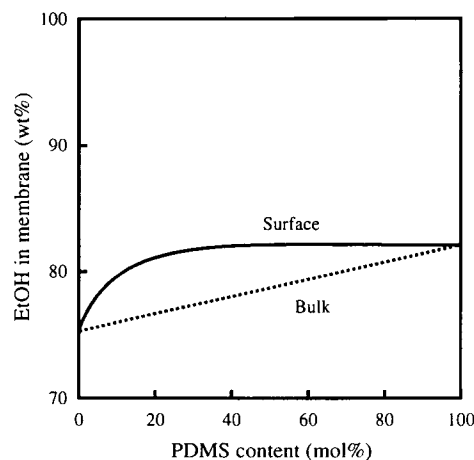


Figure 5 Relationship between the PDMS content and the theoretical ethanol concentration in the PDMS/PSt IPN membrane calculated on the basis of the Flory-Huggins equation. The feed solution is an aqueous solution of 10 wt % ethanol. The line is the theoretical ethanol concentration at the membrane surface, calculated on the assumption that the surfaces of the PDMS/PSt IPN membranes are covered with the PDMS component on the basis of the results of the surface free-energy measurements. The dashed line is total theoretical ethanol concentration in the membrane, calculated on the basis of the composition of the membrane.

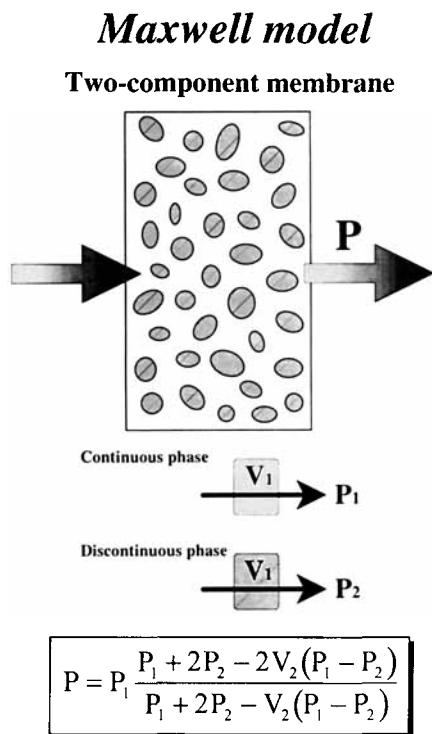


Figure 6 Conception of Maxwell's model for the permeation of aqueous ethanol solutions through membranes with microphase-separated structures consisting of a continuous phase and a discontinuous phase.

phase and a discontinuous phase as shown in Figure 6.^{49,50} We considered the relationship between the microphase-separated structure of the PDMS/PSt IPN membrane and the characteristics of permeation and separation for an aqueous ethanol solution by Maxwell's equation. When the normalized permeation rates of an aqueous ethanol solution through a continuous phase and a discontinuous phase are P_1 and P_2 , respectively, the total normalized permeation rate of an aqueous ethanol solution through the membrane, P , is represented by the volume fraction of each phase, V_1 , V_2 , as follows:

$$P = P_1 \frac{P_1 + 2P_2 - 2V_2(P_1 - P_2)}{P_1 + 2P_2 - V_2(P_1 - P_2)} \quad (6)$$

We calculated the theoretical normalized permeation rate for an aqueous ethanol solution through the PDMS/PSt IPN membrane using Maxwell's equation on the assumption that the membrane consists of a continuous PSt phase and a discontinuous PDMS phase or of a continuous PDMS phase and a discontinuous PSt phase.

The resulting theoretical normalized permeation rates are shown in Figure 7, together with experi-

mental normalized permeation rate. The theoretical normalized permeation rate calculated on the assumption of a continuous PDMS phase is much larger than that based on the assumption of a discontinuous PDMS phase. As can be seen from Table I, the PDMS component has a lower T_g than that of the PSt component. This leads us to the inference that the diffusivity of the permeants in the PDMS phase is higher than in the PSt phase. Therefore, it can be easily understood that the membrane having a continuous PDMS phase exhibits a larger theoretical normalized permeation rate than that having a discontinuous PDMS phase. On the other hand, the experimental normalized permeation rate through the PDMS/PSt IPN membrane is close to the theoretical normalized permeation rate on the assumption of the continuous PDMS phase rather than that based on the assumption of the discontinuous PDMS phase, regardless of the PDMS content. This indicates that all the PDMS/PSt IPN membranes prepared in this study have microphase-separated structures consisting of a continuous PDMS phase and discontinuous PSt phase. This conclusion is consistent with the results of the TEM observations. We previously clarified that the MMA-*g*-DMS membranes change from water- to ethanol permselectivity by the DMS content because of the changes from the discontinuous DMS phase to the continuous DMS phase. Since the PDMS component forms a continuous phase in the PDMS/PSt IPN membrane, the membrane exhibits ethanol permselectivity reflecting the characteristics of the

