

# Pervaporation Performance of Polystyrene Membrane Surface with Perfluoroalkyl Groups

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**ABSTRACT:** Research on the effect of various chemical groups on the pervaporation performance of membranes was very important for understanding the separation phenomenon. In this article, a polystyrene membrane with  $-\text{CF}_3$  groups on its surface was prepared by casting normal polystyrene (PS-H) solution with small-molecular-weight  $\alpha,\omega$ -fluoroalkyl-terminated polystyrene (S-PS-( $\text{CF}_3$ )<sub>2</sub>) on a glass plate. The amount of  $-\text{CF}_3$  groups on the surface was adjusted by changing S-PS-( $\text{CF}_3$ )<sub>2</sub> content, which was documented by X-ray photoelectron spectroscopy analysis, surface energy, and contact angle measurements. The effect of S-PS-( $\text{CF}_3$ )<sub>2</sub> content on separation performance of S-PS-( $\text{CF}_3$ )<sub>2</sub>/PS-H blend membranes for ethanol/water mixture was investigated. The results showed that water concentration in the permeate decreased with increasing S-PS-( $\text{CF}_3$ )<sub>2</sub> content; however, the permeation rate did not change until

the S-PS-( $\text{CF}_3$ )<sub>2</sub> content was increased to 1 wt %. The reason for this was attributed to the fact that a small amount of S-PS-( $\text{CF}_3$ )<sub>2</sub> enables a simple surface modification of the membrane keeping its inner structure relatively unchanged. This was confirmed by swelling degree measurements and other experiments. Comparison with our previous work showed that the  $-\text{CF}_3$  groups on the surface lowers the water permselectivity of the polystyrene membranes, whereas the  $-\text{COOH}$  groups enhance the water permselectivity. However, neither hydrophobic  $-\text{CF}_3$  nor hydrophilic groups on the membrane surface appeared to have any influence on flux. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3975–3982, 2007

**Key words:** pervaporation; polystyrene; perfluoroalkyl group; membrane; surface modification

## INTRODUCTION

Pervaporation is an energy-efficient process with which liquid mixtures can be separated by a combination of membrane permeation and evaporation.<sup>1–4</sup> It is well documented that the surface chemistry and morphology of membranes play an important role in the transport of the penetrants, since in the separation process a liquid mixture contacting the surface of a membrane is the first step according to the commonly accepted solution-diffusion mechanism. Therefore, studies of the effect of chemical groups of membrane surface on its pervaporation performance was important for understanding separation phenomenon and design of surface groups on high-performance pervaporation membranes. As reported

previously,<sup>5</sup> pervaporation performance of polystyrene membranes with carboxyl, hydroxyl, and phenyl groups on its surface were investigated and the results showed that the types of chemical groups on polystyrene membrane surface play an important role in their permselectivity. For separation of an aqueous solution of 80% ethanol, water selectivity is in the order as follows:  $-\text{COOH} > -\text{OH} > \text{phenyl}$ . However, the chemical groups on the membrane surface did not have any influence on flux.

This article focuses on the influence of hydrophobic groups of  $-\text{CF}_3$ . Polystyrene membrane surfaces with  $-\text{CF}_3$  groups were prepared by using end-fluorinated polystyrene. To adjust the content of chemical groups on the membrane surface, end-functional polymers with small molecular weight were used as surface-active components in pure normal polystyrene. The influence of  $-\text{CF}_3$  content on pervaporation performance of S-PS-( $\text{CF}_3$ )<sub>2</sub>/PS-H membranes for removing water from alcohol was investigated.

## EXPERIMENTAL

### Materials

End-functionalized polystyrene was synthesized by standard anionic polymerization. Styrene and tetra-

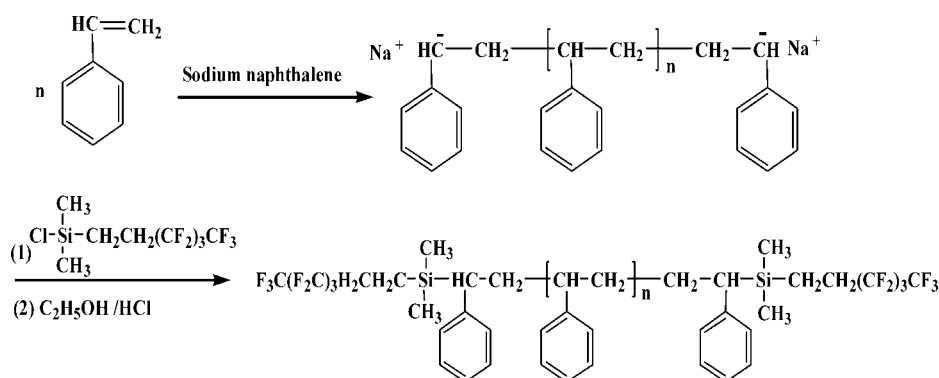
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Scheme 1

hydrofuran (THF) were purified as described elsewhere.<sup>6</sup> Sodium naphthalene was used to initiate the anionic polymerization of styrene in THF. The small-molecular-weight  $\alpha,\omega$ -fluoroalkyl-terminated polystyrene (S-PS-(CF<sub>3</sub>)<sub>2</sub>) was prepared using dimethyl (3,3,4,4,5,5,6,6,6-nonafluorohexyl) chlorosilane (Fluka Co., Switzerland) as terminator.<sup>7</sup> The structure of end-functionalized polystyrene is shown in Scheme 1. Normal polystyrene (PS-H) was purchased from Aldrich and used as received (shown in Table I). Other chemicals are from various Chinese companies. The molecular weight of samples for nuclear magnetic resonance (NMR) analysis was about 2000 g/mol.

