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CHEMICAL-MODIFIED NYLON 4 MEMBRANE FOR PERVAPORATION

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Key Words: 2-Hydroxyethyl methacrylate; Chemical grafting; Pervaporation; Pervaporation separation index; Nylon 4

ABSTRACT

A hydrophilic polymer membrane was synthesized with 2-hydroxyethyl methacrylate (HEMA) onto a Nylon 4 polymer backbone, PHEMA-g-N4. The membranes were water permselective because of the hydrophilicity, and the water permselectivity increased with increasing the degree of grafting. Permsepation of water was investigated with respect to the feed aqueous alcohol concentration, feed temperature, size of the alcohols, and degree of grafting. The separation factors of this PHEMA-g-N4 membrane were higher than those of the unmodified Nylon 4 membrane for pervaporation of aqueous ethanol solution, while the permeation rate was slightly lower. A separation factor of 98 and

a 194 g/m²·h permeation rate could be obtained. Compared with an unmodified Nylon 4 membrane, the PHEMA-*g*-N4 membrane effectively increased the pervaporation separation index for the water-ethanol mixtures on pervaporation separation.

INTRODUCTION

Recently, membrane technology has been developed in many fields. Pervaporation is an attractive separation process for the close boiling-point mixtures, heat sensitive mixtures, azeotropic mixtures, and so on [1]. The solution-diffusion model rather adequately describes the pervaporation behavior in several reports that lead to an understanding of permselectivity of a liquid mixture through a membrane depending on the different solubilities of the components toward a membrane and the diffusivity of the components in a membrane [2]. Basically, transport in pervaporation takes place in a three-step sequence: a) sorption into the membrane, b) diffusion through the membrane, and c) desorption into the vapor phase. The first two steps are considered to be selective but the third is generally a fast, nonselective step as long as the partial pressure on the permeate side is kept low [3-6]. Thus, the first two steps are mainly responsible for the permselectivity. Many experimental attempts have been made to control the specific interaction between the membrane and permeant by blending and crosslinking [7-10], copolymerization [11, 12], and surface modification [2]. Nylon 4 membranes have been regarded as a promising membrane material for separation purposes because of its excellent strength and inherent affinity to water. In previous papers we investigated various ways, such as plasma deposition [13], homografting and heterografting of ⁶⁰Co γ -ray irradiation [14, 15], and chemical grafting [16], to improve the membrane morphology and pervaporation performances of a Nylon 4 membrane which has a separation factor of 4 with a 350 g/m²·h permeation rate for a 90 wt% aqueous ethanol feed solution. We showed that inducing a hydrophilic vinyl monomer (vinyl acetate) onto a Nylon 4 membrane structure was effective in improving pervaporation performance. Thus, in the hope of further increasing permselectivity properties, a hydrophilic vinyl monomer, i.e., 2-hydroxyethyl methacrylate, was used in this article. In this paper the results of the polymerization of 2-hydroxyethyl methacrylate onto a Nylon 4 polymer backbone to improve pervaporation performances are discussed in terms of the degree of grafting, feed composition, feed temperature, molecular size of the permeating species, and degree of swelling.

EXPERIMENTAL

Materials

The Nylon 4 synthesis procedure was described previously [17]. The molecular weight of the samples, measured by a Cannon-Fenske viscometer with *m*-cresol as solvent at 25°C, was 25,000-30,000. 2-Hydroxyethyl methacrylate (HEMA) and potassium peroxydisulfate (KPS) were purified before being used. All other reagent-grade chemicals were used directly without further purification. Water was deionized and distilled.

