

# Chemical Grafted 4-Vinylpyridine onto Polycarbonate Membranes for Pervaporation

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## SYNOPSIS

4-Vinylpyridine-homografted-polycarbonate (PC-*g*-4VP) membrane was prepared for water pervaporation. The conditions of the chemical grafting reaction for synthesis PC-*g*-4VP were studied in terms of the reaction time, reaction temperature, monomer concentration, and the concentration of initiator in the reaction. The effect of feed composition, degree of swelling, and operation temperature on the pervaporation performances were investigated. It was found that water permeated through the PC-*g*-4VP membrane preferential in all range of feed compositions. The permeation rate and separation factor increased with increasing 4-vinylpyridine content in the membrane. PC-*g*-4VP membrane effectively improved both the water permeation rate and water-ethanol separation factor of the unmodified polycarbonate membrane. The total permeation rate of PC-4-VP membrane with 26.7% degree of grafting was 153 g/m<sup>2</sup> h, and the separation factor was above 6300 for a 90 wt % aqueous ethanol feed solution. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

There has been much interest in recent years in polymer membrane applied to the process of separation water from an ethanol aqueous solution. Pervaporation was used for the aqueous alcohol solution separation and the removal of water from an organic liquid, and the removal of organic contaminants from waste water.<sup>1-4</sup>

In order to improve the pervaporation performances, the membrane should be water-permselective or alcohol-permselective. The water permselective membranes must be hydrophilic substrates and allow water to permeate easily. There are many ways to prepare membranes for the above purposes: grafting a hydrophilic species onto an inert substrate,<sup>5-7</sup> blending and crosslinking,<sup>8-11</sup> copolymerization,<sup>12</sup> and synthesis of a new hydrophilic polymer.<sup>13,14</sup>

Polycarbonate (PC) possessing excellent mechanical strength has been regarded as promising

membrane material for separation. The present researchers have previously reported<sup>15</sup> the preparation of an asymmetric membrane by the wet-phase inversion process for pervaporation. The permeation rate of the asymmetric PC membrane for the pervaporation process was higher than that of the polysulfone membranes. 4-Vinylpyridine is an attractive material for the preparation of a water-permselective membrane. In this study, the water-attractive material 4-vinylpyridine and the excellent membrane material PC were prepared for the 4-vinylpyridine-homografted-polycarbonate (PC-*g*-4VP) copolymer membrane via a chemical polymerization.

The effect of 4-vinylpyridine contents on the performances of PC-*g*-4VP membranes is discussed. The effects of feed composition, degree of swelling, and operation temperatures on the pervaporation performances of copolymer membrane are studied.

## EXPERIMENTAL

### Materials

Polycarbonate (Uipilon S-2000) was supplied by Mitsubishi Gas Chemical Co. 4-Vinylpyridine

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(Merck) was distilled in vacuum at 30°C. Cyclohexanone and dichloromethane were employed as the grafting solvent and the casting solvent, respectively. Azobisisobutyronitrile (AIBN) was the initiator. Industrial-grade methanol was used as the precipitation agent.

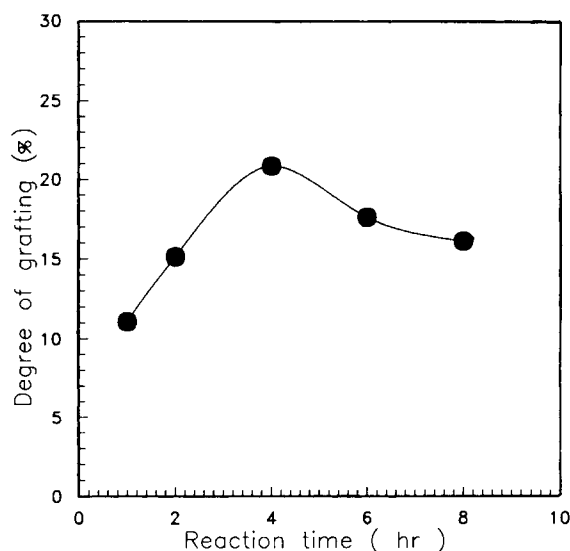
### Grafting Procedure and Membrane Preparation

