Selective Separation of Water from Aqueous Alcohol Mixtures through Functionalized Syndiotactic Poly(styrene-*co*-4-methylstyrene) Membranes by Pervaporation

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ABSTRACT: The pervaporation performances of a series of functionalized syndiotactic poly(styrene-*co*-4-methylstyrene) (SPSM) membranes for various alcohol mixtures were investigated. The syndiotactic polystyrene copolymers, poly(styrene-*co*-4-methylstyrene) (SPSM), were prepared by styrene with 4-methylstyrene using a Cp*Ti(OCH_3)$_3$/methyl aluminoxane (metallocene/MAO) catalyst. The effect of functionalization on the thermal properties and polymer structure of the SPSM membranes were also investigated. The crystallinity of the functionalized SPSM membrane is lower than that of the unfunctionalized SPSM membranes. The water molecules preferentially permeate through the SPSM membranes. Compared with unfunctionalized SPSM membranes, the functionalized SPSM membrane effectively increases the membrane formation performances and the pervaporation performances. The optimun pervaporation performance (a separation factor of 510 and permeation rate of 220 g/m^{2}h) was obtained by the bromination of SPSM (SPSMBr) membrane with a 90 wt % aqueous ethanol solution. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2247–2254, 2002

Key words: functionalization; sydiotactic poly(styrene-*co*-4-methylstyrene); pervaporation; membrane

INTRODUCTION

The separation of azeotropic mixtures, heat-sensitive compounds, and isomers is still a challenging target in the membrane separation technology. At present, the separation of the above mixtures requires the use of energy intensive processes, such as extractive and azeotropic disstillation, vacuum distillation, and solvent extraction. Pervaporation separation processes offer potentially more economical alternatives for such difficult separation mixtures. In the membrane research field, so many efforts have been made to prepare pervaporation membranes with good performance and good stability for the separation of the above liquid mixtures. Proceeding from the viewpoint of that mentioned above, many researchers have focused their attention on improving the membrane separation performance, including: membrane formation process, ^{60}Co γ-ray irradiation or plasma grafting, polymer blending, chemical grafting, and preparing new polymers.[1–8] However, the key to successful pervaporation lies in the intrinsic properties of the polymers used to prepare membranes. From this, the development of novel pervaporation membranes with good separation performance is exceedingly important, because the syndiotactic polystyrene (SPS) exhibits excellent physical properties, such as a low dielectric constant, excellent hydrolytic and dimensional stability, good heat stability, chemical resistance, as well as low specific density. It can be utilized in the electrical/electronic and automotive industry to replace existing expensive engineering plastics. However, SPS shows inferior adhesion properties, compatibility, impact resistance, and poor membrane formation.[9,10] Thus, it is inevitably limited in the scope of application as a membrane material. However, the functionalized polymers can serve as interfacial modifiers to improve their adhesion to and compatibility with other materials as well as impact resistance. Furthermore, the membrane formation properties can be improved, resulting from the introduction of the functional group into the polymer pendent group. Owing to the chemical stability of SPS, direct functionalization is difficult. Introducing 4-methylstyrene to SPS produces a copolymer that can be functionalized in benzyl groups without destroying its crystallinity.

The purpose of this work is to synthesize and characterize the functionalized syndiotactic polystyrene copolymers. The syndiotactic polystyrene copolymers, poly(styrene-*co*-4-methylstyrene) (SPSM), were prepared by styrene with 4-methylstyrene using a metallocene/MAO catalyst.[11] In addition, the effects of feed composition, the molar volume of alcohols, and the

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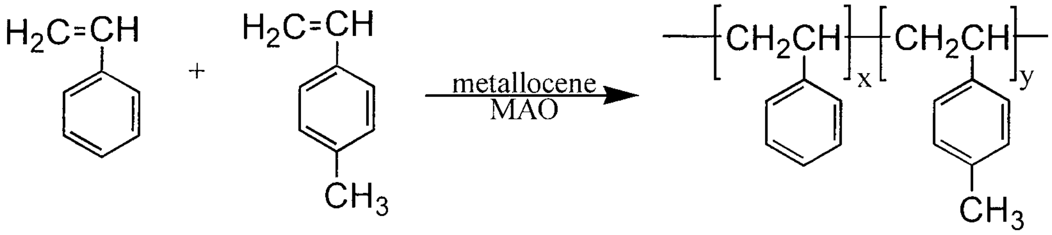


Scheme 1

feed solution temperature on the pervaporation performances of the functionalized SPSM membranes were investigated.