### Characterization

Number-average molecular weight and molecular weight distribution were determined using an Agilent 1100 (Agilent) gel-permeation chromatograph equipped with a differential refractometer detector. The proton NMR (<sup>1</sup>H NMR) spectra were recorded on a Bruker Advance AMX-500 NMR instrument in CDCl<sub>3</sub>, with tetramethylsilane as internal standard. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI-5000C ESCA system (Perkin-Elmer) with Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The Fourier transform infrared (FTIR) spectra of the films were measured on a Nicolet Avatar 370 FTIR spectrometer. The differential scanning calorimetry (DSC) measurements were performed using Pyris Diamond DSC (Perkin-Elmer Instruments). The samples were heated from about 40–250°C at a heating rate of 20°C/min. The surface morphology of the membrane was observed using a JSM-5610LF (JEOL, Japan) scanning electron microscope (SEM). The samples were coated with a 20–30 Å layer of Au prior to observation. Contact angles of water on the air-side and glass-side surfaces of the membranes were measured by the sessile drop method using DSA-10 drop sharp analysis (Krüss, Germany) at 25°C. The volume of the water drops used was always 3  $\mu$ L. The surface free energy was calculated

according to Fowkes theory<sup>8</sup> from the measured contact angles of water and diiodomethane on the samples.

Before determining contact angles of samples that had been heated in water, these samples were immediately cooled in room-temperature water for 3 min to slow the surface reconstruction during the measurements. Each time the sample was removed from water, it was dried quickly with a stream of nitrogen prior to contact angle analysis.<sup>9</sup> All reported values are the average of at least eight measurements taken at different locations of the film surface and have a typical error of the mean of  $\pm 1^\circ$ .

### Membrane preparation

The surface-modification polystyrene membranes were prepared by pouring PS-H casting solution containing a small amount of S-PS-(CF<sub>3</sub>)<sub>2</sub> with hydrophobic chain end groups on a glass plate and allowing the solvent to evaporate completely at 25°C in dried air. Prescribed amounts of polystyrene were dissolved in toluene at a concentration of 2 wt % for the preparation of casting solutions. Membrane thicknesses were measured with a thickness gauge. The resulting membranes thickness was about 40  $\mu$ m. A membrane taken off the glass plate has two surfaces that are formed under different environments. A surface of the membrane was formed in contact with the dried air, and another surface was formed in contact with the glass plate. In this article,

TABLE I  
Characterizations of Polystyrenes Used in This Study

Samples	$M_n$	$M_w$	PDI
PS-H <sup>a</sup>	$9.21 \times 10^4$	$2.48 \times 10^5$	2.67
S-PS-(CF <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	$7.51 \times 10^3$	$9.61 \times 10^3$	1.28

<sup>a</sup> Purchased from Aldrich.

<sup>b</sup> Fluorocarbon-terminated polystyrene with small molecular weight used as surface-active additives.

we denote them as the air-side surface and the glass-side surface of the membrane, respectively.

#### Degree of swelling of membranes and composition of the solution sorbed into the membranes

The experimental procedures to determine the degree of swelling (DS) of the membranes and the composition of solution sorbed into the membranes were similar to those described in Refs. 10, 11. Weighed dry membranes were immersed in an aqueous solution containing 80 wt % ethanol in a sealed vessel at 35°C to allow the membranes to reach equilibrium sorption. The membranes were then rapidly removed from the feed and carefully wiped with filter paper to remove the adherent liquid, and the membranes were weighed as quickly as possible. The DS was determined by eq. (1):

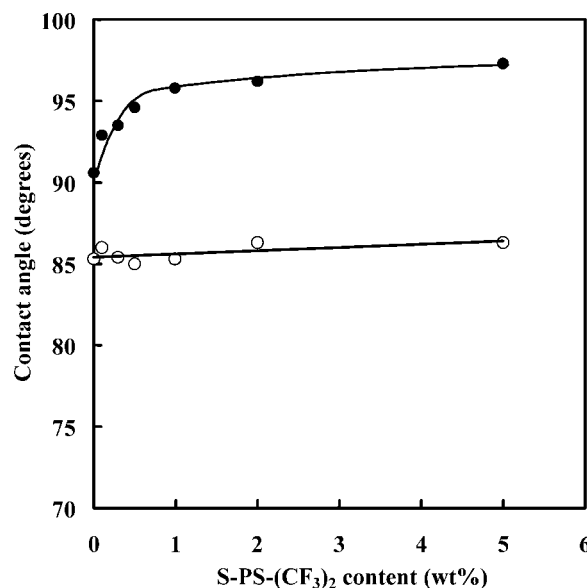
$$DS = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

where  $W_s$  is the weight of the swollen membrane and  $W_d$  is the weight of dry membrane.