The grafting procedure were carried out in 250-mL polymerization vessels. After the PC was thoroughly dissolved in the cyclohexanone, 4-vinylpyridine (4-VP) and AIBN were added to the flask. The flask was degased by three freeze-pump-thaw cycles and sealed off under a high vacuum  $< 10^{-3}$  mmHg. The grafting polymers were precipitated and extracted in ethanol and then dried in a vacuum oven for 24 h.

The PC membrane was prepared from a casting solution of grafting polymers in dichloromethane.

### Apparatus and Measurements

The pervaporation apparatus used in this study was the same as reported in the previous study,<sup>15,16</sup> the effective membrane area in each cell being 10.17 cm<sup>2</sup>. The membrane was supported by filter paper resting on a sintered stainless disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg. Most of the experiments were conducted at 25°C. The ef-



**Figure 1** Effect of reaction time on degree of grafting of PC-g-4VP. Reaction temperature, 80°C; monomer volume, 2 mL/20 mL cyclohexanone; AIBN, 0.05 g/20 mL cyclohexanone; and polymer 2 g/20 mL cyclohexanone.

fects of temperature were studied in the range of 25–55°C.

The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions and the permeates were measured by gas chromatography. (G.C. China Chromatography 8700T). The separation factor  $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$  was calculated from the following equation:

$$\alpha_{\text{H}_2\text{O}/\text{EtOH}} = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}}}{X_{\text{H}_2\text{O}}/X_{\text{EtOH}}}$$

For pervaporation,  $Y_{\text{H}_2\text{O}}$ ,  $Y_{\text{EtOH}}$  and  $X_{\text{H}_2\text{O}}$ ,  $X_{\text{EtOH}}$  are the weight fractions of water and ethanol in the permeate and feed, respectively.

The degree of swelling of the membrane was defined by the following equation:

Degree of swelling

$$= \frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}} \times 100\%$$

## RESULTS AND DISCUSSION

### Effect of Reaction Conditions on the Degree of Grafting

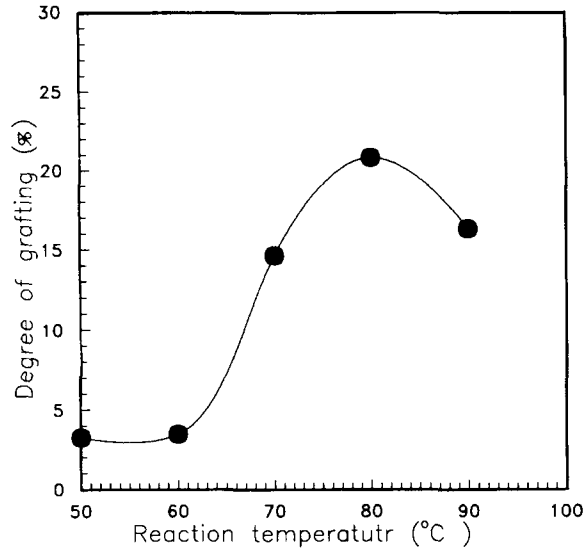
The effect of polymerization time on the degree of grafting with constant amounts of initiator, monomer, polymer solution, and reaction temperature was studied. The results are shown in Figure 1.

It shows that when the reaction time exceeds a certain limit (4 h), the degree of grafting begins to decrease. This phenomenon may be due to the degradation of P(4-VP), which occurred after 4 h reaction time.

The grafting polymerization was carried out at five different temperatures from 50 to 90°C. Figure 2 shows that the degree of grafting increases with an increase in reaction temperature up to 80°C and then declined at 90°C. In the grafting polymerization system, the monomer is competitive both in grafting and homopolymerization.<sup>17</sup> The decrease in the degree of grafting at 90°C may be due to the fact that the homopolymerization plays a more important role than grafting polymerization.