Grafting Procedure

An ampule containing the required amounts of 2-hydroxyethyl methacrylate (5–25 vol%), Nylon 4 polymer solution (5 g/100 mL formic acid), and potassium peroxydisulfate (KPS) was degassed by three freeze–pump–thaw cycles and sealed off under high vacuum ($< 10^{-4}$ torr). The sealed tube was then placed in a constant temperature bath at 80°C for 1 hour while being agitated. The reaction mixtures were poured into a large amount of distilled water and then allowed to stand at room temperature until dried at 80°C in vacuum. Conversion of monomer was calculated by means of

$$\text{Conversion of monomer (\%)} = \frac{(\text{weight of produced polymer}) - (\text{weight of ungrafted Nylon 4})}{(\text{weight of feed monomer})} \times 100$$

The degree of grafting and grafting efficiency of HEMA onto Nylon 4 after the extraction of homopolymers for 72 hours using a Soxhlet with water were calculated according to

$$\text{Degree of grafting (\%)} = \frac{(\text{weight of grafted Nylon 4}) - (\text{weight of ungrafted Nylon 4})}{(\text{weight of ungrafted Nylon 4})} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{(\text{weight of produced HEMA polymer}) - (\text{weight of homopolymer})}{(\text{weight of produced polymer})} \times 100$$

Membrane Preparation

The membrane of PHEMA-g-N4 was prepared from a casting solution of grafted copolymer in formic acid solvent. The detailed procedure is described in a previous paper [17]. After casting, the membrane was heat-treated at 70°C for 40 minutes to evaporate the solvent and to provide a suitable pore size distribution of this asymmetric membrane. The membrane thickness was in the 15 to 25 μm range.

Degree of Swelling

The degree of swelling of the membrane was defined by

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

where the weight of dry membrane and the weight of swollen membrane denote the weight of dry and solvent swollen membranes, respectively.

Apparatus and Measurements

The traditional pervaporation process was adopted [13]. The effective membrane area was 10.2 cm^2 . Most of the experiments were conducted at 25°C. The effects of temperature were studied at 25–45°C. In pervaporation, the permeation

rate was determined by measuring the weight of the permeate. The composition of the feed solutions, permeates, and solutions adsorbed in the membrane were measured by gas chromatography (G.C. China Chromatography 8700T). The separation factor $\alpha_{\text{water/alcohol}}$, was calculated from

$$\alpha_{\text{water/alcohol}} = (Y_{\text{water}}/Y_{\text{alcohol}})/(X_{\text{water}}/X_{\text{alcohol}})$$

For pervaporation, Y_{water} , Y_{alcohol} and X_{water} , X_{alcohol} are the weight fractions of water and alcohol in the permeate and feed, respectively.

RESULTS AND DISCUSSION

Effect of the Monomer Concentration on the Chemical Grafting Process

The monomer conversion, degree of grafting, and grafting efficiency in the polymerization of 2-hydroxyethyl methacrylate (HEMA) monomer onto Nylon 4 polymer backbone were estimated. The results are listed in Table 1. The data show that the degree of grafting increases with monomer concentration up to 20 vol%; beyond this concentration the degree of grafting decreases. Nevertheless, grafting efficiency decreased gradually with increasing monomer concentration. These phenomena might be due to the fact that the reaction sites in the polymerization system were increased at a higher monomer concentration. However, when the monomer concentration exceeds 20 vol%, homopolymerization is more favored than grafting polymerization. Furthermore, an increase in the concentration of monomer, which is a nonsolvent for Nylon 4, lowers the solubility of Nylon 4 in the formic acid solvent system. Additionally, monomer conversion increases with increasing monomer concentration. This is because an increase in monomer concentration increases the possibility of forming homopolymer and grafting polymers, leading to an increase in monomer conversion.

TABLE 1. Effect of Monomer Concentration on Degree of Grafting, Conversion, and Grafting Efficiency of PHEMA-g-N4 Using KPS as Initiator^a

Monomer concentration, vol%	Degree of grafting, %	Conversion, %	Grafting efficiency, %
5	26.84	35.08	92.25
10	30.13	32.89	76.41
15	57.16	35.96	72.98
20	123.4	53.97	67.56
25	104.3	45.78	59.27

^aInitiator concentration: 0.375 g KPS/100 mL solution. Polymer concentration: 5 g/100 mL solution. Reaction conditions: 80°C, 1 hour.

