

Chemical Modification of Poly(substituted-Acetylene). IV. Pervaporation of Organic Liquid/Water Mixture through Poly(1-Phenyl-1-Propyne)/ Polydimethylsiloxane Graft Copolymer Membrane

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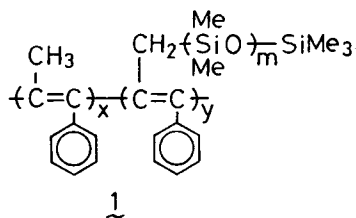
Synopsis

Poly(1-phenyl-1-propyne)/polydimethylsiloxane (PPP/PDMS) graft copolymer membranes having various PDMS content were prepared by solvent casting method, and the permeation characteristics at pervaporation were examined upon the aqueous solutions containing organic liquids such as alcohols, acetone, dioxane, acetonitrile, pyridine, and DMF. At pervaporation of ethanol/water mixture, preferential permeation of ethanol was observed for all the copolymer membranes, although PPP membrane showed water permselectivity. The permselectivity of the copolymer membrane also depended on operation temperature, but was independent on the thickness of the membrane. Furthermore, an excellent permselectivity of organic liquids was observed at the pervaporation of several organic liquid/water mixtures except in the case of DMF/water mixture. Observed high selectivity is thought to be due to the depression of the membrane swelling and the high solubility of the liquids into the membrane.

INTRODUCTION

In the membrane separation process for concentrating ethanol from its aqueous solution, it is practical to separate ethanol through an ethanol permselective membrane since ethanol is often a minor component in the solution. A polydimethylsiloxane (PDMS) membrane is well known as an ethanol permselective membrane.¹ But its selectivity at the permeation is still low according to swelling of the membrane. In addition, ultrathin membrane cannot be prepared from this material. Ishihara et al. have reported the preferential permeation of ethanol at pervaporation of ethanol/water mixture through polystyrene/PDMS graft copolymer membrane.² By using this membrane, 7 wt % aqueous ethanol solution was concentrated to an ethanol solution of 60 wt % or more. Such a high selectivity for ethanol is attributed to an increase of hydrophobicity at the membrane surface and depression of the membrane swelling.

In recent years, we have investigated the chemical modification of poly(substituted-acetylene) by introducing PDMS to afford graft copolymers containing PDMS chain in their side chain.³⁻⁵ Poly(1-trimethylsilyl-1-propyne) (PTMSP) and poly(1-phenyl-1-propyne) (PPP) have been used as the back-



bone components. It was found that PTMSP/PDMS graft copolymer membrane showed improved selectivity and stability at gas permeation³ and excellent permselectivity of ethanol from ethanol/water mixture by pervaporation technique.⁴ Our previous paper also disclosed synthesis and gas permeability of PPP/PDMS graft copolymer,⁵ of which chemical formula was shown as 1. Its chemical structure is close to those of PTMSP/PDMS and polystyrene/PDMS graft copolymers. Thus, similar excellent permselectivity for ethanol is expected in the case of PPP/PDMS graft copolymer membrane.

In this article, therefore, we describe our investigation upon the permeation and separation characteristics of the PPP/PDMS graft copolymer membrane at pervaporation of aqueous ethanol solutions. Several kinds of the graft copolymers having different PDMS content were prepared, and a detailed study on the copolymer membrane was carried out to clarify the effect of PDMS content, membrane thickness, and temperature upon the permeation. Moreover, permeation experiments of the mixtures of water and other kinds of organic liquids were also conducted to evaluate the separation property of this type of graft copolymer membrane.

EXPERIMENTAL

Materials

Starting material, PPP, was prepared according to the method of Masuda et al.⁶: 1-Phenyl-1-propyne was polymerized in toluene at 80°C with tantalum pentachloride as catalyst and tetra-*n*-butyl tin as cocatalyst. PPP thus obtained was reprecipitated several times from its toluene solution into excess amount of methanol, and was dried *in vacuo* at 80°C for 24 h before use.

PPP/PDMS graft copolymer was prepared by metalation of PPP with *n*-butyllithium followed by treating with hexamethylcyclotrisiloxane (D₃) and trimethylchlorosilane. Detailed procedure for the preparation was described in our previous paper with its characterizations.³ PDMS contents of the copolymers were controlled in 44, 56, 71, 75, and 79 mol % by changing the molar ratio of D₃ and PPP in the reaction.

Membrane Preparation

Toluene solution containing about 3 wt % of the polymer was cast on a polytetrafluoroethylene sheet and the solvent was evaporated over a period of 24 h. For the measurement of pervaporation, the polymer membrane formed was then dried *in vacuo* and cut into a square piece of 50 mm in each length. The thickness of the membrane was in the range of 30–200 μm.