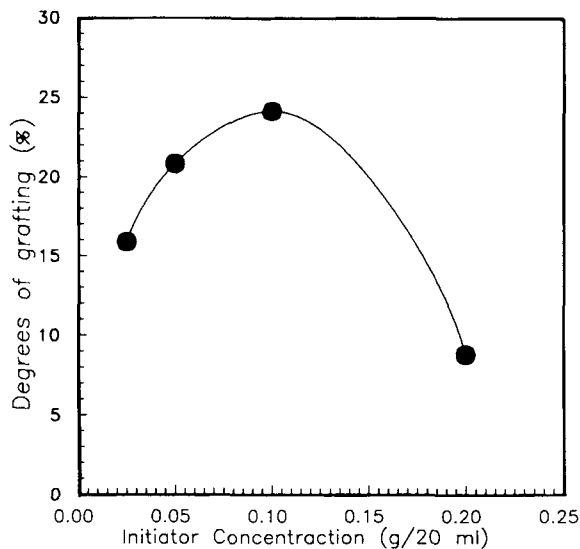
### Effects of Initiator and Monomer Concentration on the Degree of Grafting

As seen in Figure 3, the degree of grafting increased with the initiator amount up to 0.1 g/20 mL cyclohexanone and declined beyond that point. Similar



**Figure 2** Effect of reaction temperature on degree of grafting of PC-g-4VP. Reaction time, 4 h; monomer volume, 2 mL/20 mL cyclohexanone; AIBN, 0.05 g/20 mL cyclohexanone; and polymer, 2 g/20 mL cyclohexanone.

results were reported by many researchers.<sup>17-19</sup> The free radicals may create active sites for grafting from polymer backbone. The created active site and the chain transfer reaction have significant effects on the degree of grafting. However, excessive AIBN caused more active sites to form and combine with each other to give a termination reaction. The termination reaction and combination reaction reduced



**Figure 3** Effect of initiator concentration on degree of grafting of PC-g-4VP. Reaction temperature, 80°C; reaction time, 4 h; monomer volume, 2 mL/20 mL cyclohexanone; and polymer, 2 g/20 mL cyclohexanone.

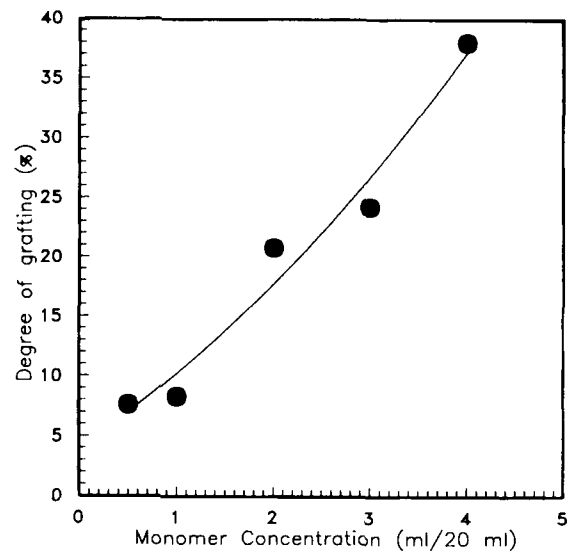
the degree of grafting. The effects of addition of a 4-VP concentration on the degree of grafting are shown in Figure 4. The increase in concentration of 4-VP results in an increase in the creation of free radical and an increase in the degree of grafting.

