

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Polyvinyl Alcohol $\gamma$ -Ray Grafted Nylon 4 Membrane for Pervaporation and Evapomeation

Juin-Yih Lai<sup>a</sup>; Rong-Yuh Chen<sup>a</sup>; Kueir Rarn Lee<sup>a</sup>

<sup>a</sup> DEPARTMENT OF CHEMICAL ENGINEERING, CHUNG YUAN UNIVERSITY, CHUNG LI, TAIWAN, REPUBLIC OF CHINA

**To cite this Article** Lai, Juin-Yih , Chen, Rong-Yuh and Lee, Kueir Rarn(1993) 'Polyvinyl Alcohol  $\gamma$ -Ray Grafted Nylon 4 Membrane for Pervaporation and Evapomeation', Separation Science and Technology, 28: 7, 1437 — 1452

**To link to this Article:** DOI: 10.1080/01496399308018049

**URL:** <http://dx.doi.org/10.1080/01496399308018049>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Polyvinyl Alcohol $\gamma$ -Ray Grafted Nylon 4 Membrane for Pervaporation and Evapomeation

JUIN-YIH LAI, RONG-YUH CHEN, and KUEIR RARN LEE

DEPARTMENT OF CHEMICAL ENGINEERING  
CHUNG YUAN UNIVERSITY  
CHUNG LI, TAIWAN 320, REPUBLIC OF CHINA

### ABSTRACT

Nylon 4, which possesses high mechanical strength and good affinity for water, can be considered as a liquid separation membrane. To improve the hydrophilicity of a Nylon 4 membrane for pervaporation and evapomeation processes, and to overcome the hydrolysis of polyvinyl alcohol (PVA), this study attempts to prepare a PVA-g-Nylon 4 membrane by  $\gamma$ -ray irradiation grafting of vinyl acetate (VAc) onto Nylon 4 membrane, followed by hydrolysis treatment. The effects of downstream pressure, irradiation dose, VAc monomer concentration, degree of grafting, feed composition, and size of alcohols on the separation of water–alcohol mixtures were studied. The surface properties of the prepared membrane were characterized by FTIR, ESCA, and a contact angle meter. A separation factor of 13.8 and a permeation rate of  $0.352 \text{ kg/m}^2\cdot\text{h}$  can be obtained for a PVA-g-Nylon 4 membrane with a degree of grafting of 21.2% for a 90-wt% ethanol feed concentration. Compared to the pervaporation process, the evapomeation process has a significantly increased separation factor with a decreased permeation rate for the same PVA-g-Nylon 4 membrane.

### INTRODUCTION

Pervaporation is an attractive separation process for a azeotropic liquid mixture where the permeating species are removed from the opposite side of a membrane as a vapor as suggested by Binning et al. (1). The solution-diffusion model rather adequately describes the pervaporation behavior, and it leads to an understanding of the permselectivity of a liquid mixture through a membrane based on the different solubilities of the components toward a membrane and the diffusivity of the components in a membrane (2–4). The membrane separation of azeotropic mixtures by pervaporation and evapomeation has been reported by various groups (1, 5–9). Research

in this field has used cellulose acetate (1, 6, 7), PTFE-*g*-*N*-vinyl pyrrolidone (9, 10), chitosan (8), and silicone rubber (11) for the membrane.

In the pervaporation process, the interaction of hydrogen bonding between the membrane material and water plays an important role in enhancing the permselectivity of water (12–15). One component of the feed mixture may be preferentially sorbed at the interface, and the strong interaction of the functional group makes for an increase of permselectivity. Poly(vinyl alcohol) is highly hydrophilic and excellent in its selectivity toward water. This feature can be used to improve the hydrophilicity of a polyamide membrane for pervaporation and evapomeation processes if the hydrolysis of PVA can be overcome. To avoid such a defect, membranes are usually modified by chemical graft,  $\gamma$ -ray irradiation grafting, and heat treatment (16–18). Nylon 4 membranes have been regarded as promising membrane materials for separation purposes because of their excellent strength and inherent affinity to water.  $^{60}\text{Co}$  irradiation, chemical graft, and plasma deposition methods have been used to improve the performance of Nylon 4 for reverse osmosis (19), ultrafiltration (20), dialysis (21), and hemodialysis (22) as reported from our laboratory.

To improve the hydrophilicity of Nylon 4 membranes for pervaporation purposes and to overcome hydrolysis of PVA, this study attempted to obtain a PVA-*g*-Nylon 4 membrane by  $\gamma$ -ray irradiation grafting VAc onto a Nylon 4 membrane, followed by hydrolysis treatment. The effects of VAc content, irradiation time, degree of grafting, feed concentration, operation temperature, and molecular size of the permeating species on the performances of pervaporation and evapomeation processes were studied.

The surface properties of the prepared membranes were characterized by FTIR, ESCA, and a contact angle meter.