The solution absorbed into the swollen membranes was completely desorbed under reduced pressure and was collected in a cold trap. The composition of the solution in the membrane was determined by gas chromatography using a Varian GC-3800 gas chromatograph.

#### Pervaporation experiments

The home-built pervaporation apparatus was described previously.<sup>12</sup> In brief, the solution was pumped across the surface of a membrane (effective area of 25 cm<sup>2</sup>) that was supported by a stainless steel frit. On the permeate side of the membrane, a vacuum pressure of 70 Pa was applied, and the permeate was collected in one of two liquid nitrogen-cooled traps. Feed solution was usually pumped across the membrane at a flow rate of 20 mL/min. To accurately monitor the time-dependence pervaporation performances of the membrane, it is necessary to collect the permeate within a short time as possible. For this purpose, a special sample tube was used to collect the permeate, in which a smaller amount of permeate could be easily taken to conduct the GC analysis. The collected permeate was weighed accurately by an electric balance, with sensitivity of 0.0001 g. Both sides of membrane were used as a separation face (contacting the feed solution) to distinguish the effect of surface structure on pervaporation performance. Water concentrations in the permeate and flux were used to evaluate the pervaporation performance of the membranes. All pervaporation experiments were repeated at least three



**Figure 1** Relationship between S-PS-(CF<sub>3</sub>)<sub>2</sub> content and the contact angles of water on the glass-side (○) and the air-side (●) surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes.

times to ensure reproducibility of the measurements. The errors inherent in these permeation measurements ranged within a few percent for the permeation rates through the membranes.

## RESULTS AND DISCUSSION

### Polymer characterization

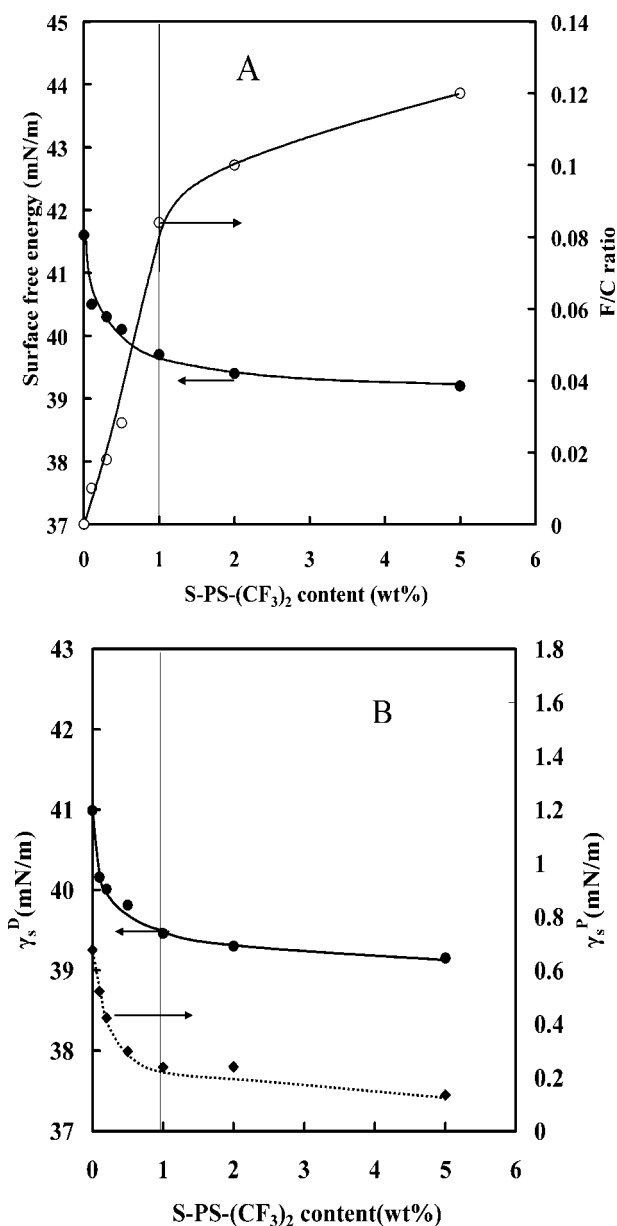
From the <sup>1</sup>H NMR spectrum of the end-functionalized polymer with dimethyl(3,3,4,4,5,5,6,6,6-nonafluorohexyl)chlorosilane, the single peak appearing at  $\delta = 0.50$  ppm can be assigned as the hydrogen on —CH<sub>3</sub> adjacent to Si (see Scheme 1). This result is identical to that reported by Tanaka et al.<sup>7</sup> The molecular weights and molecular weight distribution of end-functionalized polystyrenes were shown in Table I.