EXPERIMENTAL

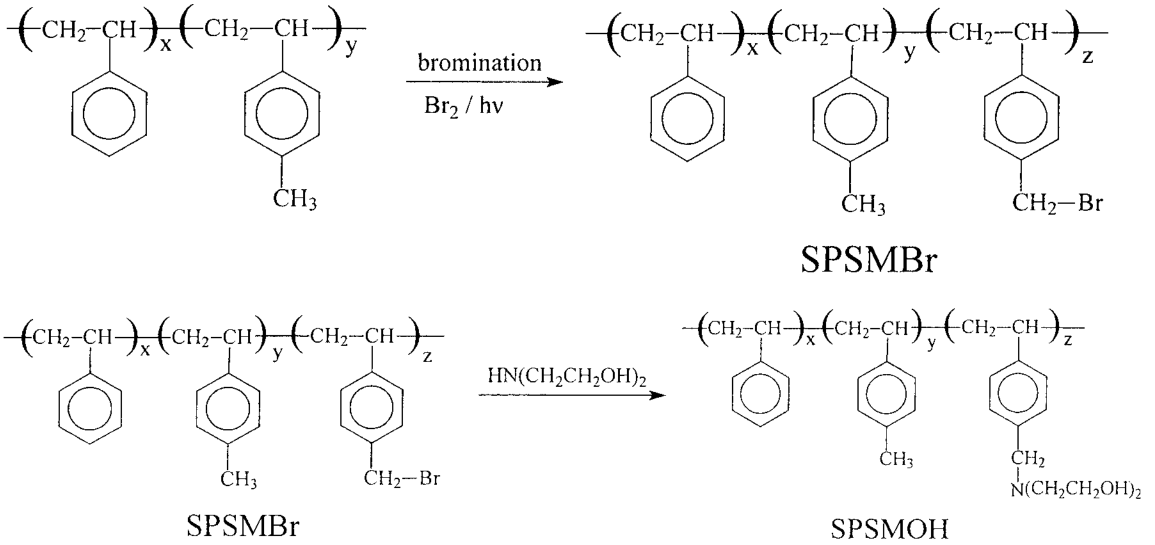
Material

Synthesis of syndiotactic poly(styrene-*co*-4-methylstyrene)(SPSM)

The copolymerization were carried out in a 5-L steel autoclave (Parr) with a stirrer at constant pressure (H_2/N_2). Styrene (1800 mL) and 4-methylstyrene (180 mL) were poured into the reactor via a canula. Triisobutylaluminum (TIBA, 4.8 mmol) and methylaluminoxane (MAO, 13.4 mmol) was then charged into the reaction vessel. The reaction vessel was heated to 70°C before 6.75×10^{-5} mol of Cp*Ti(OCH_3)$_3$/methyl aluminoxane (metallocene/MAO) catalyst was added. The reaction was conducted for 50 min and terminated by adding a sodium hydroxide/methanol solution after cooling. The resulted copolymer was purified by Soxhlet extraction with methyl ether ketone for 24 h. The product was filtered and then dried in a vacuum oven at 110°C for at least overnight. The resulted copolymer contained about 2.8 mol % of 4-methylstyrene with the melting point being 244°C. The GPC results indicated a weight averaged molecular weight (M_w) of 54,000. The reaction is shown in the Scheme I.

Functionalization of the SPSM copolymer

The bromination reaction of the SPSM copolymer (SPSMBr) is that mixtures of SPSM copolymer (9 g) and solvent cyclohexane (150 mL) were introduced into a three-necked flask, then reflux at 72°C for 1 h under nitrogen atmosphere. The aqueous bromine solution (0.021 mL) was diluted with cyclohexane to 1 mL, then add to the above solution by a drop funnel in 20 min. The photolytical method (90 W light source) was used to proceeding the bromination reaction. The reaction was terminated by the addition of a solution of NaOH/MeOH. The SPSMBr product was washed with water and methanol, then dried in a vacuum system at 60°C. In addition, a nucleophilic substitution of the pendant (—CH_2Br) group on the SPSMBr backbone using diethylene glycolamine (SPSMOH) was shown in Scheme II. SPSMBr (1.1 g) and THF/Toluene (v/v = 1/1) 40 mL were introduced into a three-necked flask, then reflux at 72°C for 0.5 h under nitrogen atmosphere. A solution of diethylene glycolamine was prepared by dissolving diethylene glycolamine (0.17 g) in 5 mL of isopropanol. It was added to the



Scheme 2

above solution, then reflux at 90°C for 16 h under nitrogen atmosphere. The SPSMOH product was precipitated in excess of methanol and dried in a vacuum system at 70°C for 16 h.