The existence of HEMA grafting onto Nylon 4 was confirmed by FTIR spectrophotometrically. Figure 1 shows the spectra of (a) unmodified Nylon 4, (b) PHEMA-g-N4 with 57.16% degree of grafting, and (c) PHEMA-g-N4 with 104.3% degree of grafting. Comparison of spectra (a) and (b) shows that a new absorption peak at 1738 cm^{-1} , which corresponds to C=O stretching in HEMA, appeared in spectra (b). Thus, this peak confirms that grafted chains exist in the Nylon 4 matrix. The relative absorbance of A_{1738}/A_{1545} was evaluated by measuring the ratio of C=O absorption at 1738 cm^{-1} (A_{1738}) to the amide II band absorption at 1545 cm^{-1} (A_{1545}). The 1545 cm^{-1} absorbance was at almost the same level for every spectra and is used as a reference because it was independent of the degree of grafting. It shows that the relative absorbance increases with an increasing degree of grafting, i.e., 0, 0.98, and 1.17 for spectra (a), (b), and (c), respectively [14]. These results not only confirm that the HEMA monomer is grafting onto the Nylon 4 backbone but also agree with the results in Table 1.

Effect of Degree of Grafting on Membrane Morphology

The morphology of the PHEMA-g-N4 membrane was measured by scanning electron microscopy (SEM, Model Hitachi S-570). The membrane was mounted on a brass cylinder, freeze-dried under vacuum, and rendered electrically conductive

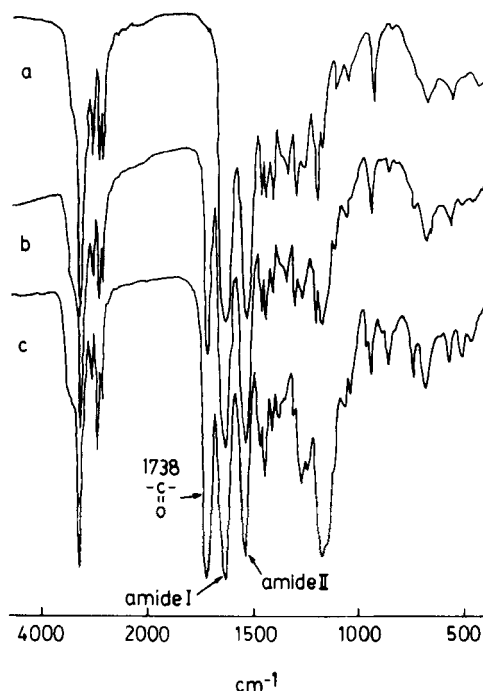


FIG. 1. FTIR spectra of (a) unmodified Nylon 4 membrane, (b) PHEMA-g-N4 membrane with degree of grafting 57.16%, and (c) PHEMA-g-N4 membrane with degree of grafting 104.3%.

by coating it with gold. It was viewed in a scanning electron microscope operating at an accelerating voltage of 20 kV. Figure 2(A)–(E) shows surface views of the PHEMA-*g*-N4 membranes with various degrees of grafting. From Fig. 2, we can observe that membrane denseness increases with an increasing degree of grafting from 26.84 to 104.3%. Additionally, a brittle membrane was obtained at a 123.4% degree of grafting. These results will influence the pervaporation performance of the PHEMA-*g*-N4 membrane for the separation of alcohol–water mixtures.