### Surface characterization

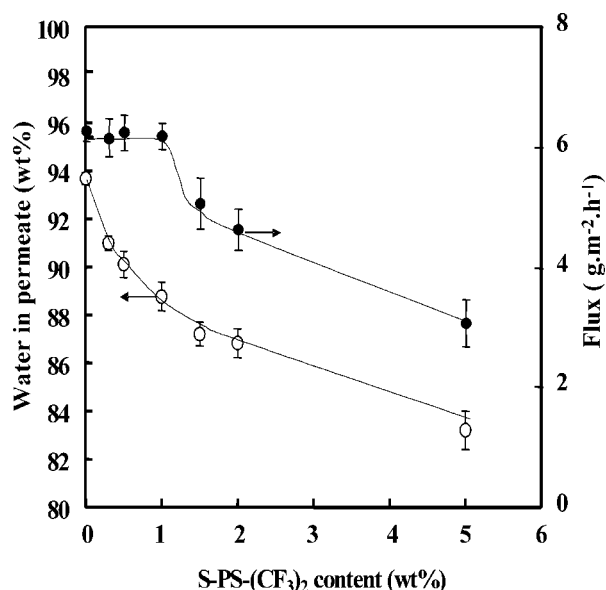
Contact angle measurement is one of the most sensitive and effective methods to probe surface structure of polymer with 5–10 Å of surface sensitivity.<sup>13</sup> The surface contact angles for water on S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H blend membranes were measured, and Figure 1 shows the relationship between S-PS-(CF<sub>3</sub>)<sub>2</sub> content and the contact angle of water on the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H blend membranes. It is apparent that the contact angle of water on the air-side surface of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes increased rapidly following the addition of S-PS-(CF<sub>3</sub>)<sub>2</sub> content within the range of 0–1 wt %, and then increased slightly as the

S-PS-(CF<sub>3</sub>)<sub>2</sub> content exceeded 1 wt %. However, the contact angle on the glass-side surface did not change. The wettability change of a multifunctional polymer surface in the surface formation process is known to be associated with the change in surface functional-group composition when no other disturbing factors are present. These factors can include surface roughness,<sup>14</sup> and surface crystallinity.<sup>15</sup> The sample surfaces under investigation appeared smooth and showed no difference between the air-side and the glass-side in surface morphology when they were examined under SEM. Furthermore, DSC results showed that S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H films appeared totally amorphous, which is the same as observed for PS film studied by FTIR transmission measurement.<sup>16</sup> Surface energies of different side surfaces of the samples were estimated from contact angle measurements using a technique described by Fowkes.<sup>8</sup> Figure 2 shows the relationship between the estimated surface energies and S-PS-(CF<sub>3</sub>)<sub>2</sub> content of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes. The value for the PS-H film was similar to the reported one.<sup>16</sup> With increasing S-PS-(CF<sub>3</sub>)<sub>2</sub> content, the surface free energy of the air-side decreased rapidly [Fig. 2(A)]. At a S-PS-(CF<sub>3</sub>)<sub>2</sub> content over 1 wt %, however, the surface free energy of the air-side surface was almost constant at about 39.5 mN/m and decreased by 2 mN/m relative to that of pure PS-H membrane. At the same time, it is found in Figure 2(B) that adding S-PS-(CF<sub>3</sub>)<sub>2</sub> mainly results in a decrease in the dispersive component of surface free energy. However, the surface energy of the glass-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes was about 42.3 mN/m and did not change with S-PS-(CF<sub>3</sub>)<sub>2</sub> content. The surface chemistry of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes was studied with XPS. In agreement with the findings by Tanaka et al.,<sup>7</sup> a pronounced increase in fluorine photoemission at about 691 eV was found in an XPS spectrum of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H film relative to the PS-H film. The atomic ratios of fluorine to carbon (F/C) near the air-side of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes are shown in Figure 2(A). Adding S-PS-(CF<sub>3</sub>)<sub>2</sub> up to 1 wt % resulted in a dramatic increase in F/C. The F/C ratio on the air-side surface with a S-PS-(CF<sub>3</sub>)<sub>2</sub> content of more than 1 wt % increased slowly despite greatly increasing the S-PS-(CF<sub>3</sub>)<sub>2</sub> content. However, the F/C ratio on the glass-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub> was 0.0013, which was almost negligible compared to that on its air-side surface. These observation can be attributed to the fact that the hydrophobic -CF<sub>3</sub> group of S-PS-(CF<sub>3</sub>)<sub>2</sub> is mainly localized at the air-side surfaces. Such surface localization of chain-end groups of polymers is caused by the minimization of the interfacial free energy.<sup>17</sup> The low energy end group -CF<sub>3</sub> that diffused preferentially to the air-side surface has also been docu-

mented by other analysis techniques, such as neutron reflection (NR), nuclear reaction analysis, static secondary ion mass spectroscopy.<sup>18–21</sup> In addition, since a -CF<sub>3</sub> component in the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane is very hydrophobic, its localization at the air-side surface makes the membrane surface more thermodynamically stable.<sup>17</sup> The relatively constant surface free energy means that the amount of S-PS-(CF<sub>3</sub>)<sub>2</sub> at the air-side surface was almost saturated. These results suggested that S-PS-(CF<sub>3</sub>)<sub>2</sub> was preferentially concentrated near the surface and was saturated near the surfaces of the membranes with a



**Figure 2** Effect of S-PS-(CF<sub>3</sub>)<sub>2</sub> content on the surface free energy and the atomic ratio of fluorine to carbon (F/C) (A), the dispersive (γ<sub>s</sub><sup>D</sup>) and polar (γ<sub>s</sub><sup>P</sup>) components of surface free energy (B) of the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes.