### Effect of Degree of Grafting on Pervaporation Performance

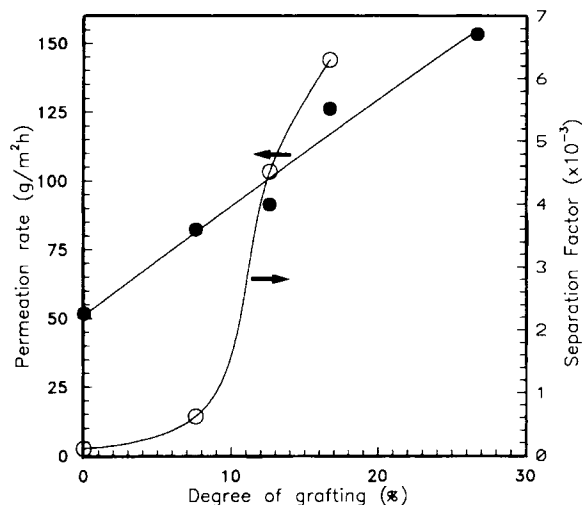
In order to investigate the effect of 4-vinylpyridine content in the membrane on the pervaporation performance, the pervaporation testing was carried out with 90 wt % feed ethanol concentration. As shown in Figure 5, the permeation rate and the separation factor increase with an increase in the degree of grafting. It is indicated that the high 4-vinylpyridine content in the membrane strongly affects the membrane transport properties.

The swelling and sorption tests were studied to further understand the relationship between the 4-vinylpyridine content in the membrane and pervaporation performance. The effect of degree of grafting on the degree of swelling for the PC-g-4VP membrane was shown in Figure 6. The degree of swelling increases with the degree of grafting. This may be due to the hydrophilicity of the PC-g-4VP membrane increases with increasing degree of grafting.

The swelling degree of PC-g-4-VP membranes with degree of grafting in the range of 7.6–26.7% was higher than that of PC by 2–6%. It is indicated

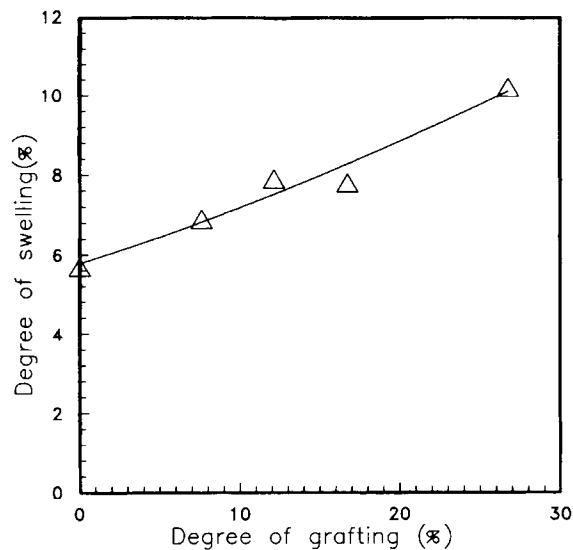


**Figure 4** Effect of monomer concentration on degree of grafting of PC-g-4VP. Reaction temperature, 80°C; reaction time, 4 h; AIBN, 0.05 g/20 mL cyclohexanone; and polymer, 2 g/20 mL cyclohexanone.



**Figure 5** Effect of degree of grafting on pervaporation performances of PC-g-4VP membranes. Feed, 90 wt % ethanol aqueous solution; operation temperature, 25°C; and operation pressure, 7 mmHg.

that 4-vinylpyridine content in the membrane presented a higher degree of swelling than the pure PC membrane. The tendency of the permeation rate was similar to that of the equilibrium degree of swelling. It is considered that the mobility of the polymer chain was increased as the degree of swelling of membranes and the permeation rate of the solution increased. Additionally, the higher degree of swelling supplied the excess volume to offer the permeants easy diffusion through the membrane. Thus, the



**Figure 6** Effect of degree of grafting on degree of swelling of PC-g-4VP membrane. Feed: 90 wt % ethanol aqueous solution and operation temperature: 25°C.