## EXPERIMENTAL

### Material

Nylon 4 was synthesized by the  $\text{CO}_2$ -initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidone as the catalyst (19). The molecular weights of Nylon 4, as measured by a Cannon-Fenske viscometer with *m*-cresol as the solvent at 25°C, ranged from 20,000 to 22,000. Formic acid and normal propyl alcohol, supplied by Nihon Shiyaku Industries Co., were used as a medium solvent and a casting solvent, respectively. Vinyl acetate was supplied by Merck Co., and it was separated from the hydroquinone stabilizer by vacuum distillation. The distilled monomer was stored in a brown glass bottle at  $-10^\circ\text{C}$ .

### Membrane Preparation

The pervaporation membrane substrate was prepared from a formic acid casting solution of Nylon 4 with *n*-propanol added as a swelling agent. The membrane was formed by casting the solution on a glass plate to a pre-determined thickness. The glass plate was heat treated at 70°C for 40 minutes to evaporate the solvent and to provide pores of a suitable size.

### Heterograft Copolymerization

The pure Nylon 4 membrane was dried in vacuum and weighed, then placed in a glass tube, and the grafting monomer solution was poured onto the membrane to completely soak it. Graft copolymerization was carried out by irradiation with  $^{60}\text{Co}$   $\gamma$ -rays at room temperature at a dose rate of 0.1 Mrad/h. After irradiation, the crude graft membrane was kept in a Soxhlet apparatus with acetone for more than 48 hours in order to extract any PVAc homopolymer. For hydrolysis, the PVAc-*g*-Nylon 4 membrane was treated with 0.5 N aqueous sodium hydroxide solution at room temperature for 3 hours. The degree of hydrolysis was confirmed by the infrared peak at  $1738\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  vibration in VAc) disappearing in Fig. 2(f).

The degree of grafting was calculated by

degree of grafting (D.G.)

$$= \frac{(\text{weight of grafted Nylon 4}) - (\text{weight of Nylon 4})}{\text{weight of Nylon 4}}$$

where the “weight of Nylon 4” and the “weight of grafted Nylon 4” denote the weight of dry and grafted-polymerized membrane, respectively.

### Apparatus and Measurements

Normal pervaporation and evapomeation set-up configurations were used. In pervaporation the feed solution is in direct contact with the membrane, whereas the feed is not in contact with the membrane and only vapor is supplied to the membrane in evapomeation. The cell was stainless steel, and circulation of the liquid was over the membrane. The membrane area in contact with the feed solution was  $10.2\text{ cm}^2$ . The membrane was supported by filter paper resting on a sintered stainless disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg, and the permeate was collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography (G. C. China Chromatography 8700 T). The permeation rate was determined by the weight of the permeate.

The separation factor was calculated from the following equation:

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

In pervaporation,  $X_{\text{water}}$ ,  $X_{\text{alcohol}}$ ,  $Y_{\text{water}}$ , and  $Y_{\text{alcohol}}$  are weight fractions of water and alcohol in the feed and the permeate, respectively. In evaporation,  $X_{\text{water}}$  and  $X_{\text{alcohol}}$  are weight fraction of water and ethanol vapor in the feed solution, and  $Y_{\text{water}}$  and  $Y_{\text{alcohol}}$  are weight fraction of water and alcohol in the permeate.

FT-IR spectra were obtained at  $4\text{ cm}^{-1}$  resolution using a Bomem MB-100 FT-IR. Face contact angles were obtained on a Kyowa Kaimenkagaku Co. CA-D meter for measuring the water contact angle with membranes at room temperature. Electro spectroscopy for chemical analysis (ESCA) spectra were obtained by using a Perkin-Elmer PHI 590 AM spectrometer with a  $\text{MgK}_{\alpha}$  x-ray source.

### Swelling Degree Measurement

Clean and dried membranes of known weights were immersed in the feed solution at room temperature for 24 hours in order to reach equilibrium swelling. These pieces were rapidly removed from the bottle, blotted to remove the surface solvent, and placed on a weighing scale. The first reading was taken 40 seconds following removal of the membrane from the mixture, and four to five readings were made at 10 second intervals. The weight of the solvent-swollen membrane was obtained by extrapolating the initial portion of the experimental curve to the zero line (23). The degree of swelling was calculated by the following equation:

$$\text{degree of swelling} = \frac{(\text{weight of swollen Nylon 4}) - (\text{weight of Nylon 4})}{\text{weight of Nylon 4}}$$

where "weight of Nylon 4" and "weight of swollen Nylon 4" denote the weights of dry and solvent-swollen membranes, respectively.