**Figure 3** Effects of the S-PS-(CF<sub>3</sub>)<sub>2</sub> content on the water concentration of the permeate (○) and flux (●) through S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes by pervaporation (35°C). An aqueous solution of 80 wt % ethanol as a feed solution was permeated from the air-side surface (permeation I) of the membranes. The data were obtained from the permeate collected within about 30 min of the beginning of pervaporation.

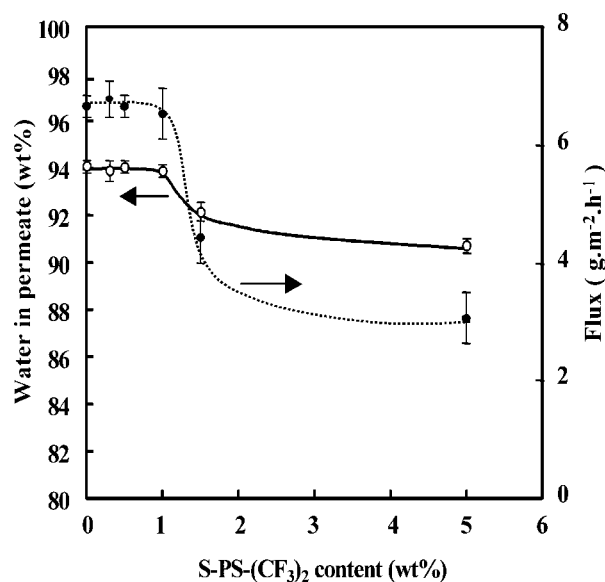
S-PS-(CF<sub>3</sub>)<sub>2</sub> content of 1 wt %. When the S-PS-(CF<sub>3</sub>)<sub>2</sub> content is more than 1 wt %, the inner structure of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane will be affected. It is worth noting that the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes have a chemically asymmetric structure, so that the air-side of the membrane has a more hydrophobic surface than the glass-side. Such an asymmetric structure of a pervaporation membrane must have a strong effect on the characteristics of permeation and separation during pervaporation.

According to the results given earlier, it should be assumed that when the amount of end-functionalized polystyrenes added was less than 1 wt %, most of the end-functionalized polystyrene was concentrated at the membrane surface and the inner structure of the membranes consisted mainly of the PS-H network. Consequently, adding a small amount of S-PS-(CF<sub>3</sub>)<sub>2</sub> enables a simple surface modification of the membrane keeping its inner structure relatively unchanged. This observation is almost the same as for PDMS-*b*-PDEAA/PDMS and PDMS-*b*-PNHFM/PDMS membranes reported by Uragami and coworkers.<sup>22</sup>

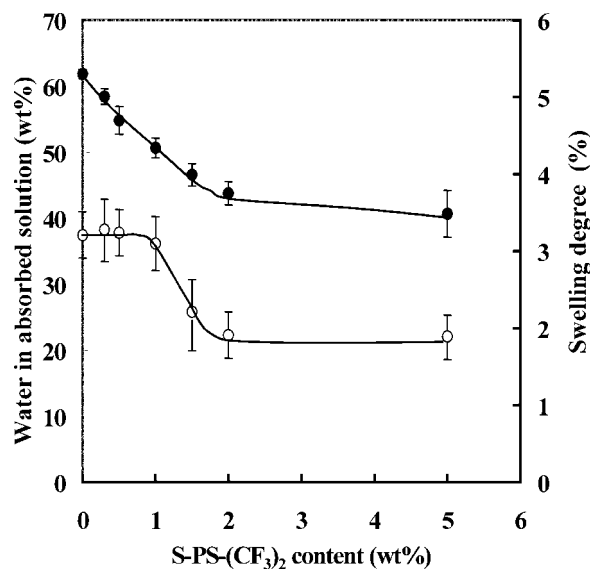
#### Effect of —CF<sub>3</sub> content of membrane surface on pervaporation performance of membranes