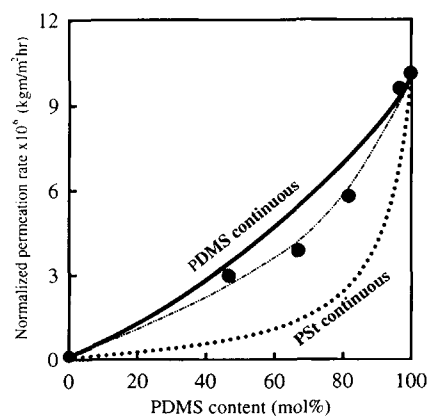


Figure 7 Relationship between PDMS content and normalized permeation rate of an aqueous solution of 10 wt % ethanol through the PDMS/PSt IPN membranes by pervaporation: (—) theoretical normalized permeation rate in the case that the PDMS phase is continuous; (-----) theoretical normalized permeation rate in the case that the PSt phase is continuous by Maxwell's equation.

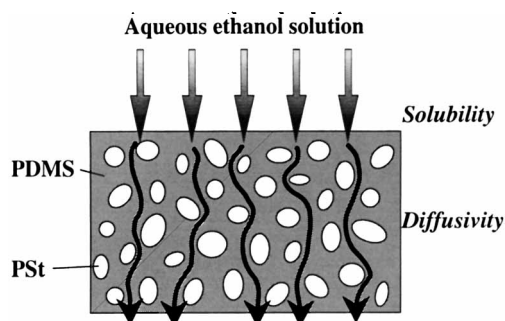


Figure 8 Tentative illustration on the relationship between the microphase-separated structures of the PDMS/PSt IPN membranes and the permselectivity for an aqueous ethanol solution.

PDMS component, regardless of the PDMS content. Furthermore, the localization of the PDMS component on the membrane surface is an important factor in providing the excellent ethanol permselectivity, as the localized PDMS component at the membrane surface gives rise to the more preferential incorporation of ethanol than water. The permeability and selectivity for aqueous ethanol solutions through the PDMS/PSt IPN membranes can be explained by the tentative permeation mechanism shown in Figure 8. In the solution process of the permeants into the PDMS/PSt IPN membrane, ethanol is more predominantly sorbed into the membrane than is water, because the membrane surface covered with the PDMS component has a much stronger affinity for ethanol than for water. In the diffusion process, furthermore, the ethanol and water sorbed in the PDMS/PSt IPN membrane prefer to diffuse in the continuous PDMS phase rather than the discontinuous PSt phase due to lower T_g of PDMS than that of PSt. As a result, the PDMS/PSt IPN membranes shows ethanol permselectivity at a similar level to the PDMS membrane, regardless of the PDMS content.

CONCLUSIONS

The characteristics of permeation and separation for aqueous ethanol solutions through PDMS/PSt IPN membranes by pervaporation were investigated from the standpoint of their microphase-separated structures. All the PDMS/PSt IPN membranes had a microphase-separated structure in which PSt domains exist in a continuous PDMS phase. An aqueous solution of 10 wt % ethanol through the PDMS/PSt IPN by pervaporation was concentrated to about 50 wt %. The PDMS/PSt IPN membranes

with PDMS content of more than 40 wt % showed ethanol permselectivity to the same extent as did the PDMS membrane. Furthermore, the mechanical properties of the PDMS/PSt IPN membranes could be improved by the introduction of PSt without lowering the ethanol permselectivity of the PDMS membrane. The permeation mechanism of aqueous ethanol solutions through the PDMS/PSt IPN membranes was discussed on the basis of solution-diffusion theory and Maxwell's model.