Pervaporation

Pervaporation of organic liquid/water mixtures through the membrane was carried out in an ordinary manner using a stainless steel cell² at the temperature range between 18 and 73°C. The permeation area of the membrane in contact with liquid was 9.6 cm². The feed solution of the organic liquid/water mixture was circulated on the upper side of the membrane, and the pressure of the lower side was maintained at about 0.5 mm Hg. Composition and flux of the permeating mixture were determined by a gas chromatograph connected directly to the pervaporation cell, in order to avoid the effect of moisture on the determination of pervaporation characteristics.

The permeation rate P (g m/m² h) was calculated by a correction of the flux for the thickness of the membrane. The separation factor, which was a measure of the preferential permeation of component A, was also defined as the concentration ratio Y_A/Y_B in the permeate divided by the concentration ratio X_A/X_B in the feed. A and B indicate organic liquids and water, respectively.

Ethanol, methanol, *n*-propanol, *i*-propanol, acetone, dioxane, acetonitrile, pyridine, and dimethylformamide (DMF) were used as the organic liquids in this study.

RESULTS AND DISCUSSION

Pervaporation of Ethanol/Water Mixture

Figure 1 shows permeation composition curves of aqueous ethanol solution at 30°C through PPP/PDMS graft copolymer membranes having different PDMS contents in comparison with PPP membrane. In the case of PPP membrane, preferential permeation of water was observed at every ethanol composition in feed. In general, most of poly(substituted-acetylene) mem-

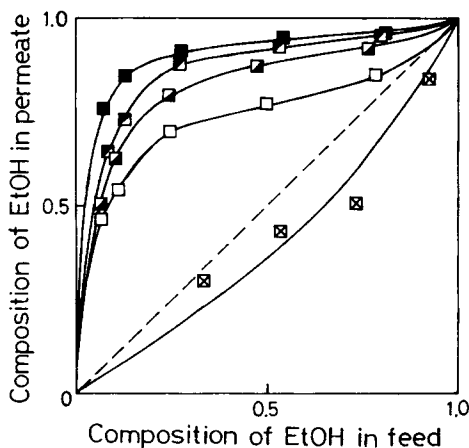


Fig. 1. Permeation composition curves of ethanol/water mixture through PPP membrane (▧) and PPP/PDMS graft copolymer membranes: (□) 56/44; (■) 44/56; (▧) 29/71; (●) 21/79.

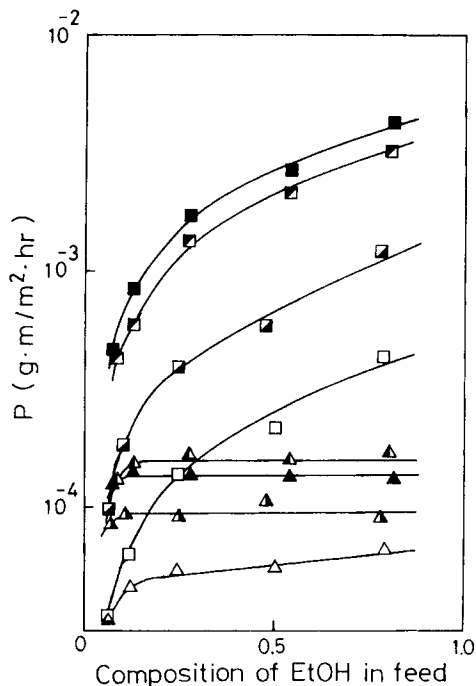


Fig. 2. Plots of permeation rates P_{EtOH} and $P_{\text{H}_2\text{O}}$ against feed composition of ethanol/water mixture through PPP/PDMS graft copolymer membranes: (\square, Δ) 56/44; ($\blacksquare, \blacktriangle$) 44/56; (\square, Δ) 29/71; ($\blacksquare, \blacktriangle$) 21/79.

branes are known to show preferential permeation of water at pervaporation of aqueous ethanol solution except in the case of PTMSP membrane.⁷ On the contrary, as shown in Figure 1, preferential permeation of ethanol was observed for all the PPP/PDMS graft copolymer membranes. The composition of ethanol permeated through the graft copolymer membranes increased with increase of the PDMS content. In particular, 7 wt % aqueous ethanol solution was concentrated to over 75 wt % by using the copolymer membrane containing 79 mol % of PDMS composition, whereupon the separation factor assumed about 40 and the permeation rate was 5.73×10^{-4} g/m² h.