Characterization

^{1}H-NMR spectra were measured at 30°C on a NMR spectrometer (Bruker AM-200 MHz). Differential scanning calorimetry analysis was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter in the flowing nitrogen (60 cm^3/min) at a heating rate of 20°C/min. The molecular weights of the polymers were determined using a Waters 150CV, which was equipped with three μStyragel HT columns and operated at 140°C.

Membrane preparation

The polymer membrane was prepared from a casting solution containing 5 wt % of polymer in $CHCl_3$. Casting the solution onto a glass plate to a predetermined thickness using a Gardener knife at room temperature formed the membranes. The glass plate was then heated at 70°C for 1 h. The average thickness of the membranes is about 30 μm.

Pervaporation experiments

A traditional pervaporation apparatus was used in this study.[12] The effective membrane area was 10.17 m^2. A vacuum pump maintained the downstream pressure at 3–5 mmHg. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions, permeates, and solutions absorbed in the membrane were measured by gas chromatography (GC; China Chromatography 8700). The separation factor was calculate from

$$\alpha_{H_2O/EtOH} = \frac{Y_{H_2O}/Y_{EtOH}}{X_{H_2O}/X_{EtOH}}$$

where Y_{H2O}, Y_{EtOH}, and X_{H2O}, X_{EtOH} are the weight fraction of water and ethanol in the permeate and feed, respectively.

Degree of swelling

The clean and dried membranes with known weights were immersed in ethanol feed concentration at 25°C for 24 h to reach equilibrium swelling. These pieces were rapidly remove the surface solvent, and placed on a weighting scale. The first reading was taken at 40-s intervals. The weight of the solvent swollen membrane was obtained by extrapolating the initial potion of the experimental curve to the zero line. The degree of swelling of the membrane was defined by the following equation:

$$\text{Degree of swelling} = (W_w - W_d)/W_d \times 100\%$$

where W_d and W_w denote the weight of dry and swollen membranes, respectively.

Contact angle measurement

The contact angle of water was measured by a FACE contact angle meter (CA-D type, Kyowa Interface Science Co. Ltd) at 25°C and 60% relative humidity.

RESULTS AND DISCUSSION

Properties

Figure 1 shows the typical ^{1}H-NMR spectra of the SPSM copolymer. According to Figure 1, the resonance at 6.42–6.55 ppm and 2.24 ppm are peculiar to the protons of benzene ring and the methyl protons of 4-methylstyrene, respectively. Thus, the relative intensity at 6.42–6.55 ppm and 2.24 ppm can be used to estimate the composition of SPSM copolymer. In this article, a SPSM copolymer containing styrene and 4-methylstyrene are 79 and 21 mol %, respectively, was used to further investigate the pervaporation separation performances. The spectrum of the bomination of SPSM (SPSMBr) copolymer is shown in Figure 2. It shows a new peak at 4.41 ppm, which corresponds to the methylene protons (bond;CH_2Br) on the 4-methylstyrene. As a result, a 2.1 mol % bromination SPSM copolymer was obtained. In addition, the DSC results are shown in Table I. It can be seen that the temperature (the peak temperature) and the area of the crystal fusion decreases as the SPSM copolymer possessed functionalization. The results presented in Table I can be interpreted as the degree of crystallization decreases as the SPSM copolymer possessed functionalization. Furthermore, the thermal gravimetric analysis was run on the SPSM and SPSMBr copolymers, as show in Figure 3. It shows that the decomposition temperature, at which 10% loss of mass was observed, for these copolymers was higher than 350°C. Thus, a syndiotatic polystyrene copolymers (SPSM and SPSMBr) with high thermal stability was obtained in this article.