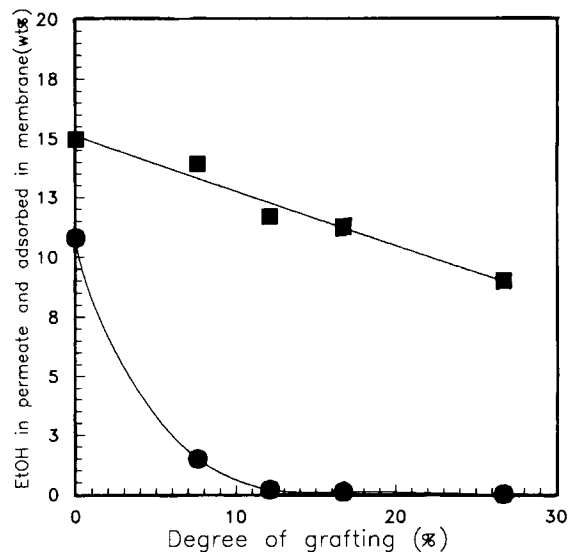
permeation rate increased with increasing degree of swelling. These results correspond to the data presents in Figure 5 very well.

Figure 7 shows the influence of the degree of grafting on the ethanol concentration in the permeate and adsorbed in the membrane for the PC-g-4VP membrane. The ethanol sorption in the membrane and in the permeate decreased with increasing degree of grafting for the PC-g-4VP membrane. Additionally, it shows that the ethanol concentration of the sorption in the membrane is higher than that of the permeate through the membrane. This trend is due to the fact that the small-size water predominantly diffused through the PC-g-4VP membrane. Furthermore, comparing the ethanol sorption in the grafting membrane with the pure PC membrane, it was found that the ethanol sorption in the grafting membrane was remarkably lower than that of the PC membrane. These phenomena can be explained by the fact that the 4-vinylpyridine content in the grafting membrane had strongly interacted with the water molecules in the feed solution.

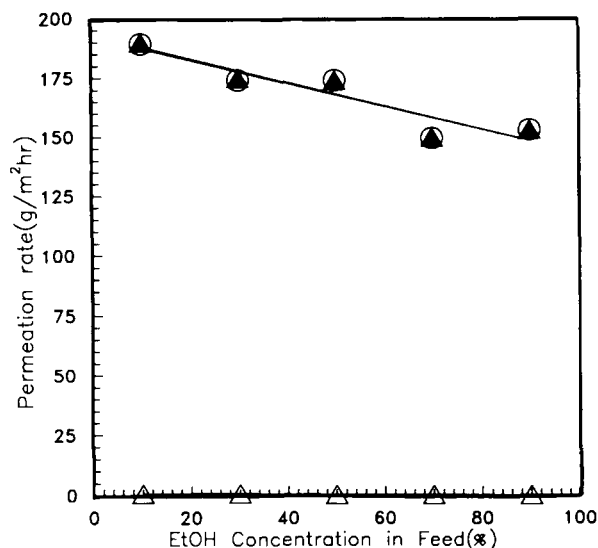
#### Effect of the Feed Concentration on Pervaporation Performances

The effect of the feed ethanol composition in the range of 10–90 wt %, on the pervaporation performances for the PC-g-4VP membrane with 26.7% degree of grafting is shown in Figure 8.

The total permeation rate decreased with an in-



**Figure 7** Effect of degree of grafting on the ethanol concentration in permeate and adsorbed in the membrane for PC-g-4VP membrane. (●) permeate and (■) adsorbed.



**Figure 8** Effect of the feed composition on the pervaporation performances of PC-g-4VP (D.G. = 26.7%) membrane. ( $\blacktriangle$ ) water, ( $\triangle$ ) ethanol, and ( $\circ$ ) total.

crease in the ethanol feed concentration. A similar trend of the individual permeation rate of water and ethanol was obtained at the same time. These results imply that the diffusivity of ethanol through the grafting membrane depends slightly on the feed concentration because of its low affinity to the grafted membrane. However, water molecule shows a relatively large concentration dependence. This is attributable to the water swelling of the PC-g-4VP membrane with a 26.6% degree of grafting. The water permeation rate of the grafting membrane was approximately equal to the total flux.