Figure 2 shows relation between the ethanol compositions in feed and the permeation rates of each component at the pervaporation experiments for PPP/PDMS graft copolymer membranes. In every case, the permeation rate of ethanol increased with increase of the alcohol content in feed. On the other hand, the permeation rate of water was almost constant at every composition in feed except in low concentration range of ethanol. Furthermore, permeation rate of ethanol increased with increase of the PDMS content of the graft copolymer. These phenomena indicate that these membranes have good affinity toward ethanol and high hydrophobicity. In general, excessive enhancement of the affinity of the polymer membrane for ethanol may lead to the decrease of the selectivity owing to the membrane swelling in a high ethanol composition region in feed. In fact, though a crosslinked PDMS membrane is well known as an ethanol permselective membrane, the selectivity for ethanol diminishes, especially when the composition of ethanol in feed

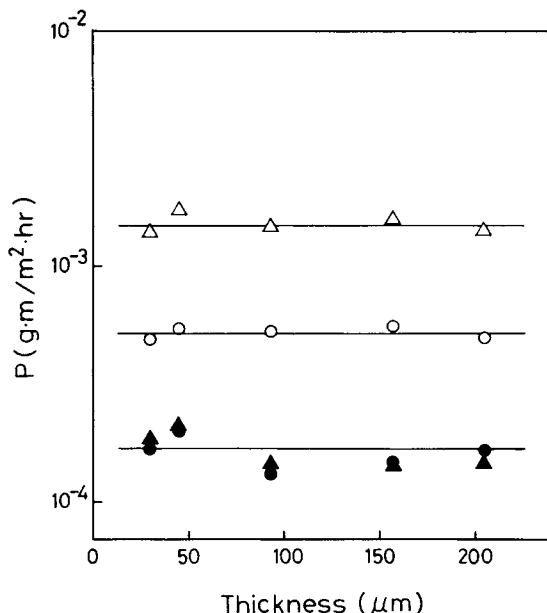


Fig. 3. Effect of membrane thickness on the permeation rates P_{EtOH} and $P_{\text{H}_2\text{O}}$ for the pervaporation of 15 wt % (○, ●) and 50 wt % (△, ▲) aqueous ethanol solution through PPP/PDMS graft copolymer membrane.

exceeds 70 wt %.¹ At the concentration range, considerable swelling of the membrane was observed owing to its high affinity for ethanol. On the other hand, PPP/PDMS graft copolymer membranes were not swollen by water, pure ethanol, and water/ethanol mixture even if the PDMS content was 79 mol %. This is one of the reasons why these membranes have such a high ethanol permselectivity. The almost constant permeation rate of water at every composition in feed as shown in Figure 2 is also due to little swelling of the membrane even by ethanol.

Figure 3 shows effect of membrane thickness on permeation rates of ethanol and water at the pervaporation of 15 and 50 wt % aqueous ethanol solution through PPP/PDMS graft copolymer membrane containing 75 mol % of PDMS composition. It was confirmed that both permeation rates of ethanol and water were independent of the thickness of the copolymer membrane, which was in the range of 30–200 μm. Further, the separation factor α was also constant with an alteration in the membrane thickness. Thus, a proportional increase of flux is observed with a decrease of the membrane thickness. If an ultrathin membrane can be prepared from this graft copolymer, a very high flux is expected with high α .

Figure 4 shows effect of operating temperature on permeation rates of ethanol and water and separation factor at the pervaporation of 7 wt % aqueous ethanol solution through the copolymer membrane containing 75 mol % of PDMS composition. The operating temperature was changed between 18 and 73°C. The permeation rates of ethanol and water increased simply as the temperature increased, whereas separation factor assumed the maximum value, 29, at 50°C. Accordingly, it is very effective to use this