Effect of functionalization on the pervaporation performance of the SPSM membrane

Pervaporation of aqueous ethanol mixtures through SPSM, SPSMBr, and SPSMOH membranes are discussed in this section. It is interesting to compare the pervaporation performances of the functionalized SPSM membranes for aqueous ethanol solution sepa-

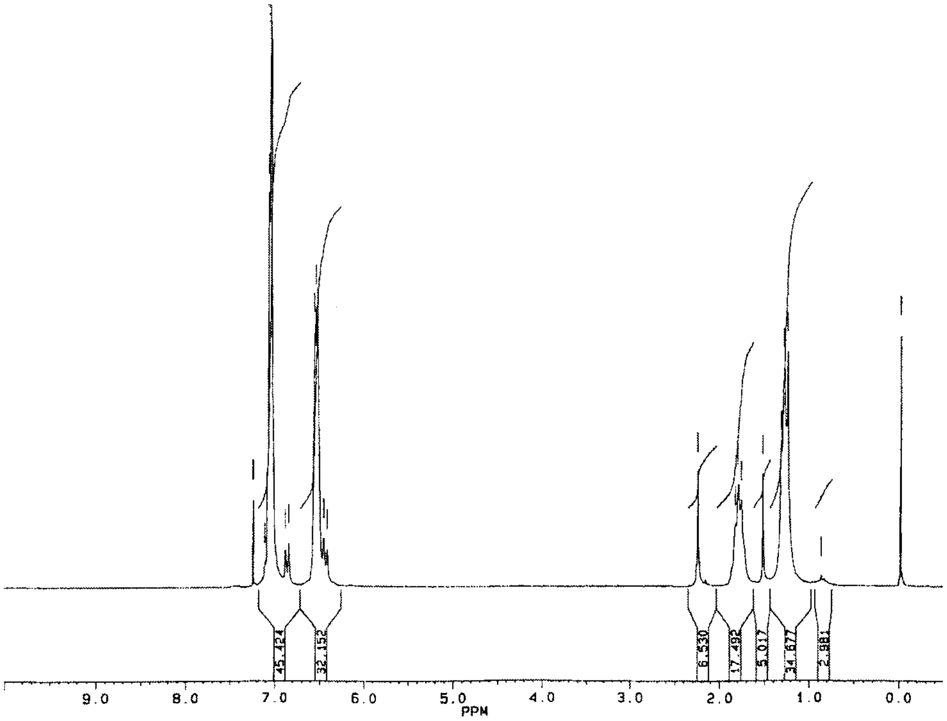


Figure 1 Typical ^{1}H-NMR spectrum of the SPSM copolymer.

ration with that of the unfunctionalized SPSM membrane. The functionalized membrane performances for pervaporation separation of aqueous ethanol solution, being at a relatively high level, are listed in Table II. Compared with permeation rate of SPSM membrane, the SPSMBr and SPSMOH membranes showed significant improvement. These phenomena might be due to the fact that the bromination reaction and then by a nucleophilic substitution of the pendant (—CH_2Br) group on the SPSMBr backbone using diethylene glycolamine (SPSMOH) seems to result in a relaxation structure of the membranes. Hence, the permeation rate increases as the SPSM membrane proceeding a functionalization reaction. In addition, the water con-