## RESULTS AND DISCUSSION

### Effect of Total Dose on the Degree of Grafting

The graft polymerization reaction was carried out by  $\gamma$ -ray irradiation induced in the VAc aqueous solution at a constant dose rate of  $0.1\text{ Mrad/h}$  for various time periods to give a total dose in the range of  $0.5$  to  $4\text{ Mrad}$ . Figure 1 shows that the degree of grafting increases as the total dose increases up to  $2\text{ Mrad}$ , reaches a maximum, and then decreases for the range of  $0.5$  to  $4\text{ Mrad}$ . It also shows that the degree of grafting increased with increasing VAc monomer concentration in the range of  $5$

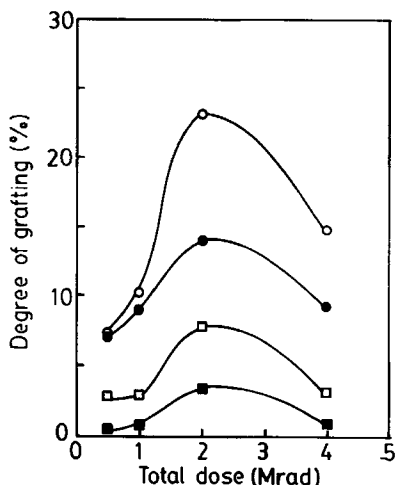


FIG. 1 Effect of total dose and monomer concentration on the degree of grafting. Dose rate, 0.1 Mrad/h. Medium solvent, EtOH:H<sub>2</sub>O = 5:3 vol%. VAc concentration, 5 vol% (■), 16 vol% (□), 30 vol% (●), 45 vol% (○).

to 45 vol%. These phenomena might be due to the fact that degradation took place at a higher total dose and that the gel effect was more pronounced at a higher concentration of VAc monomer. This result suggests the optimized condition for the best degree of grafting is 45 vol% VAc content.

Figure 2 shows the FT-IR spectra of pure Nylon 4 before and after  $\gamma$ -ray irradiation induced various VAc monomer concentrations. The PVAc-g-Nylon 4 membrane shows a sharp peaks at  $1738\text{ cm}^{-1}$  (typical of  $\text{C}=\text{O}$  vibrations),  $1242\text{ cm}^{-1}$   $\nu(\text{—O—C—})$ , and  $1025\text{ cm}^{-1}$   $\nu(\text{—C—O—C—})$  due

to the VAc which is not found in a pure Nylon 4 membrane. The relative absorbance  $A_{1738}/A_{1475}$  was evaluated by measuring the ratio of  $\nu(\text{C}=\text{O})$  absorbance at  $1738\text{ cm}^{-1}$  ( $A_{1738}$ ) to the  $\delta_s(\text{—CH}_2\text{—})$  band absorbance at  $1475\text{ cm}^{-1}$  ( $A_{1475}$ ). The absorbance at  $1475\text{ cm}^{-1}$  ( $\text{—CH}_2\text{—}$  groups) remained at almost the same level for every spectra, and it was used as a reference because it was independent of the degree of grafting. The relative absorbance increases with an increasing degree of grafting (Table 1). These results not only confirmed that the VAc monomer is already grafting onto the membrane structure, but they also agreed with the conclusions from Fig. 1. However, after hydrolysis of the PVAc-g-Nylon 4 membrane with

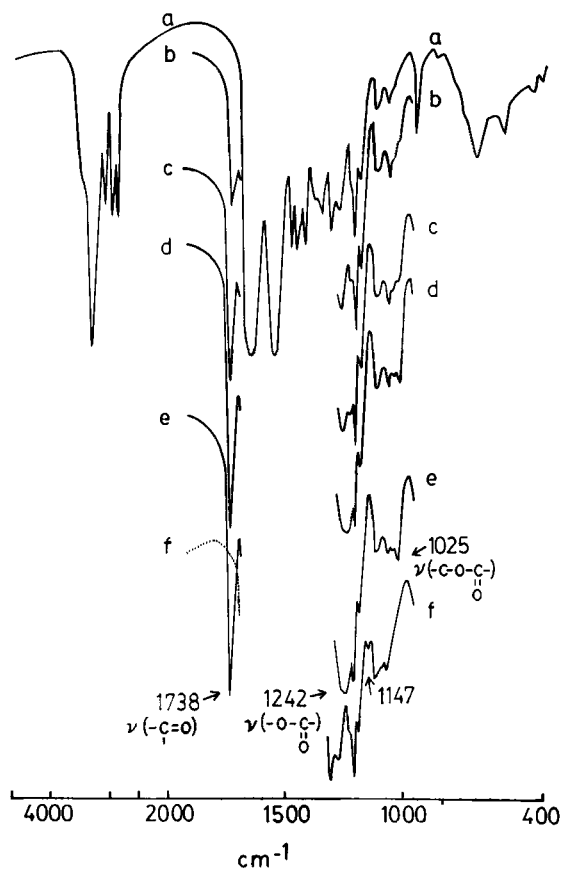


FIG. 2 FT-IR spectra of VAc heterografted Nylon 4 membranes with various VAc vol% concentrations. Total dose: 2 Mrad. Pure Nylon 4 membranes (a), VAc 5 vol% (b), VAc 16 vol% (c), VAc 30 vol% (d), VAc 45 vol% (e), three hours of hydrolysis of a membrane with 45 VAc vol% (f).