In general, membrane hydrophilicity increases as the hydrophilic monomer is

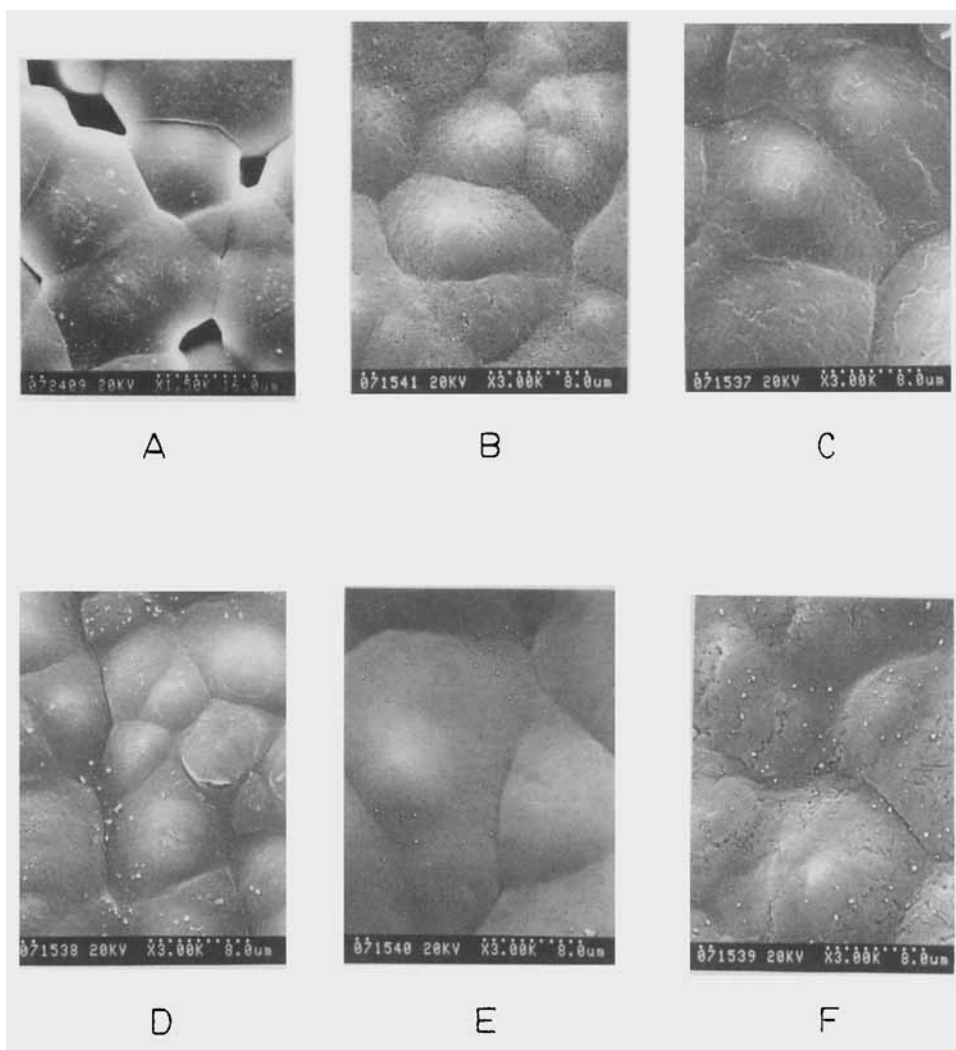


FIG. 2. Scanning electron micrographs of membrane surface: (A) unmodified Nylon 4 membrane, (B) PHEMA-*g*-N4 membrane with degree of grafting 26.84%, (C) PHEMA-*g*-N4 membrane with degree of grafting 30.13%, (D) PHEMA-*g*-N4 membrane with degree of grafting 57.16%, (E) PHEMA-*g*-N4 membrane with degree of grafting 104.3%, and (F) PHEMA-*g*-N4 membrane with degree of grafting 123.4%.

TABLE 2. Effect of the Degree of Grafting of the PHEMA-g-N4 Membrane on the Water Contact Angle, Permeation Rate, and PSI Value

Degree of grafting, %	Permeation rate, g/m ² ·h	Water contact angle, degrees	Pervaporation Separation Index
0	350	61	1,400
26.84	218	66	6,950
30.13	210	68	8,400
57.16	205	68	18,100
104.3	194	76	18,900
123.4	206	78	14,100

added to the polymer matrix, and hydrophilicity reduces the water contact angle. However, in this paper we observe the opposite phenomena with the water contact angle increasing and the permeation rate decreasing with an increase in the degree of grafting. The results are listed in Table 2. These phenomena might be due to the fact that PHEMA chains incorporated into the Nylon 4 structure form entanglements and/or crosslinking between the PHEMA chains, thus reducing the hydrophilicity and free volume of the PHEMA-g-N4 membrane. Moreover, membrane denseness increases with increasing degree of grafting, resulting in a permeation rate decrease. Figure 2 agrees very well with the results indicated in Table 2.