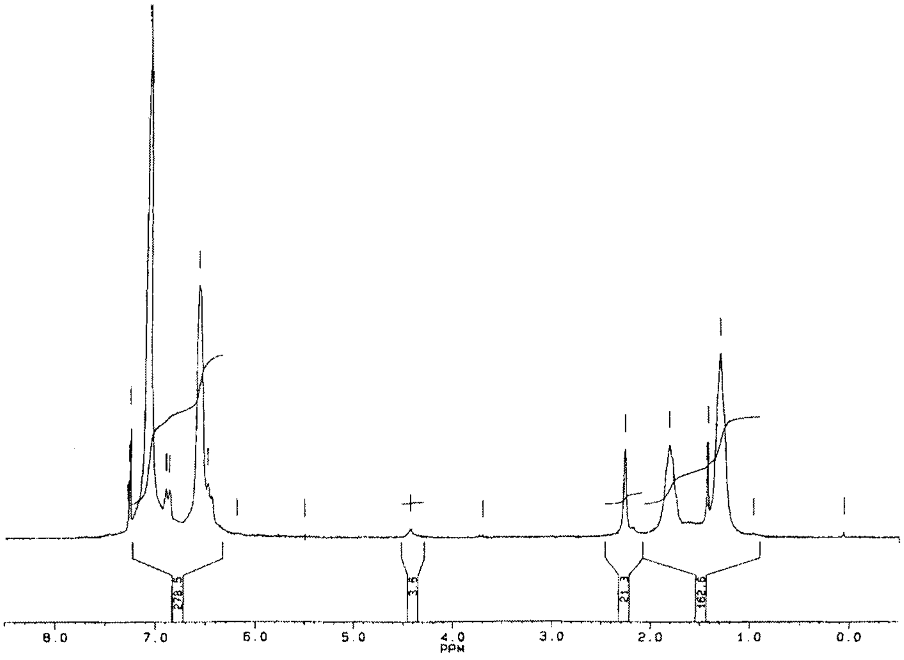


Figure 2 Typical ^{1}H-NMR spectrum of the SPSMBr copolymer.

TABLE I
Heat of Crystal Fusion and Melting Temperature for SPSM, SPSMBr, and SPSMOH Copolymers

Copolymer	T_m (°C)	Heat of Crystal Fusion (J/g)
SPSM	244.7	21.7
SPSMBr	221.4	17.5
SPSMOH	236.5	15.9

TABLE II
Effect of Functionalization of the SPSM Membranes on the Pervaporation Performances[a]

				Durability Test			
				Three Days		One Month	
Membrane	Water Contact Angle (deg)	*F*	α	*F*	α	*F*	α
SPSM	96	170	195	brittle	1	brittle	1
SPSMBr	88	220	510	220	510	220	510
SPSMOH	82	189	441	274	281	585	117

[a] SPSM: syndiotactic poly(styrene-*co*4-methylstyrene).
SPSMBr: bromination of SPSM.
SPSMOH: nucleophilic substitution of the pendant (—CH_2Br) group on the SPSMBr backbone using diethylene glycolamine.
Feed:90 wt % aqueous ethanol solution at 25°C.
F: Permeation rate (g/m^{2}h); α: Separation factor.

tact angle of the SPSM, SPSMBr, and SPSMOH membranes are 96, 88, and 82°, respectively. This indicates that the hydrophilicity of the SPSMBr and SPSMOH membranes is higher than that of the SPSM membrane. Thus, the permeation rate of the former is higher than that of the latter for a water permselective system. Furthermore, the membrane durability was tested for 90 wt % ethanol solution. When the time of pervaporation experiments over 3 days, the brittle phenomenon appear in the SPSM membrane, resulting in remarkable decline of selectivity. However, no decline occurs for 1-month testing of SPSMBr membrane. In addition, the permeation rate increases and the separation factor decreases with the operation time increases for the SPSMOH membrane. These phenomena might be due to the fact that the SPSMOH membrane with higher hydrophilicity and loosen structure, resulting in the plasticizing effect increases. Thus, a high stability pervaporation membrane was prepared by using the bromination procedure. Thus, the SPSMBr membrane was chosen to further investigate in the following section.

The effect of composition of feed on the pervaporation performances for the SPSMBr membranes is shown in Figure 4. The separation factor and permeation rate increase as the feed concentration of ethanol increase for the above membranes. These phenomena can be explained by the plasticizing effect of ethanol. Generally, hydrophobic membranes have stronger interaction with alcohol than with water. The degree of swelling of SPSMBr membranes also increases with increasing ethanol concentration, as shown in Figure 5. When the ethanol concentration in the feed solution is higher, the amorphous regions of the membrane are more swollen. Hence, the polymer chain become more flexible, thus decreasing the energy required for diffusive transport through the membrane, resulting in the permeation rate increases with the ethanol concentration in the feed solution. Furthermore, when the degree of swelling of the membrane in the mixture was large, water permeated through the membrane despite its low affinity toward the membrane. Thus, the separation factor increased with increasing the feed ethanol concentration.