0.5 N NaOH aqueous solution at room temperature for 3 hours, the peak at  $1738\text{ cm}^{-1}$  disappears. This result is also shown in Fig. 2(f).

### Analyzing the Surface Properties of the PVA-g-Nylon 4 Membrane

In order to investigate the surface properties of the PVA-g-Nylon 4 membrane, an ESCA study was performed and the contact angle was measured, as shown in Table 1. The relative peak intensity ratio  $O_{1s}(538)/$

TABLE 1  
ESCA Peak Ratio ( $O_{1s}/N_{1s}$ ) and Water Contact Angle of  
PVA-g-Nylon 4 Membranes<sup>c</sup>

D.G. (%)	Relative <sup>a</sup> absorbance $A_{1738}/A_{1475}$	Relative <sup>b</sup> peak intensity $O_{1s}(538)/N_{1s}(400)$	Contact angle of water (degree)
0.00	0.0	2.7	88
2.7	0.7	1.8	87
7.3	1.4	4.3	82
15.6	2.3	6.2	81
21.2	3.1	19.8	78

<sup>a</sup>PVAc-g-Nylon 4 membrane (total dose: 2 Mrad).

<sup>b</sup>Hydrolysis condition: 0.5 N NaOH solution, 3 hours.

<sup>c</sup>Energy range:  $C_{1s}(280\text{--}295)$  eV,  $O_{1s}(528\text{--}540)$  eV,  $N_{1s}(397\text{--}406)$  eV.

$N_{1s}(400)$  at a higher degree of grafting is larger than that at a lower degree of grafting, and the contact angle of the former is lower than that of the latter. This phenomenon may be because the hydroxy group on the graft layer of the PVA-g-Nylon 4 membrane increases and the relative peak intensity at 533 eV generally increases. This analysis, based on the relative peak intensity of  $N_{1s}(400)$  eV, is practically unchanged in these grafted membranes (23). Perhaps the VAc monomer is increasingly introduced into the pure Nylon 4 membrane as their relative peak intensity ratio increases. The contact angle measurement was performed in order to detect the change of surface hydrophilicity of the PVA-g-Nylon 4 membrane, which was expected to increase with an increasing degree of grafting. On the other hand, receding contact angles are a measure of the wettability of higher energy portions of the solid surface. For example, the contact angles of water for a pure Nylon 4 membrane and a PVA-g-Nylon 4 membrane with a degree of grafting of 21.2% are 88 and 78, respectively. This indicates that the affinity of grafted membranes for water is higher than that of pure Nylon 4 membranes. These phenomena are probably due to the fact that the hydroxy group on the graft layer of the PVA-g-Nylon 4 membrane increases, resulting in the hydrophilicity of PVA-g-Nylon 4 membrane enhancement.

### Effect of Downstream Pressure on Pervaporation Process

Figure 3 shows the effect of downstream pressure on the performances of PVA-g-Nylon 4 membranes with a 21.2% degree of grafting for a 90-wt% ethanol aqueous feed solution. The permeation rate and separation factor were approximately independent of downstream pressure for pres-



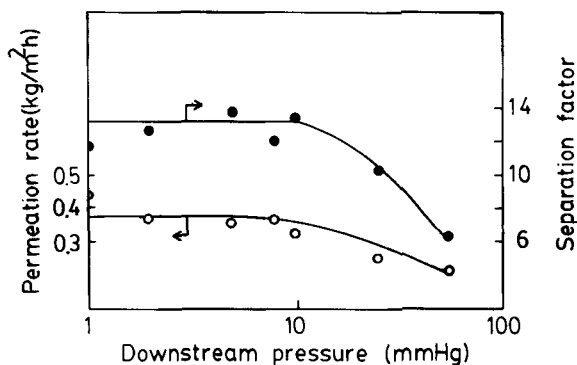


FIG. 3 Effect of downstream pressure on pervaporation through PVA-g-Nylon 4 membranes with D.G. = 21.2% (feed concentration, 90 wt%; operation temperature, 25°C).

sures lower than 10 mmHg. However, both of them decreased sharply above 10 mmHg. Since the downstream pressures above 10 mmHg are comparable with the partial pressure at 25°C with 59 and 23.7 mmHg for ethanol and water, respectively, the evaporation of these liquids from the membrane surface should be suppressed under high pressure. This suggests that a reasonable downstream pressure should be lower than 10 mmHg in this study.