This section describes the relationship between —CF<sub>3</sub> content on the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes surfaces and their separation characteristics. An

aqueous solution of 80 wt % ethanol was permeated from the air-side surface (permeation I) and the glass-side surface (permeation II) of the membranes by pervaporation. The air-side surface of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes faced the feed in a pervaporation cell in the case of permeation I, and the glass-side surface faced the feed side in permeation II. Figure 3 shows the effect of the S-PS-(CF<sub>3</sub>)<sub>2</sub> content on the permeation rate and the water concentration in the permeate passing through the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes by pervaporation. The data suggest that PS-H membranes are water-permselective membranes. The water concentration in the permeate decreased gradually from 93.6% to 83% with increasing S-PS-(CF<sub>3</sub>)<sub>2</sub> content from 0% to 5 wt %. However, a notable difference was found when the glass-side surface of the membranes faced the feed as shown in Figure 4. In this case, the water concentration in the permeate was not affected when increasing the content of S-PS-(CF<sub>3</sub>)<sub>2</sub> in the range of 0–1 wt %, but decreased when the S-PS-(CF<sub>3</sub>)<sub>2</sub> content exceeded 1 wt %. There was no obvious difference in the permeation rate of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes between permeations I and II. As shown in Figures 3 and 4, the flux of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes did not change with S-PS-(CF<sub>3</sub>)<sub>2</sub> content within the range of 0–1 wt %, whereas the flux decreased when the S-PS-(CF<sub>3</sub>)<sub>2</sub> content was higher than 1 wt %.



**Figure 4** Effects of S-PS-(CF<sub>3</sub>)<sub>2</sub> content on the water concentration of the permeate (○) and flux (●) through S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes by pervaporation (35°C). An aqueous solution of 80 wt % ethanol as a feed solution was permeated from the glass-side surface (permeation II) of the membranes. The data were obtained from the permeate collected within about 30 min of the beginning of pervaporation.



**Figure 5** Effects of S-PS-(CF<sub>3</sub>)<sub>2</sub> content on the swelling degree (○) and the water concentration in the absorbed solution (●) of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes.  $T = 35^{\circ}\text{C}$ ; solution: an aqueous solution of 80 wt % ethanol.

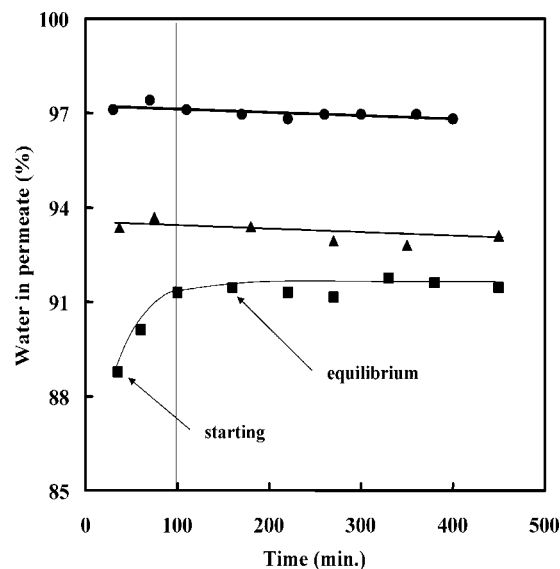
On the basis of the solution-diffusion theory, the effect of asymmetric surface-modification of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes on their permeability and selectivity can be explained as follows. As described in the previous section, the air-side surface of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes becomes more hydrophobic by adding a small amount of S-PS-(CF<sub>3</sub>)<sub>2</sub>, and the hydrophobicity remains relatively constant when the S-PS-(CF<sub>3</sub>)<sub>2</sub> content is more than 1 wt %. In the solution process of permeation I, the hydrophobic air-side surface strongly prevents water molecules in the feed solution from being sorbed into the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes. As a result, the relative solubility of ethanol molecules is enhanced because of the considerably reduced solubility of water molecules. Ethanol molecules concentrated at the membrane surface can diffuse easily in the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes. However, when increasing the S-PS-(CF<sub>3</sub>)<sub>2</sub> content to more than 1 wt %, some S-PS-(CF<sub>3</sub>)<sub>2</sub> will be kept in the bulk of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane. The diffusivity of water and ethanol is then more strongly reduced in the bulk of the membrane due to existence of S-PS-(CF<sub>3</sub>)<sub>2</sub>, which results in decreasing the flux. This hypothesis might be supported by swelling degree measurements. Figure 5 shows that the water concentration in the solution absorbed membrane decreased with increasing S-PS-(CF<sub>3</sub>)<sub>2</sub> content. This means that the sorbed selectivity to water of the membrane decreased with increasing S-PS-(CF<sub>3</sub>)<sub>2</sub> content. The swelling degrees remained constant as the S-PS-(CF<sub>3</sub>)<sub>2</sub> content increased to 1 wt % and decreased when the S-PS-(CF<sub>3</sub>)<sub>2</sub> content exceeded 1 wt %.