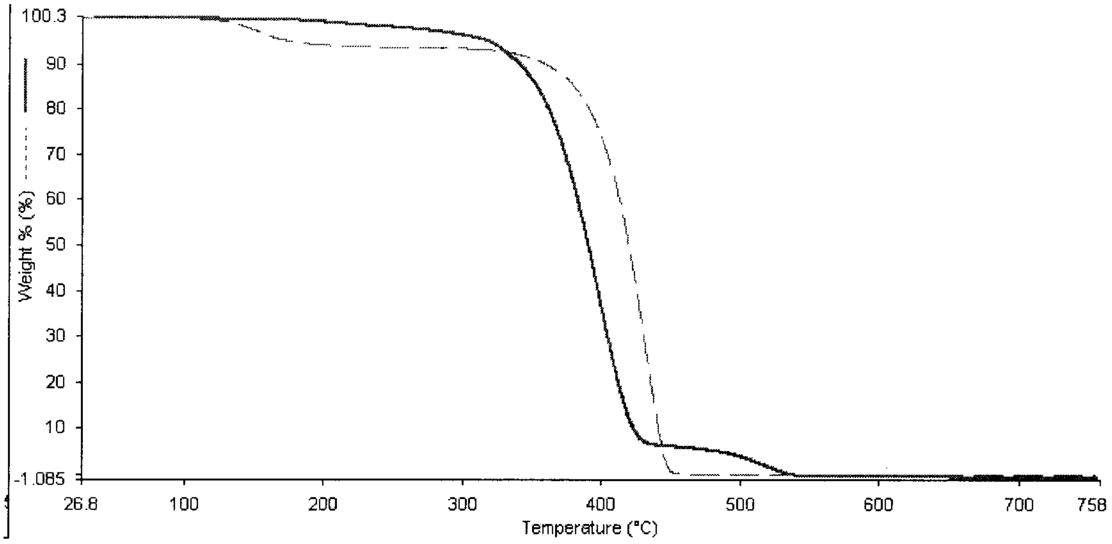


Figure 3 TGA curves for the SPSM and SPSMBr copolymer in nitrogen (heating rate:10°C/min). (—) SPSMBr, (···) SPSM.

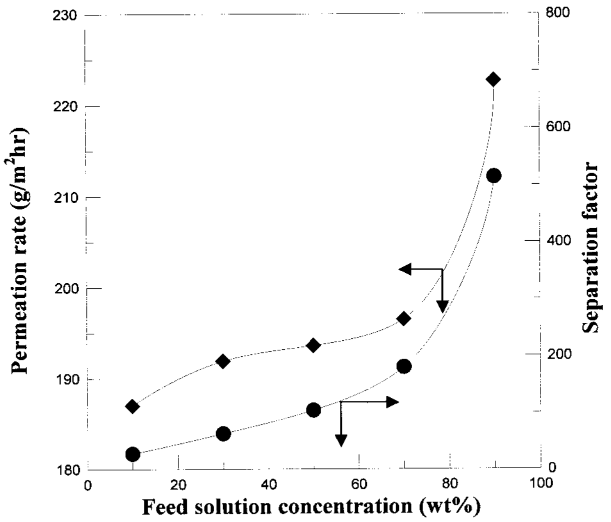


Figure 4 Effect of composition of feed on the pervaporation performances for the SPSMBr membranes at 25°C.

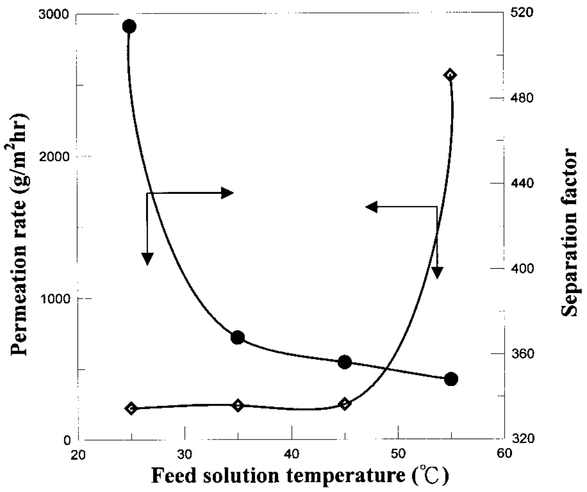


Figure 6 Effect of the feed solution temperature on the pervaporation performances for a 90 wt % aqueous ethanol solution through the SPSMBr membranes.