Figure 9 shows the effect of feed ethanol concentration on the degree of swelling through the grafting membrane and the unmodified membrane. The degree of swelling increases with increasing ethanol concentration in the feed mixture through the PC-g-4VP membrane. These results confirm the results indicated in Figure 8 very well. In addition, an opposite result of the unmodified PC membrane was observed. This phenomena might be due to the plasticization effect of ethanol on the hydrophobic unmodified PC membrane. On the contrary, the degree of the PC membrane showed the opposite result.

The effect of the feed ethanol concentration on the pervaporation performance was shown in Figure 10. The sorption in the grafted membrane and in the unmodified PC membrane increased with increasing feed ethanol concentration. The sorption composition curves lie under the diagonal line indicating that the water molecules were selectively dissolved into the membrane. The sorption of

ethanol in the unmodified PC membrane was higher than that of the grafted membrane. These phenomena can be explained by the fact that the affinity between the ethanol and the grafted membrane is higher than that of the affinity between the ethanol and the unmodified PC membrane.

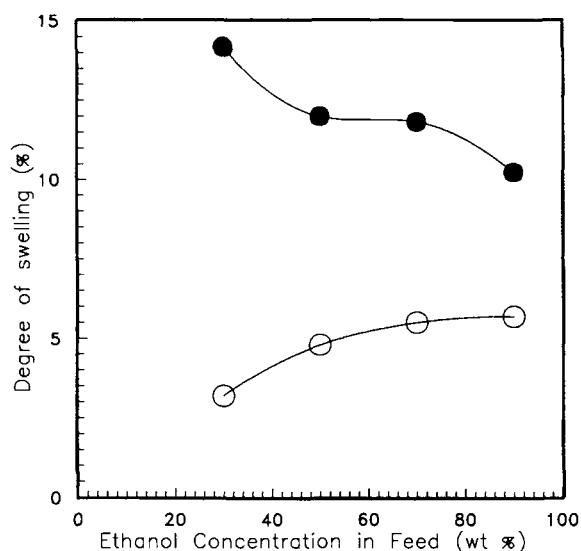
The higher hydrophilicity of the grafted membrane facilitated the water transport through the grafted membrane better than through the unmodified polycarbonate membrane.

### Effect of Operation Temperature on Pervaporation Performance

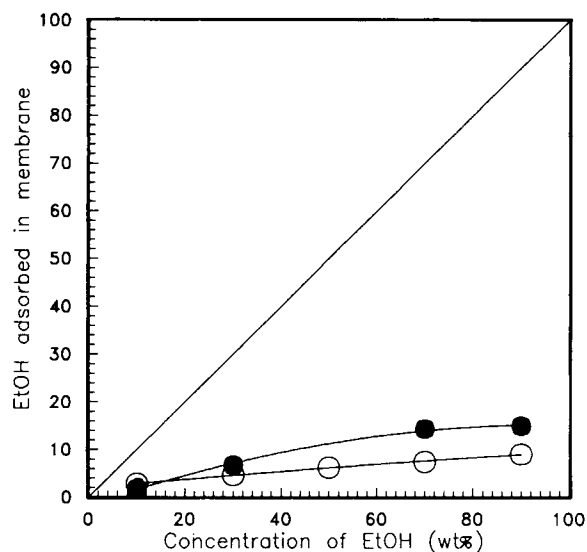
The effect of the operation temperature on the pervaporation performance of the grafting membrane was shown in the Figure 11. The permeation rate increased with an increase in the operation temperature in the range of 25–55°C. The separation factor remained almost constant as the operation temperature increased. These results might be due to the fact that the increases of swelling of the matrix at higher temperature results in increased polymer segmental motions.