### Effect of Degree of Grafting on Pervaporation Performances

Pervaporation testing was carried out with a 90-wt% ethanol feed concentration through membranes with different degrees of grafting. The separation factor increases with an increasing degree of grafting, as shown in Fig. 4. This may be due to the hydroxy group increasing as the degree of grafting increases. The hydrogen-bonding interaction between hydroxy group and water molecular in the feed solution became strong, resulting in a high permselectivity of water. The hydrophilicity of PVA-g-Nylon 4 increases with an increasing degree of grafting for a low degree of grafting, and the surface density of the PVA-g-Nylon 4 membrane evidently increases for a degree of grafting higher than 14%. Consequently, for a degree of grafting higher than 14%, the surface density change played a more important role. Furthermore, in Figure 2(f) the FT-IR spectra shows that the new  $1147\text{ cm}^{-1}$  band is sensitive to crystallization of the graft polymer layer (PVA), and a linear relationship has been established between intensity and the hydroxy group on the PVA-g-Nylon 4 membrane (24). Compare these results with Fig. 4: the surface density increases with

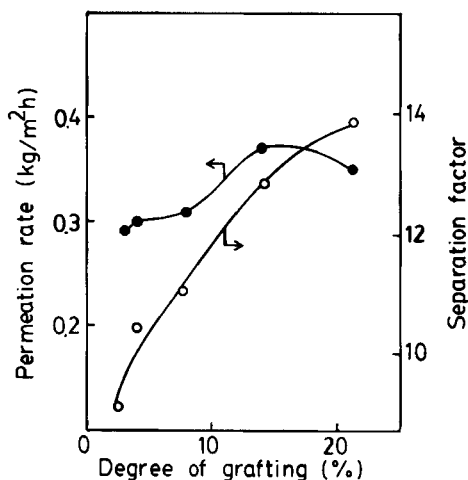


FIG. 4 Effect of degree of grafting on permeation rate and separation factor through PVA-g-Nylon 4 membranes (feed ethanol concentration, 90 wt%; operation temperature, 25°C; downstream pressure, 3 mmHg).

crystallization, resulting in a decreasing permeation rate for a higher degree of grafting.

### Effect of Feed Concentration on Pervaporation Performances

According to the solution-diffusion model, preferential sorption plays an important role in determining the permselectivity. Figure 5 shows the water permeation curves of the ethanol–water mixture through an ungrafted Nylon 4 membrane and PVA-g-Nylon 4 membranes with different degrees of grafting. It is observed that the concentration of water permeated through the modified grafted membranes was higher than that through ungrafted membranes. The higher permselectivity is attributed to the higher hydrophilicity of the hydroxy groups on the graft polymer layer (PVA) of the PVA-g-Nylon 4 membranes. The hydroxy group concentration increases with a higher degree of grafting, and the permselectivity of water is always higher.

Figure 6 shows that the degree of swelling increases with decreasing feed ethanol concentration. This might be because interaction between the hydroxy group and the water molecular of the feed solution increases with increasing water content in the feed solution. The effect of feed ethanol concentration on the permeation rate and separation factor are shown in

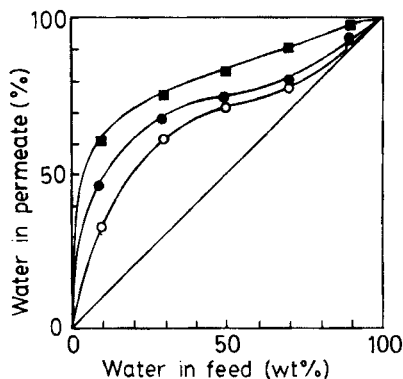


FIG. 5 Water fraction in permeate vs water fraction in feed for pervaporation process. Ungrafted Nylon 4 membranes ( $\circ$ ), PVA-g-Nylon 4 membranes with D.G. = 3.2% ( $\bullet$ ), and PVA-g-Nylon 4 membranes with D.G. = 21.2% ( $\blacksquare$ ).

Fig. 7. This demonstrates that the separation factor for both ungrafted Nylon 4 membranes and PVA-g-Nylon 4 membranes increases with D.G. = 21.2%, and that the permeation rate decreases with an increasing concentration of ethanol in the feed solution. The separation factor of PVA-g-Nylon 4 membranes is much higher than that of ungrafted Nylon 4 membranes. For example, the 13.8 separation factor of PVA-g-Nylon 4 membrane for 90 wt% feed ethanol concentration is four times larger than that of ungrafting membrane, whereas the permeation rate does not change. These results can be explained by the fact that the higher hydro-

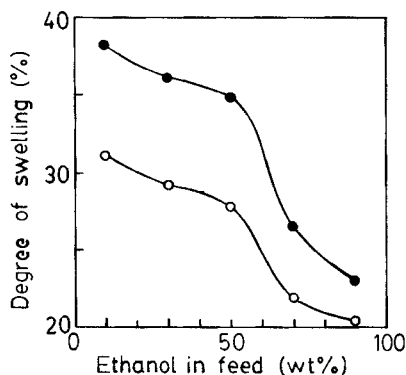


FIG. 6 Effect of feed ethanol concentration on degree of swelling: pure Nylon 4 membranes ( $\circ$ ) and PVA-g-Nylon 4 membranes with D.G. = 21.2% ( $\bullet$ ).