Effect of the feed solution temperature on the pervaporation performances

The effect of feed solution temperature on the permeation rates and separation factors for pervaporation of 90 wt % aqueous ethanol solutions through the SPSMBr membranes are shown in Figure 6. It shows that the permeation rate increases and the separation factor decreases as the feed solution temperature increases. From these phenomena it may be assumed that the increases of swelling of the membrane matrix at higher temperature results in increased polymer segmental motions. According to the free volume theory,[13] the random thermal motion of polymer chains in the amorphous region produces free volume. As temperature increases, the frequency and amplitude of the chain jumping increase and the resulted free volume becomes larger; therefore, the permeation of the permeating molecules and the associated molecules through the SPSMBr membrane becomes easier, resulting in increasing total permeation rate. The data from experiments of swelling also support the above deduction: the degree of swelling of membranes increases with increasing temperature for SPSMBr membranes, as shown in Figure 7. Additionally, the partial pressure of ethanol in the vapor phase increases with increasing the feed solution temperature, resulting in the membrane further swelling. This facilitates the transport of ethanol molecules along with water, thus reducing the separation factor.

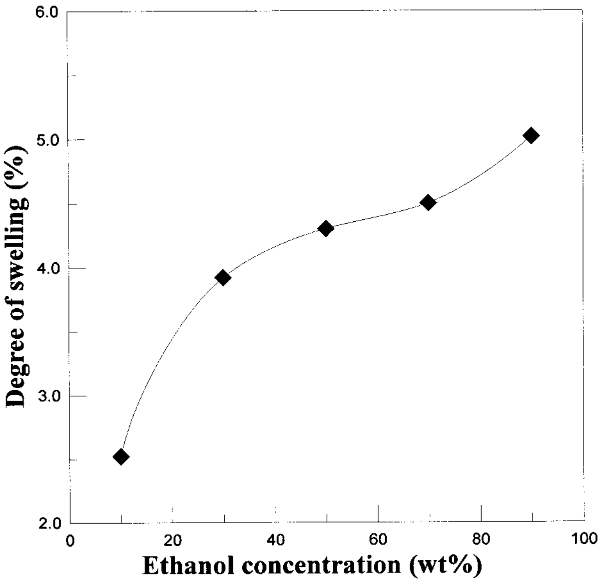


Figure 5 Effect of composition of feed on the degree of swelling for the SPSMBr membranes at 25°C.

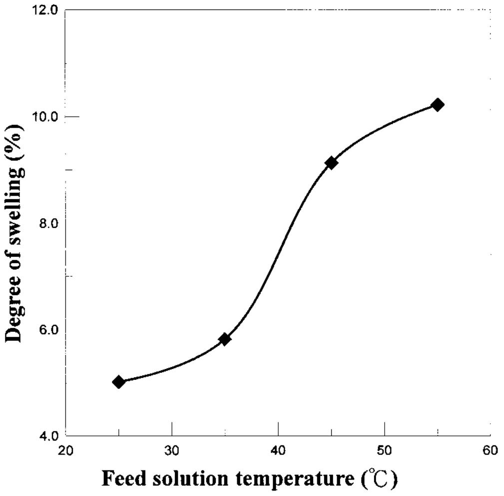


Figure 7 Effect of the feed solution temperature on the degree of swelling for a 90 wt % aqueous ethanol solution through the SPSMBr membranes.

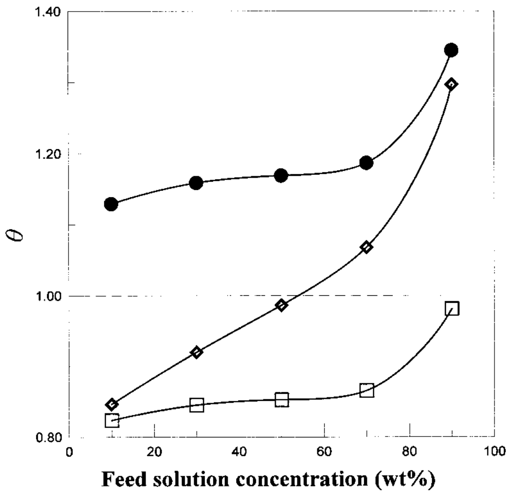


Figure 8 Effect of feed ethanol concentration on the permeation ratio (θ) at 25°C. (◇) θ_t; (●) θ_{EtOH}; (□) θ_{H2O}.