Effect of Degree of Grafting on Pervaporation Performances

The effect of the degree of grafting on the permeation rates and separation factors for pervaporation of 90 wt% aqueous solutions through PHEMA-g-N4 membrane are shown in Fig. 3. The permeation rate decreases as the degree of

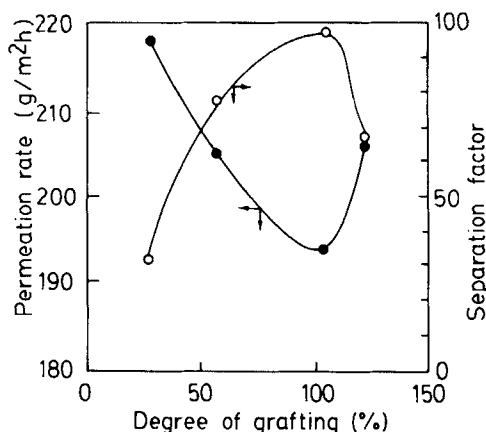


FIG. 3. Effect of degree of grafting on permeation rate and separation factor through PHEMA-g-N4 membrane with 90 wt% aqueous ethanol solution.

TABLE 3. The Pervaporation Performances of Modified Nylon 4 Membrane with Various Modified Methods for 90 wt% Aqueous Ethanol Feed Solution

Membrane	Separation factor	Permeation rate, g/m ² ·h	Pervaporation Separation Index	Ref.
Unmodified N4	4.0	350	1,400	This work
PHEMA- <i>g</i> -N4	97.6	194	18,900	This work
PVA- <i>p</i> -N4 ^a	13.5	420	5,600	13
PVA-homo- <i>g</i> -N4 ^b	7.3	691	5,000	14
PVA-hetero- <i>g</i> -N4 ^c	13.9	358	4,900	15

^aPlasma deposition, 10 W/20 min.

^b⁶⁰Co γ -ray irradiation homografting with a 42.2% degree of grafting.

^c⁶⁰Co γ -ray irradiation heterografting with a 21.2% degree of grafting.

grafting increases, but the separation factor increases with the degree of grafting up to 104.3% and then decreases. These phenomena might be due to the fact that the membrane surface begins to form microcracks when the degree of grafting exceeds 104.3%. These results correspond well with the result indicated in Fig. 2 and Table 2. The denser entanglement and/or crosslinking structure of the PHEMA-*g*-N4 membrane results in a Pervaporation Separation Index (PSI; permeation rate product separation factor) of 18,900 for the PHEMA-*g*-N4 membrane with a 104.3% degree of grafting, i.e., the best pervaporation performance for an ethanol-water mixture solution for the PHEMA-*g*-N4 membrane. Compared with the pervaporation performances of the various modified Nylon 4 membranes listed in Table 3, the chemically modified Nylon 4 membranes show a significant improvement [13–15]. Comparison of the results of the unmodified Nylon 4 membrane with the

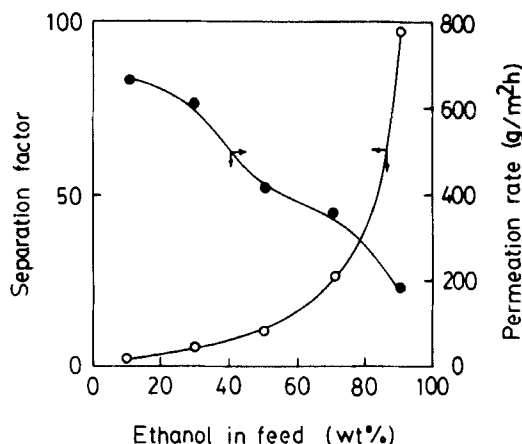


FIG. 4. Effect of feed composition on pervaporation performances for PHEMA-*g*-N4 membrane with 104.3% degree of grafting.