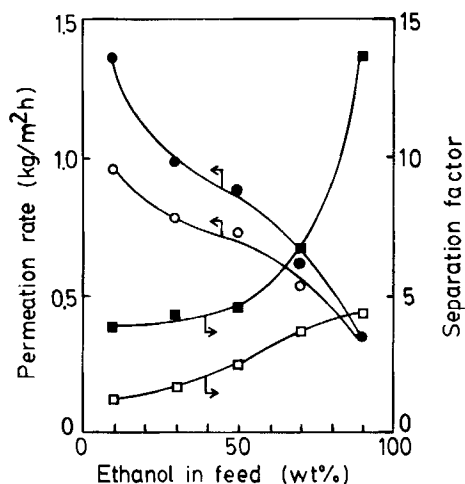


FIG. 7 Effect of feed ethanol concentration on pervaporation performances. Ungrafted Nylon 4 membranes ( $\square$ ,  $\circ$ ) and PVA-g-Nylon 4 with D.G. = 21.2% ( $\blacksquare$ ,  $\bullet$ ).

philicity of the hydroxy group is obtained on the grafted membranes (Fig. 5). Moreover, the permeation rate for a grafted membrane is also higher than that of an ungrafted Nylon 4 membrane but only for a 90-wt% ethanol feed concentration. Recently, a new crosslinked PVA membrane was prepared by Huang and his coworker (15); its  $0.030 \text{ kg/m}^2\cdot\text{h}$  permeation rate is lower than that of the PVA-g-Nylon 4 membrane, but the separation factor is opposite. According to Fig. 6, the swelling of the membranes was remarkable, and the permeation characteristics, as shown in Fig. 7, strongly depend on the degree of swelling of the membranes. The mobility of the polymer chain was increased by swelling, and the permeability is governed by the degree of swelling. The result is worth mentioning because the permeation rate and the separation factor are generally competitive in the membrane process.

However, both higher permeation rate and higher selectivity than those of ungrafted Nylon 4 membrane can be obtained by VAc heterografted Nylon 4 membrane. The heterografting surface modification technique is a very useful tool for improving pervaporation characteristics.

### Pervaporation Characteristics of Graft-Polymerized Membranes for Different Alcohol–Water Systems

The dependence of both the permeation rate and the separation factor on the molecular size and shape of the permeating species with various

TABLE 2  
Effect of the Degree of Grafting on Permeation Rate ( $P$ ) and Separation Factor ( $\alpha$ ) of Alcohol–Water Mixtures with PVA-*g*-Nylon 4 Membranes<sup>c</sup>

D.G. (%)	Methanol		Ethanol		<i>n</i> -Propanol		<i>tert</i> -Butanol	
	$P^a$	$\alpha^b$	$P$	$\alpha$	$P$	$\alpha$	$P$	$\alpha$
3.6	0.785	2.5	0.291	8.9	0.097	33.2	0.086	104.7
7.8	0.703	3.0	0.309	11.0	0.115	57.9	0.097	347.8
13.9	1.034	2.8	0.372	11.7	0.242	99.3	0.087	412.1
21.2	0.770	2.9	0.358	13.9	0.103	257.2	0.089	717.1

<sup>a</sup>Permeation rate, kg/m<sup>2</sup>·h.

<sup>b</sup>Separation factor,  $\alpha$ .

<sup>c</sup>Operation conditions: feed concentration, 90 wt% ethanol; downstream pressure, 3–5 mmHg; temperature, 25°C.

graft-polymerized membranes are shown in Table 2. It is observed that an increase of the number of carbon atoms in an alcohol molecule results in an increase of the separation factor but a decrease of the permeation rate. These phenomena can be explained by the molecular size and shape of the alcohol.

The molecular length,  $\bar{L}$  (in angstroms), of methanol, ethanol, and *n*-propanol are 2.9, 4.2, and 5.4, respectively. The separation factor was found to depend on the molecular length for this linear alcohol system, and it was also found that the permeation rate increased as the molecular length decreased. The permeation rate of *tert*-butanol is lower than that of *n*-propanol, which may be 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.

### Evapomeation

The performances of aqueous ethanol solution through PVA-*g*-Nylon 4 membranes by pervaporation and evapomeation are shown in Table 3 and Fig. 8.