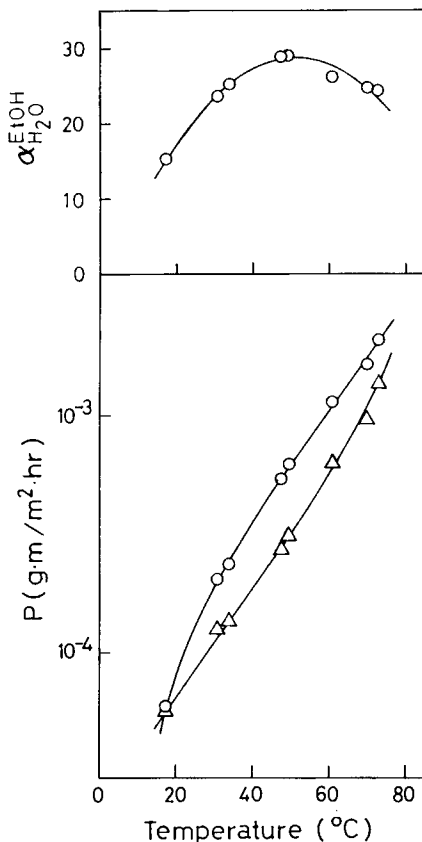


Fig. 4. Effect of temperature on permeation rates P_{EtOH} (○), P_{H_2O} (△), and separation factor $\alpha_{H_2O}^{EtOH}$ for the pervaporation of 7 wt % aqueous ethanol solution through PPP/PDMS graft copolymer membrane.

membrane at about 50°C for the separation of ethanol/water mixture in view of the highest selectivity, as well as the high flux.

Pervaporation of Organic Liquid / Water Mixtures

Figures 5 and 6 show permeation composition curves of various alcohol/water and other organic liquid/water mixtures at pervaporation at 30°C through PPP/PDMS graft copolymer membrane containing 75 mol % of PDMS composition. As shown in the figures, all the organic liquids used in this work were efficiently separated from their aqueous solution except for DMF.

It was found that the permeation characteristics of alcohols were different from each other depending upon the kind of alcohol, as shown in Figure 5. When the concentration of alcohols was below 30 wt %, the separation factor increases with increase of molecular size of alcohol in the following order: methanol < ethanol < *n*-propanol \approx *i*-propanol. On the contrary, in the range of over 30 wt %, the order was reversed. Thus, it is considered from this result that, in the region of low concentration of alcohols, preferential permeation of

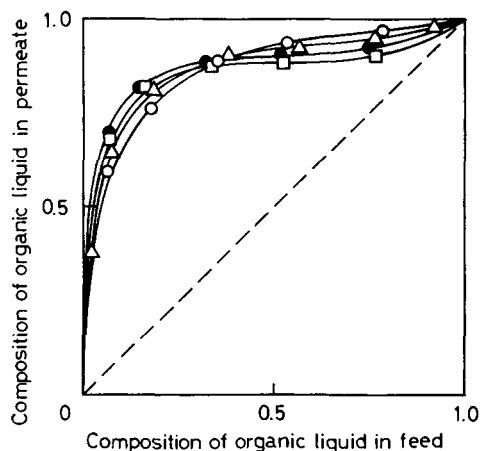


Fig. 5. Permeation composition curves of organic liquid/water mixture through PPP/PDMS graft copolymer membrane. Organic liquid: (○) methanol; (△) ethanol; (□) *n*-propanol; (●) *i*-propanol.

alcohols is accelerated as the affinity of alcohols toward the membrane increases, and, in the region of the high concentration, the membrane would swell to some extent by the alcohol of more hydrophobic, such as *n*-propanol and *i*-propanol. Other than alcohols, acetone, acetonitrile, dioxane, and pyridine were efficiently separated from their aqueous solutions, as shown in Figure 6. The copolymer membrane was not disrupted nor even swollen by every organic liquid used in the permeation experiments. However, in the case of DMF/water mixture, preferential permeation of water was observed at 53°C. Below the temperature, DMF did not permeate through the membrane. The observed low permselectivity of DMF would be explained by its low vapor pressure. Accordingly, the permeation characteristic of DMF/water mixture cannot be simply compared with that of other volatile organic liquids/water mixtures.

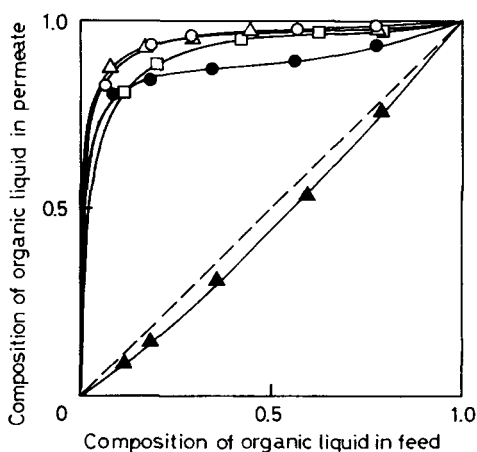


Fig. 6. Permeation composition curves of organic liquid/water mixture through PPP/PDMS graft copolymer membrane. Organic liquid: (○) acetone; (△) acetonitrile; (□) dioxane; (●) pyridine; (▲) dimethylformamide.