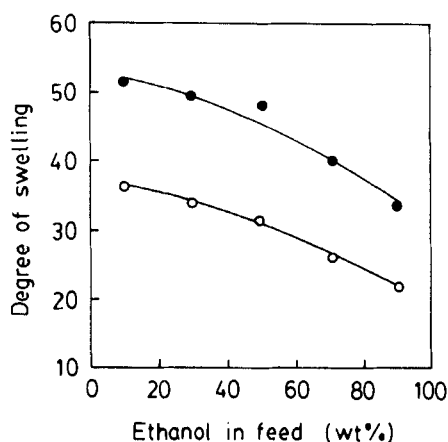


FIG. 5. Effect of feed ethanol concentration on the degree of swelling (○) of unmodified Nylon 4 membrane; (●) PHEMA-g-N4 membrane with degree of grafting 104.3%.

PHEMA-g-N4 membrane shows a significant improvement of the separation factor and the PSI value.

Effect of Feed Composition on Pervaporation Performances

The effect of the ethanol concentration of the feed mixture on the permselectivity of the PHEMA-g-N4 membrane with a 104.3% degree of grafting was investigated at 25°C. The results are shown in Fig. 4. This figure indicates that the permeation rate decreases from 667 to 194 g/m²·h and the separation factor increases from 2.0 to 97.6 with an ethanol concentration increasing from 10 to 90 wt%. These results can be explained by the degree of swelling of the membrane.

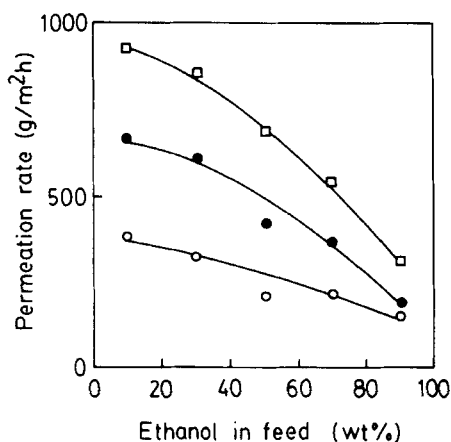


FIG. 6. Effect of feed composition on the total permeation rate with varying temperature: (○) 15°C, (●) 25°C, (□) 35°C.

TABLE 4. Activation Energy of Permeation of Water-Ethanol Mixtures through the PHEMA-g-N4 Membrane with a 104.3% Degree of Grafting

Feed concentration, wt%	Activation energy, kcal/mol
10	6.51
30	6.68
50	5.65
70	7.76
90	8.93

That is, the degree of swelling of the PHEMA-g-N4 membrane decreases with increasing ethanol concentration as shown in Fig. 5, and its curve corresponds well with the permeation rate curve of the PHEMA-g-N4 membrane. When the swelling ratio of the membrane in the mixture was large, ethanol permeated the membrane in spite of its low affinity toward the membrane. That is, excessive swelling due to the selective solvent (water) causes a nonselective solvent (ethanol) to permeate through the membrane and lowers the selectivity. Furthermore, the degree of swelling of the PHEMA-g-N4 membrane with a degree of grafting of 104.3% is much higher than that of the unmodified Nylon 4 membrane. These phenomena might be due to the fact that the interaction between the water molecules of the feed solution and the hydroxy group of the PHEMA-g-N4 membrane increases with increasing water content in the feed solution.

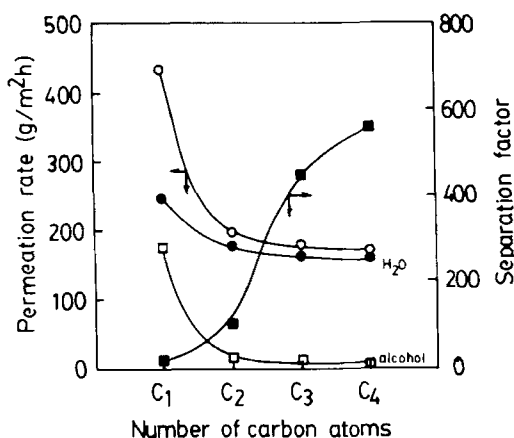


FIG. 7. Effect of molecular shape of alcohol on permselectivity of PHEMA-g-N4 membrane with 90 wt% aqueous alcohol solution: (○) total permeation rate, (●) permeation rate of water, (□) permeation rate of alcohol, and (■) separation factor.