This explanation was confirmed further by the results as shown in Figure 4. Both the swelling

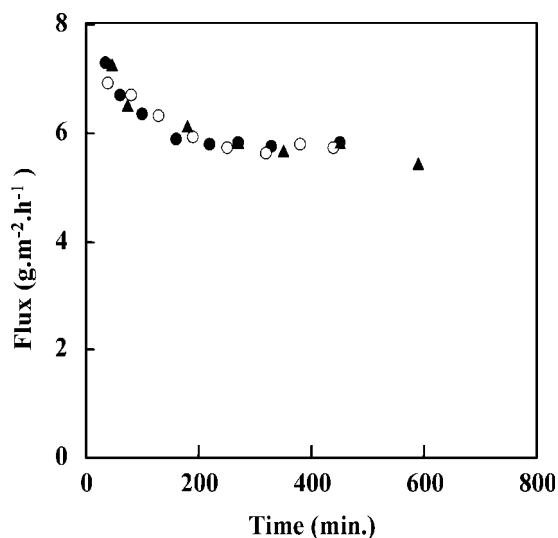
degree and the water concentration of the permeate passing through the glass-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes decreased when the S-PS-(CF<sub>3</sub>)<sub>2</sub> content was more than 1 wt %. These observation may be attributed to a change in the inner structure of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane relative to the membrane with less than 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub>. Some S-PS-(CF<sub>3</sub>)<sub>2</sub> remained in the bulk which results in decreasing the diffusivity and absorbed selectivity to water and the flux of the S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes. This is identical to the result observed by surface characterization.

### A comparison of -CF<sub>3</sub> groups with other chemical groups on polystyrene membrane surfaces

In this section, the pervaporation performance of a polystyrene membrane with -CF<sub>3</sub> groups on its surface was compared with that of the membrane surface with carboxyl groups as reported previously<sup>5</sup> and the results are shown in Figures 6 and 7. These result indicate that -CF<sub>3</sub> groups on the membrane surface lowered the water permselectivity of the PS-H membrane and the water concentration was 5% lower as 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub> was added into the PS-H membrane. -COOH groups on the membrane surface enhanced the water permselectivity of the PS-H membranes. The water concentration was 3% higher when 1 wt % S-PS-(COOH)<sub>2</sub> was added into PS-H membrane. Furthermore, it is interesting to note that the water concentration in the permeate



**Figure 6** Effects of the operating time on the water concentration of the permeate through the air-side surface of PS-H membrane (▲), the glass-side surface of S-PS-(COOH)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(COOH)<sub>2</sub> (●) (see Ref. 5); the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub> (■) during pervaporation (35°C). Feed: an aqueous solution of 80 wt % ethanol.

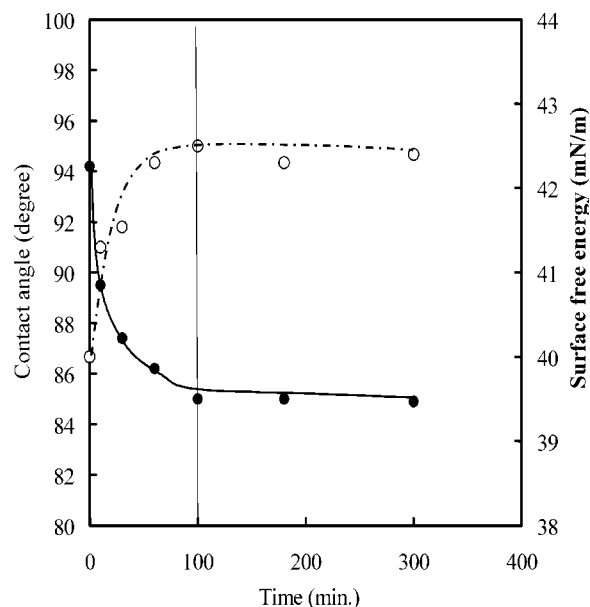


**Figure 7** Effects of the operating time on the flux through the air-side surface of polystyrene membrane (▲), the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub> (○) and the glass-side surface of S-PS-(COOH)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(COOH)<sub>2</sub> (●) (see Ref. 5) during pervaporation (35°C). Feed: an aqueous solution of 80 wt % ethanol.

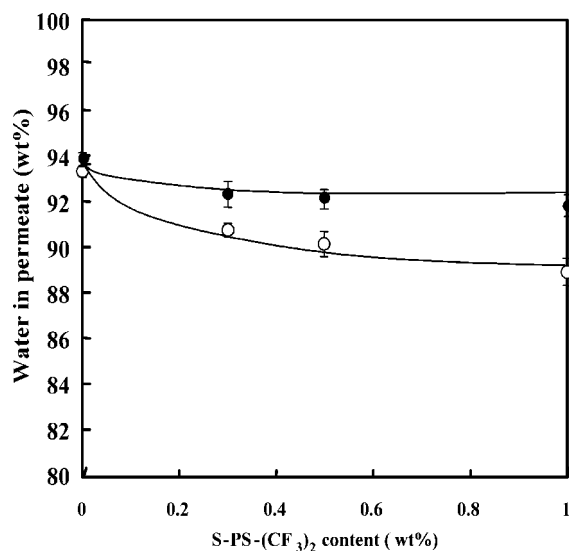
through air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes increased rapidly with operating time and finally reached an equilibrium value. A well-known ethanol-permselective membrane, poly(1-trimethylsilyl-1-propyne) membrane, showed a decrease in separation factor to ethanol with increasing operating time.<sup>23</sup> However, no change occurs when the glass-side surface of S-PS-(COOH)<sub>2</sub>/PS-H membrane was used as the separation face. At the same time, surface modification of polystyrene membranes does not influence their permeability as shown in Figure 7. Therefore, the effects of surface chemical groups of polystyrene membrane on the membrane permselectivity for an ethanol aqueous solution can be explained as follows: -COOH on the glass-side surface of S-PS-(COOH)<sub>2</sub>/PS-H membrane makes the membrane surface very hydrophilic, so that more water molecules are preferentially incorporated into the membrane surface due to their stronger affinity. However, the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes at which the very hydrophobic -CF<sub>3</sub> of S-PS-(CF<sub>3</sub>)<sub>2</sub> is localized prefers the predominant incorporation of ethanol molecules because of the lower hydrophilicity of ethanol. Therefore, the surface modification of the polystyrene membrane by small-molecular-weight end-functionalized polystyrene can control the selectivity of the solution process without changing the diffusion process in the permeation of an aqueous ethanol solution. Thus, the hydrophobic groups on the membrane surface lower the water permselectivity whereas hydrophilic groups enhance the water permselectivity.