The water is predominantly permeated through the grafted membranes in both methods. Additionally, the permeation rates were found to increase with a decrease of the ethanol concentration in the feed solution. However, the permeation rate of evapomeation is lower than that of pervaporation. These results might be due to the fact that the membrane was in direct contact with the feed solution and swollen for the pervaporation process but that of the evapomeation process was not. This supports the assumption that the grafted membranes in evapomeation can have a quite dense struc-

TABLE 3  
Comparison of Permeation Rate and Separation Factor of Ethanol-Water Solution through the Grafted-Polymerized Membrane (D.G. = 21.2%) by Pervaporation and Evapomeation<sup>a</sup>

Feed concentration (wt%)	Pervaporation		Evapomeation	
	Permeation rate (kg/m <sup>2</sup> ·h)	Separation factor	Permeation rate (kg/m <sup>2</sup> ·h)	Separation factor
90 (90.8) <sup>b</sup>	0.352	13.8	0.054	154.4 (169.3)
70 (77.3)	0.618	6.7	0.062	52.1 (78.5)
50 (67.7)	0.886	4.6	0.068	37.8 (71.8)
30 (60.4)	0.988	4.3	0.068	34.6 (117.7)
10 (43.9)	1.358	3.9	0.074	17.5 (119.5)

<sup>a</sup>Operation temperature: 25°C.

<sup>b</sup>Ethanol in vapor in weight %.

ture. Thus, the diffusivity of the permeating species during the diffusion process in evapomeation is lower. Furthermore, the separation factors of PVA-g-Nylon 4 membranes in evapomeation are much higher than those of the membranes used in pervaporation. For example, the 154.4 separation factor with the 0.054 kg/m<sup>2</sup>·h permeation rate of PVA-g-Nylon 4 membranes in evapomeation can be obtained for a 90-wt% ethanol concentration under a 3–5 mmHg operating pressure. The permeation rate and

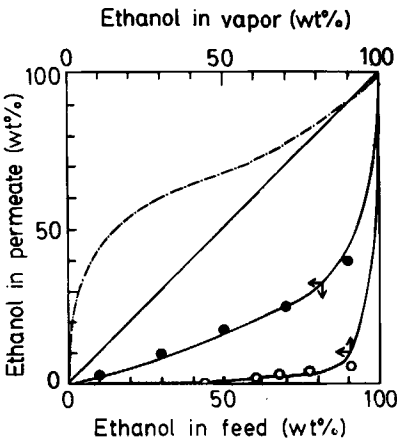


FIG. 8 Effect of ethanol concentration in the permeate through the PVA-g-Nylon 4 membranes with D.G. = 21.2%. Pervaporation (●) and evapomeation (○). The broken curve is for vapor-liquid equilibrium concentration.

separation factor are 0.352 kg/m<sup>2</sup>·h and 13.8, respectively, for the pervaporation process under the same operating condition (see Table 3). This suggests that the evapomeation method is effective in increasing the separation factor for alcohol–water separation.

### Effect of Temperature

The above-mentioned pervaporation runs were conducted at 25°C. In order to study the effect of temperature, the pervaporation experiments were carried out in the 15 to 45°C range. The experimental values are shown in Table 4. The permeation rate increases with increasing temperature, corresponds to the general tendency. It is observed that there is a minimum separation factor for all feed concentrations in the 15 to 45°C range. Figure 9 shows that the permeation rate is inversely proportional to the absolute temperature relationship, and this indicates that the experimental results agree very well with Arrhenius equation. The activation

TABLE 4  
Experimental Values of Feed and Permeate Concentration and Permeation Rate and Separation Factor at Various Temperatures (PVA-g-Nylon 4 membranes with D.G. = 21.2%)

<i>T</i> (°C)	Feed concentration (wt% EtOH)	Permeation concentration (wt% EtOH)	Permeation rate (kg/m <sup>2</sup> ·h)	Separation factor, α
15	90.3	36.4	0.287	16.2
	70.9	21.3	0.333	9.1
	49.4	15.2	0.551	5.5
	11.0	2.6	0.903	4.6
25	90.3	39.6	0.352	13.8
	70.9	25.0	0.451	6.7
	49.4	17.6	0.886	4.6
	11.0	3.1	1.354	3.9
35	90.3	39.5	0.589	14.2
	70.9	23.7	0.671	7.9
	49.4	16.6	1.256	4.9
	11.0	2.8	1.928	4.3
45	90.3	34.5	0.765	17.6
	70.9	23.8	1.176	7.5
	49.4	16.4	1.789	4.9
	11.0	2.7	2.629	4.4

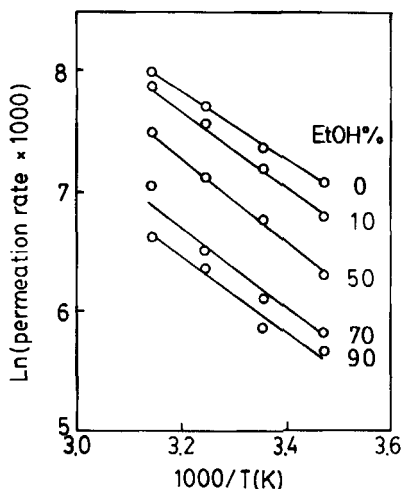


FIG. 9 Effect of temperature on permeation rate of PVA-g-Nylon 4 membranes with D.G. = 21.2% for different ethanol–water concentrations (in wt%).

energies of ethanol–water permeating through the grafted membrane were calculated to be 5.9–7.4 kcal/mol.