TABLE 5. Activation Energy of Permeation and Swelling Degree of Water-Alcohol Mixtures through the PHEMA-*g*-N4 Membrane with a 104.3% Degree of Grafting

Aqueous alcohol solution	$L,^a \text{ \AA}$	Activation energy, kcal/mol	Swelling degree, %
Methanol	2.9	4.09	56
Ethanol	4.2	5.04	35
<i>n</i> -Propanol	5.4	5.21	29
<i>tert</i> -Butanol	—	5.59	17

^aMolecular length.

Effect of Temperature on Pervaporation Performance

The effect of temperature and feed composition on the total permeation rate is shown in Fig. 6. The total permeation rate increases with increasing temperature and with decreasing ethanol concentration of the feed solution. These results might be due to the plasticizing effect of the permeants and the interaction between the permeants and polymer. As the temperature increases, the interaction becomes weaker, so that the plasticizing effect can be recovered. However, strong interactions can be formed at low temperature and reduce the plasticizing effect. The activation energy for permeation of an aqueous alcohol solution through a PHEMA-*g*-N4 membrane can be obtained from the Arrhenius plot. The data are presented in Table 4. From the data in this table, the activation energy of PHEMA-*g*-N4 is found to be in the 5.65 to 8.93 kcal/mol range. These results indicate that the permeation mechanisms for aqueous alcohol solution through the PHEMA-*g*-N4 membrane are the same for both types of modified Nylon 4 membranes, i.e., PVA-*p*-N4 and PVA-homo-*g*-Nylon 4 reported previously [13, 14]. Similar results were observed by Mochizuki et al. [18].

Pervaporation Properties of the PHEMA-*g*-N4 Membrane for Different Alcohol-Water Mixtures

According to the solution-diffusion mechanism [2], the size of the permeating species is important in both the solution and diffusion processes. The pervaporation performances of a 90 wt% of aqueous alcohol solution through the PHEMA-*g*-N4 membrane are shown in Fig. 7. An increase in the separation factor and a decrease in the permeation rate occurs as the number of carbon atoms in the alcohol increases. These results can be explained by the molecular size and shape of the alcohol.

Consequently, the larger separation factor for the higher linear alcohol may be explained by the molecular size. Additionally, the permeation rate of *tert*-butanol is lower than that of the *n*-propanol, which may be due to the steric hindrance of the former being higher than that of the latter. Figure 7 also shows the individual

permeation rates of alcohol and water for a PHEMA-g-N4 membrane with a 90 wt% aqueous alcohol solution. The permeation rate of alcohol decreases rapidly from 175 to 2.6 g/m²·h for methanol and *tert*-butanol, respectively. These phenomena confirm the effect of the molecular size and shape of the alcohol mentioned above. Moreover, the activation energy of the 90 wt% aqueous alcohol solution through the PHEMA-g-N4 membrane is in the 4.09 to 5.59 kcal/mol range. The data are presented in Table 5. The activation energy and molecular length are of the same order as is the separation factor for this system. In order to further prove the above results, the effect of the aqueous alcohol solution on the degree of swelling of the PHEMA-g-N4 membrane are also presented in Table 5. These results correspond well with the results from the permeation rate study of the PHEMA-g-N4 membrane, as indicated in Fig. 7.

CONCLUSIONS

In previous papers we investigated various ways, such as plasma deposition and ⁶⁰Co γ -ray irradiation, to improve the membrane morphology and pervaporation performances of Nylon 4 membranes. In this study we use the chemical grafting method to modify the Nylon 4 membrane for enhanced ethanol dehydration. The separation factor of the PHEMA-g-N4 membrane is found to be significantly higher than that of the unmodified Nylon 4 membrane for an aqueous ethanol feed concentration in the 10 to 90 wt% range. A separation factor of 98 and a permeation rate of 194 g/m²·h can be obtained for the PHEMA-g-N4 membrane with a 104.3% degree of grafting. The permeation rate decreases with increasing membrane denseness. The activation energy of the aqueous alcohol solution through the PHEMA-g-N4 membrane is of the same order as the alcohol molecular size.

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