REFERENCES

1. R. Y. M. Huang, *Pervaporation Membrane Separation Processes*, Elsevier, Amsterdam, 1991.
2. K. C. Hoover and S. T. Hwang, *J. Membr. Sci.*, **10**, 253 (1982).
3. S. Kimura and T. Nomura, *Membrane*, **8**, 177 (1983).
4. M. H. V. Mulder, J. O. Hendrikman, H. Hegeman, and S. C. Smolders, *J. Membr. Sci.*, **16**, 269 (1983).
5. H. J. C. Hennepe, D. Bargeman, M. H. V. Mulder, and C. A. Smolders, *J. Membr. Sci.*, **35**, 39 (1987).
6. K. Ishihara, R. Kogure, and K. Matsui, *Kobunshi Ronbunshu*, **43**, 779 (1986); **45**, 653 (1988).
7. Y. Nagase, Y. Takamura, and K. Matsui, *J. Appl. Polym. Sci.*, **42**, 185 (1991).
8. W. J. Ward, W. R. Browall, and R. M. Salemann, *J. Membr. Sci.*, **1**, 99 (1976).
9. S. Takegami, H. Yamada, and S. Tsujii, *J. Membr. Sci.*, **75**, 93 (1992).
10. S. Okamoto, A. Butsuen, S. Tsuru, S. Nishioka, K. Tanaka, H. Kita, and S. Asaoka, *Polym. J.*, **19**, 747 (1987).
11. T. Masuda, B.-Z. Tang, and T. Higashimura, *Polym. J.*, **18**, 565 (1986).
12. K. Ishihara, Y. Nagase, and K. Matsui, *Makromol. Chem. Rapid Commun.*, **7**, 43 (1986).
13. Y. Nagase, S. Mori, and K. Matsui, *J. Appl. Polym. Sci.*, **37**, 1259 (1989).
14. Y. Nagase, K. Ishihara, and K. Matsui, *J. Polym. Sci. Polym. Phys. Ed.*, **28**, 377 (1990).
15. Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, *J. Appl. Polym. Sci.*, **43**, 1227 (1991).
16. T. Uragami and H. Shinomiya, *Macromol. Chem.*, **192**, 2293 (1991).
17. T. Uragami and T. Morikawa, *Macromol. Chem. Rapid Commun.*, **10**, 287 (1989); *J. Appl. Polym. Sci.*, **44**, 2009 (1992).
18. W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1968.
19. L. Le Duc, L. P. Blanchard, and S. L. Malhotra, *J. Macromol. Sci.-Chem. A*, **14**, 389 (1980).
20. G. L. Gaines, *Macromolecules*, **14**, 208 (1981).
21. K. J. Quinn and J. M. Courtney, *Br. Polym. J.*, **20**, 25 (1988).

22. A. Z. Okkema, D. J. Fabrizio, T. G. Grasel, S. L. Cooper, and R. J. Zdrahala, *J. Biomater.*, **10**, 23 (1989).
23. F. S. Fu and J. E. Mark, *J. Polym. Sci. Polym. Phys.*, **26**, 2229 (1988).
24. D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 1978, Vols. 1 and 2.
25. D. Klemmner and K. C. Frisch, *Polymer Alloys*, Plenum Press, New York, 1977.
26. L. H. Sperling, *Macromol. Rev.*, **12**, 141 (1977).
27. D. Klemmner, *Angew. Chem.*, **90**, 104 (1978).
28. Y. S. Lipatov and L. M. Sergeeva, *Interpenetrating Polymeric Networks*, Naukova Dumka, Kiev, 1979.
29. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
30. L. H. Sperling, in *Polymer Blends; Processing, Morphology, and Properties*, M. Kryszyewski, A. Galeski, and E. Martuscelli, Eds., Plenum Press, New York, 1984, Vol. 2.
31. D. A. Thomas and L. H. Sperling, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 2, p. 1.
32. H. Djomo, J. M. Widmaier, and G. C. Meyer, *Polymer*, **24**, 1415 (1983).
33. V. Nevissas, J. M. Widmaier, and G. C. Meyer, *J. Appl. Polym. Sci.*, **36**, 1467 (1988).
34. L. H. Sperling and H. D. Sarge, *J. Appl. Polym. Sci.*, **16**, 3041 (1972).
35. J. R. Ebdon, D. J. Hourston, and P. G. Klein, *Polymer*, **25**, 1633 (1984); **27**, 1807 (1986).
36. B. McGarey and R. W. Richards, *Polymer*, **27**, 1315 (1986); *Br. Polym. J.*, **19**, 111 (1987).
37. S. R. Jin, J. M. Widmaier, and G. C. Meyer, *Polymer*, **29**, 346 (1988).
38. X. W. He, J. M. Widmaier, J. E. Herz, and G. C. Meyer, *Polymer*, **30**, 364 (1989); **33**, 866 (1992).
39. T. Miyata, T. Takagi, T. Kadota, and T. Uragami, *Macromol. Chem. Phys.*, **196**, 1211 (1995).
40. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).
41. K. Nakamae, T. Miyata, and N. Ootsuki, *Makromol. Chem. Rapid Commun.*, **14**, 413 (1993).
42. V. Huelck, D. A. Thomas, and L. H. Sperling, *Macromolecules*, **5**, 340 (1972); **5**, 348 (1972).
43. A. A. Donatelli, L. H. Sperling, and D. A. Thomas, *Macromolecules*, **9**, 671 (1976); **9**, 676 (1976).
44. T. Uragami and T. Morikawa, *Macromol. Chem.*, **190**, 399 (1989).
45. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
46. M. H. V. Mulder, T. Franken, and C. A. Smolders, *J. Membr. Sci.*, **22**, 55 (1985).
47. H. Okuno, T. Nishida, and T. Uragami, *J. Polym. Sci. Polym. Phys.*, **33**, 299 (1995).
48. F. W. Altena and C. A. Smolders, *Macromolecules*, **15**, 1491 (1982).
49. R. M. Barrer, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic Press, London, 1968, Chap. 6.
50. A. E. Barnabeo, W. S. Creasy, and L. M. Robeson, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1979 (1975).

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