## CONCLUSIONS

The grafting of VAc onto Nylon 4 was confirmed by an FTIR study, and the amount of hydroxy group on the membrane surface was characterized by ESCA.

The separation factor and permeation rate of ungrafted Nylon 4 membrane are both improved with a PVA-g-Nylon 4 membrane in the range of 10 to 90 wt% ethanol feed concentration. A separation factor of 13.8 and a permeation rate of 0.352 kg/m<sup>2</sup>·h can be obtained with a PVA-g-Nylon 4 membrane with a degree of grafting of 21.2%. Compared with the pervaporation process, the evapomeation process has a significantly increased separation factor with a decreasing permeation rate for the same PVA-g-Nylon 4 membrane.

For both ungrafted and PVA-g-Nylon 4 membranes, the permeation rates increase with increasing feedwater content, which causes a swelling effect.

The permeation rates in the operating temperature range of 15–45°C are found to follow the Arrhenius law. There is a minimum separation factor for all feed concentrations in the temperature range considered.



The separation factor of the PVA-g-Nylon 4 membrane increases as the degree of grafting increases due to an increase of the hydroxy group. The permeation rate increases with an increasing degree of grafting up to 14% and then decreases.

$\gamma$ -Ray irradiation grafting of VAc onto a Nylon 4 membrane has proved promising for improving the pervaporation performances of an ungrafted Nylon 4 membrane.

### ACKNOWLEDGMENT

The authors wish to thank the National Science Council of the Republic of China for financial support (NSC81-0405-E033-01).

### REFERENCES

1. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, **53**, 45 (1961).
2. M. H. V. Mulder and C. A. Smolders, *J. Membr. Sci.*, **17**, 289 (1984).
3. M. H. V. Mulder, A. C. M. Franken, and C. A. Smolders, *Ibid.*, **23**, 41 (1985).
4. S. Hwang and K. Kammermeyer (Eds.), *Membranes in Separation* (Techniques of Chemistry, Vol. 7), Wiley-Interscience, New York, 1975.
5. P. Aptel, N. Challard, and J. Neel, *J. Membr. Sci.*, **1**, 271 (1976).
6. E. Nagy, O. Borlai, and A. Ujhidy, *Ibid.*, **7**, 109 (1980).
7. R. C. Binning and R. J. Lee, U.S. Patent 2,953,520 (September 20, 1960).
8. T. Uragami and K. Takigawa, *Polymer*, **31**, 668 (1990).
9. P. Aptel, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **18**, 351 (1974).
10. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *Ibid.*, **16**, 1061 (1973).
11. K. C. Hoover and S. T. Hwang, *J. Membr. Sci.*, **10**, 253 (1982).
12. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **18**, 365 (1974).
13. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Polym. Sci., Part A*, **24**, 1585 (1986).
14. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
15. R. Y. M. Huang and C. K. Yeom, *J. Membr. Sci.*, **51**, 273 (1990).
16. T. O. Nguyen, A. Essamri, R. Clement, and J. Neel, *Makromol. Chem.*, **188**, 1973 (1987).
17. Y. S. Kang, S. W. Lee, U. Y. Kim, and J. S. Sim, *J. Membr. Sci.*, **51**, 215 (1990).
18. M. Wesslein, A. Heintz, and R. N. Lichtenthaler, *Ibid.*, **51**, 181 (1990).
19. J. Y. Lai, T. C. Chang, Z. J. Wu, and T. S. Hsieh, *J. Appl. Polym. Sci.*, **32**, 4709 (1986).
20. A. Jong, T. C. Chang, and J. Y. Lai, *Ibid.*, **36**, 87 (1988).
21. J. Y. Lai and C. C. Chou, *Ibid.*, **37**, 1465 (1989).
22. J. Y. Lai, C. Y. Shih, and S. M. Tsai, *Ibid.*, **43**, 1431 (1991).
23. T. Hirotsu and M. Isayama, *J. Membr. Sci.*, **45**, 137 (1989).
24. C. A. Finch, *Polyvinyl Alcohol Properties and Applications*, Wiley, New York, 1973.

Received by editor December 2, 1991