### Comparison of the Pervaporation Performance with Previous Study

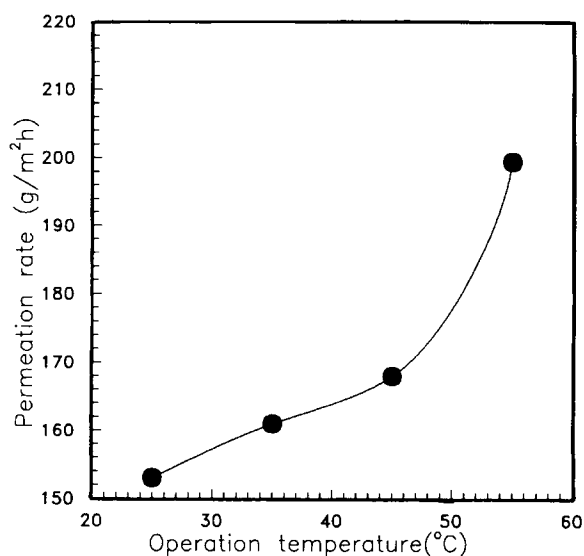
For comparison with the grafted membrane, a poly(4-vinylpyridine) membrane,<sup>20</sup> a PTFE-g-PVP membrane,<sup>21</sup> and an asymmetric PC membrane<sup>15</sup>



**Figure 9** Effect of the feed ethanol concentration on degree of swelling through the grafting membrane and unmodified membrane. ( $\circ$ ) PC and ( $\bullet$ ) PC-g-4VP (D.G. = 26.7%).



**Figure 10** Effect of the feed ethanol concentration on the pervaporation performances. (○) PC and (●) PC-*g*-4VP (D.G. = 26.7%).



**Figure 11** Effect of operation temperature on pervaporation performance of PC-*g*-4VP (D.G. = 26.7%) membrane. Feed, 90 wt % ethanol aqueous solution and operation pressure, 7 mmHg.

were used. As shown in Table I, the poly(4-vinylpyridine) membrane presented the highest flux but lower separation factor, the PTFE-*g*-PVP membrane had a higher permeation rate and a lower separation factor, and the asymmetric PC membrane presented the lowest permeation rate and a higher separation factor. However, compared with the previous studies the PC-*g*-4VP membrane evidently increases the separation factor for the pervaporation separation of aqueous alcohol feed solution. In addition both permeation rate and separation factor of the PC-*g*-4VP membrane were higher than that of the unmodified asymmetric PC membrane. The pervaporation performances of grafting membranes are quite stable during operation period in this study for at least 96 h. This grafting method provided an easy process to improve the high pervaporation performance of the membrane.

## CONCLUSION

A water-perselective grafting membrane can be prepared from a chemical grafting method by controlling the reaction conditions. The specific interaction between permeates and the grafted membrane play an important role in the pervaporation performance. A separation factor above 6300 and a 153 g/m<sup>2</sup> h permeation rate can be obtained for the PC-*g*-4VP membrane with a degree of grafting 26.7% for 90 wt % ethanol feed concentration. The separation factor and permeation rate of the unmodified PC membrane are 116 and 51 g/m<sup>2</sup> h, respectively. The incorporation of the grafting membrane obtained not only improves the separation factor but also increases the permeation rate of the 4-vinylpyridine grafting on the PC membrane.

**Table I** Comparison of Pervaporation Performance for This Study

Membrane Material	ETOH (%)	<i>T</i> (°C)	<i>P</i> (torr)	Total Flux (g/m <sup>2</sup> h)	Separation Factor	Ref.
P4VP <sup>a</sup>	80	25	13	9700	20.5	20
PTFE-P4VP <sup>b</sup>	90	20	—	1700	1.9	21
PC <sup>c</sup>	90	25	7	55	1421	15
PC-P4VP	90	25	7	153	> 6300	This study

<sup>a</sup> Crosslinking membrane.

<sup>b</sup> Degree of grafting = 50%.

<sup>c</sup> Asymmetric membrane.

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