TABLE I
Results of Pervaporation of Organic Liquid/Water Mixtures through PPP/PDMS
Graft Copolymer Membrane and the Values of Contact Angle of the Liquid
on the Membrane Surface

Organic liquid	Composition (wt %)		$\alpha_{\text{water}}^{\text{organic}}$	P (g m/m ² h)	Contact angle (°)
	Feed	Permeate			
Acetonitrile	7.90	87.3	80.2	1.70×10^{-3}	51.9
Acetone	6.31	82.8	71.4	1.58×10^{-3}	20.5
Pyridine	8.41	80.4	44.7	9.09×10^{-4}	59.6
Dioxane	11.4	80.9	33.0	1.00×10^{-3}	52.5
<i>i</i> -Propanol	7.02	69.7	30.5	7.25×10^{-4}	19.7
<i>n</i> -Propanol	6.97	67.8	28.1	6.05×10^{-4}	19.5
Ethanol	7.28	63.9	22.5	5.53×10^{-4}	28.6
Methanol	6.64	59.0	20.2	5.04×10^{-4}	56.8

Table I indicates typical pervaporation results of aqueous low concentrating solutions of organic liquid through PPP/PDMS graft copolymer membrane and the values of contact angle by the liquids on the surface of the membrane. In this table, organic liquids are listed in their order of separation factor. In particular, the separation factors α for acetonitrile and acetone solutions exceeded 70 and 80, respectively, whereupon the 6–8 wt % feed solution was concentrated to over 80 wt % in the permeate. Further, the permeation rates P reached over 1×10^{-3} g m/m² h. This value of P indicates that if the ultrathin membrane of ca. 1 μm thickness can be prepared, the flux of the permeate will be over 1 kg/m² h. Such an excellent permselectivity of organic liquids at the pervaporation through the copolymer membrane might be attributed to the surface property of the membrane. In order to evaluate the affinity of the membrane for the liquid components, the contact angle by each liquid on the surface of the membrane was measured as listed in Table I. The values of contact angle of the organic liquids used in this work were in the range of 19–60°, whereas that of water was 98.6°. It can be assumed from these values that the graft copolymer membrane has good affinity toward these organic liquids and also high hydrophobicity. This is one of the reasons why such a high selectivity is observed in the pervaporation experiments. However, there is no linear relationship between the values of separation factor and those of contact angle.

In order to elucidate the difference of separation factors at the pervaporation of various organic liquids/water mixtures, the separation factors were plotted against solubility parameter of each liquid component. Figure 7 shows the relation between the separation factors α listed in Table I and the solubility parameters⁸ δ of each liquid component. As shown in this figure, the separation factor increased with decrease of the solubility parameter of each organic liquid, in other words, with increase of the difference between the solubility parameter of the liquids and that of water. In general, a noncrystalline polymer will dissolve in a solvent of similar δ without the necessity of solvation, chemical similarity, association, or any special directed intermolecular force.⁸ In fact, δ of tetrahydrofuran, a good solvent to dissolve the copolymer, was 9.1, and δ 's of acetonitrile and acetone (the highest α was

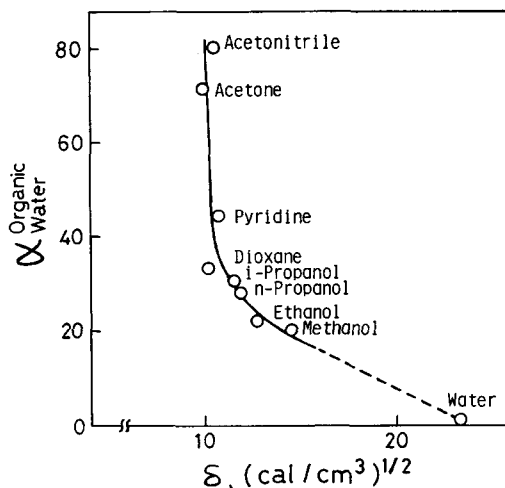


Fig. 7. Plots of separation factor $\alpha_{\text{Organic/Water}}$ in Table I against solubility parameter δ for the pervaporation of organic liquid/water mixture through PPP/PDMS graft copolymer membrane.

observed on their aqueous solution) were 10.5 and 9.9, respectively. Thus, it is predicted that the solubility parameter of the graft copolymer membrane is near that value of acetonitrile or acetone. Consequently, it is considered that such a difference of selectivity for organic liquids is mainly attributed to a difference of solubility of the liquids to the membrane.

This study allows us to expect that this type of graft copolymer membrane is employed in the practical applications, such as the separation or concentration of organic liquid from their aqueous solutions.

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