Permeation ratio (θ)

For the pervaporation of binary mixtures the pervaporation ratio (θ_t) is defined as the ratio of the actual permeation rate (Q) to its ideal permeation rate ($Q°$) by Huang et al.[14,15] When the feed alcohol solution exhibits an ideal permeation behavior, the permeation ratio should be equal to unity. The value of the permeation ratio may be higher or lower than unity for nonideal permeation. If the permeation ratio of a system is higher than unity, the system can be said to exhibit a "permeation enhancement effect," while a value lower than unity indicates a "permeation depression effect." Figure 8 shows the permeation ratio vs. feed composition for the SPSMBr membrane. The θ_t values are less than unity at low feed compositions (<50 wt %), indicating the existence of interactions between the permeates and the SPSMBr membrane. Therefore, the interaction effect dominates over the plasticizing effect on the polymer membrane so that the permeation rate is smaller than the ideal permeation rate. However, when the feed solution concentration is higher than 50 wt %, the plasticizing effect of the permeates (ethanol) becomes dominant and results in permeation enhancement. Thus, the permeation ratio θ_t is higher than unity at higher feed concentration. Furthermore, Figure 8 also shows that the permeation ratios of ethanol are higher than unity in the range of 10–90 wt % aqueous ethanol solutions, suggesting that the interaction between the ethanol molecules in the feed and the SPSMBr membrane is higher than that between water and the SPSMBr membrane. Thus, the permeation ratio θ_t increases rapidly for a feed solution with high ethanol concentration.

Effect of feed alcohol mixtures on the pervaporation performances of SPSMBr membrane

The pervaporation performances of a 90 wt % aqueous alcohol solution through the SPSMBr membrane are shown in Figure 9. An increase in the separation factor and a decrease in the permeation rate occur as the number of carbon atoms in the alcohol increases. According to the solution/diffusion mechanism, the size of the permeating species is important in both the solution and diffusion processes. Thus, the molar volumes of the alcohol can explain these phenomena. The molar volumes of methanol, ethanol, *n*-propanol, and *t*-butanol are 40.7, 58.68, 75.14, and 94.88 ml/mol, respectively. The separation factor was found to depend on the molecular length of linear alcohols. Additionally, the permeation rate of *t*-butanol is lower than that of *n*-propanol, possibly because the steric hindrance of the former is higher than that of the latter. A higher separation factor and a lower permeation rate are achieved for a higher molecular weight alcohol.

CONCLUSION

The functionalization procedure is effective in enhance the pervaporation performances of the SPSM membrane. Especiallly, the optimun pervaporation performance (a separation factor of 510 and permeation rate of 220 g/m^{2}h) was obtained by the bromination of SPSM (SPSMBr) membrane with a 90 wt % aqueous ethanol solution. The separation factor and permeation rate increase as the feed concentration of ethanol increase for the SPSMBr membranes. At lower feed ethanol concentration, the interaction effect dominates over the plasticizing effect on the SPSMBr membrane so that the permeation rate is smaller than the

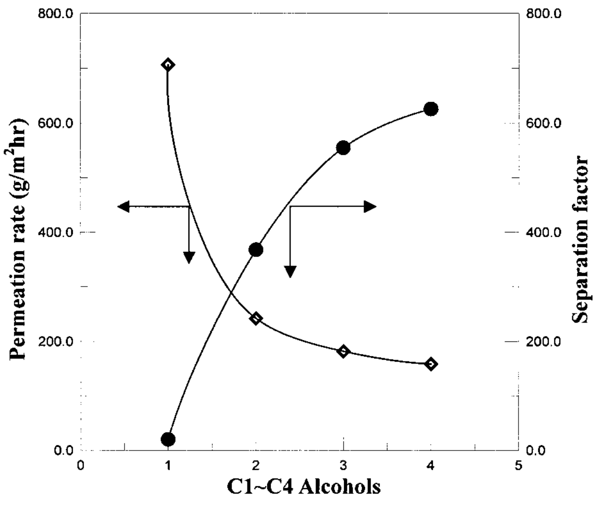


Figure 9 Effect of feed alcohol mixtures on the pervaporation performances for a 90 wt % aqueous alcohol mixtures at 25°C through the SPSMBr membrane.

ideal permeation rate. However, when the feed solution concentration is higher than 50 wt %, the plasticizing effect of the permeates (ethanol) becomes dominant and results in permeation enhancement.

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