Polymer surfaces are dynamic, both temperature- and environment-dependent.<sup>24,25</sup> The polymeric surface has the capacity to modify its structure in contact with the surrounding medium and will attain an equilibrium state corresponding to a minimal interfacial free energy between the two media,<sup>17</sup> which has been documented by various analytical techniques.<sup>26,27</sup> The contact angle of the air-side of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane against water as a function of time is shown in Figure 8. The results indicate that the contact angle decreased with time and reached an equilibrium value as the sample was immersed in water for 100 min. This is identical to water contact angles for fluorosilane-terminated polystyrene as a function of its time in contact with saturated water vapor.<sup>28</sup> At the same time, the surface free energy of the membrane increased with time in water, which corresponds to the pervaporation results as shown in Figure 6. Therefore, the reason for this may be attributed to that hydrophobic -CF<sub>3</sub> at the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane turn to bulk leaving the phenyl groups projecting out of the surface to form a "relative hydrophilic conformation" when the air-side surface contacts the feed mixture. This corresponds to the results observed by XPS and NR,<sup>7</sup> where discernible segregation of the chain ends was not observed at the surface when the  $\alpha,\omega$ -fluoroalkyl-terminated polystyrene film was annealed in boiled water.

Figure 9 shows the effect of S-PS-(CF<sub>3</sub>)<sub>2</sub> content in S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes on the equilibrium and the starting water concentration in the permeate



**Figure 8** Time versus the contact angle of water (●) and surface free energy (○) on the air-side surface of S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membrane with 1 wt % S-PS-(CF<sub>3</sub>)<sub>2</sub> after immersion in water at 35°C.



**Figure 9** Effect of S-PS-(CF<sub>3</sub>)<sub>2</sub> content in S-PS-(CF<sub>3</sub>)<sub>2</sub>/PS-H membranes on the equilibrium (●) and starting (○) water concentration in permeate. Feed: an aqueous solution of 80% ethanol; T: 35°C.

as shown in Figure 6. The results show that this difference increases with increasing amount of —CF<sub>3</sub> groups, namely S-PS-(CF<sub>3</sub>)<sub>2</sub> content. Since the surface reconstruction will happen during pervaporation, the pervaporation performance at the starting point and equilibrium point are indicative of different structures on the membrane surface. With more —CF<sub>3</sub> groups on the membrane surface, a greater difference exists on the membrane surface before and after surface reconstruction, which results in greater change taking place during pervaporation.

This investigation showed that reconstruction of the membranes surface with hydrophobic groups during pervaporation had a profound effect on their separation performance. Surface reconstruction of the membranes is a factor that should be taken into account during the preparation of ethanol-permselective pervaporation membranes.

## CONCLUSIONS

Polystyrene membrane surfaces with various —CF<sub>3</sub> group contents were prepared by adding small-molecular-weight  $\alpha,\omega$ -fluoroalkyl-terminated (S-PS-(CF<sub>3</sub>)<sub>2</sub>) polystyrene into normal polystyrene as a surface active component, which was documented by XPS analysis, surface energy, and contact angle measurements. The addition of a small amount of S-PS-(CF<sub>3</sub>)<sub>2</sub> made the air-side surface of the PS-H membranes very hydrophobic, keeping the inner structure of the PS-H membrane relatively unchanged, because S-PS-(CF<sub>3</sub>)<sub>2</sub> was mainly concentrated at the air-side surface. The —CF<sub>3</sub> groups on the membrane surface lowered the water-permselectivity of polystyrene membranes

during pervaporation separation of ethanol–water mixture, but did not affect the membrane permeation rate. At the same time, permselectivity of the membrane surface with the —CF<sub>3</sub> groups was affected greatly by surface reconstruction during pervaporation, which must be an important consideration in the surface design and modification of ethanol-permselective pervaporation membranes.

By comparison with our previous work, an initial conclusion can be made that surface chemical groups of polystyrene membranes can greatly influence permselectivity. Hydrophilic groups improve the water permselectivity of the PS-H membrane and hydrophobic groups give the inverse results. However, they did not have any influence on permeation rate.

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