Plasma Graft Polymerization of N,N-Dimethylaminoethyl Methacrylate and Water–Ethanol Separation by Pervaporation Through the Grafted Membranes

TOSHIHIRO HIROTSU* and AKITO ARITA†

Research Institute for Polymers and Textiles, 1-1-4, Higashi, Tsukuba, Ibaraki 305, Japan

SYNOPSIS

N,N-dimethylaminoethyl methacrylate was graft-polymerized onto the porous polypropylene films of Celgard 2400 and 2500 which have been previously surface-activated by glow discharge plasmas. The grafting was dependent on various factors both in the plasma pretreatment and the post-polymerization with the monomer. The reaction was discussed from the aspects of the dependences of graft polymerization on discharge power, plasma pretreatment period, etc. When the grafting exceeded a critical amount depending on the size of pores on the substrate film, pervaporation of water–ethanol separation functioned through these grafted membranes. The water permselectivity was improved by the ammonium ionization of the pendant N,N-dimethylamino group using dimethyl sulfate or chloroacetic acid, although the increase of pervaporation performance was not so high as those previously obtained by the grafted poly(sodium acrylate)-type membranes. Pervaporation characteristics of these membranes were discussed from the ionized states of the permselective layers analyzed by IR and ESCA.

INTRODUCTION

Graft polymerization is possible with some vinyl monomers onto the polymeric substrates which have been previously treated by glow discharge plasma. Such processes have been applied to polymer modification because of the durable properties with the grafted layers. For example, the surface hydrophilicity of polyester fabrics improved by graft polymerization with acrylic acid,[1] the dyeing properties improved by graft polymerization of fluorine monomers,[2] etc. have been reported. Water-permeable or semipermeable membranes have been obtained by plasma graft polymerization of hydrophilic monomers, such as acrylamide and 2-acrylamide-2-methylpropane sulfonic acid.[3,4] We have applied this plasma graft polymerization technique to the prep-

aration of pervaporation membranes for the purpose of water–ethanol separation, and observed the water permselectivity of the membranes grafted with acrylic acid,[5] methacrylic acid,[6] acrylamide–acrylic acid,[7] 2-hydroxyethyl methacrylate,[8] etc.

When the mixture solvents were subjected to evaporation through a membrane (i.e., pervaporation), the more soluble and diffusive component preferentially permeates across the membrane (e.g., water through hydrophilic membranes), and as a result separation of the mixtures is achieved. Nowadays, such membrane separation process is applied for the practical use of dehydration from aqueous organic solutions by hydrophilic membranes such as crosslinked poly(vinyl alcohol).

One of the important merits of plasma-grafted membranes for pervaporation lies in the structure. The permselective layer made of the graft polymer is formed on the mechanically stable substrate films through the chemical bond, i.e., the permselective layer is in a kind of the immobilized state, and therefore the more durable separation properties

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may be obtained with the product membranes. The more hydrophilic graft polymers like poly(acrylic acid) can be incorporated in the separation membranes for dehydration, and such a permselective layer, in which water is more soluble and diffusible, leads to the effective pervaporation membranes. In fact, some of the plasma-grafted membranes showed higher permeation rates with higher water permselectivity. The permselectivity attributed to the hydrophilic graft polymer layers was dependent on the chemical structure. When the polymer layer was ionized in the form of carboxylates of Na, K, and Li salts, the permselectivity of water was in general improved. As these anionic membranes had the better pervaporation efficiency for water separation, our concern was next directed to the cationic membranes. For the precursor of these cationic membranes, N,N-dimethylaminoethyl methacrylate (DMAEMA) was selected as a monomer of plasma graft polymerization onto the porous polypropylene films. The terminal N,N-dimethylamino group of the grafted layer was transferred to the ammonium-ion structure through the reaction with dimethyl sulfate (Me_2SO_4) or chloroacetic acid (ClAcOH), and the membranes for pervaporation was prepared.

In the present paper, we would like to report the results of plasma graft polymerization of DMAEMA and the pervaporation characteristics for water–ethanol separation through these product membranes with relating to the chemical structure of the permselective layer.

EXPERIMENTAL

Materials

DMAEMA (Tokyo Kasei Kogyo) was purified by distillation in vacuum. Porous polypropylene films (Celgard 2400, 2500) were used for the substrates of graft polymerization. According to the manufacturer's manual, the average pore size is 200×2000 Å and 400×4000 Å, respectively, for these two types of substrate films. They were subjected to plasma pretreatments as supplied, and the pervaporation membranes were constructed.

Plasma Graft Polymerization

The apparatus and the reaction procedure of plasma graft polymerization have schematically described previously.[7] A substrate porous polypropylene film (6×6 cm) was placed in a cylindrical reactor (3 cm i.d. and 24 cm length), and treated with a plasma

(0.02 torr) at first. The glow discharge plasma was generated inductively by the radio frequency of 13.56 MHz. For the present work, no special gas such as argon and nitrogen was supplied but the residual gas in the system was used for the plasma source. After the termination of glow discharges, the aqueous solution (40 mL) of DMAEMA which had previously been degassed in vacuum was introduced in the reactor through the stopcock without the contact of activated substrate films to air. The graft polymerization was then made in vacuum by shaking in a water bath under fixed temperature and reaction period conditions. Since the whole graft polymerization process was conducted in vacuum, the deactivation of the activated polymer radicals by oxygen in air could be avoided. After the reaction, the grafted film was taken out from the reactor, and washed with deionized water and soaked overnight in water to remove the unreacted monomer and homopolymers. The grafting was evaluated by the weight increase in vacuum-dried states and given in mg/cm^2.

Quaternary-Ammonium Ionization

The plasma-grafted membranes of DMAEMA were dipped in a 2 wt % solution of Me_2SO_4 or ClAcOH in water–ethanol (50/50) at room temperature for about 20 min and quaternary-ammonium ionization of the terminal dimethylamino group was made. The ammonium ionization was confirmed by IR.

Pervaporation

Water–ethanol separation characteristics of these grafted membranes were evaluated by pervaporation as follows. The graft polymerized membranes with the effective area of 12.56 cm^2 were set in a stainless steel holder, and pervaporation was carried out by evacuating one side of the membrane using the aqueous ethanolic solution with the concentration range of 0–90 wt % for feed. The permeates were collected in a cold trap in liquid nitrogen, and permeation rate or flux (Q, $kg/m^2/h$) was obtained from the increasing rate of the weight. Concentration of water and ethanol was analyzed, respectively, for feeds and permeates by the peak intensity of gas chromatogram measured by a Model GC-14A (Shimadzu) equipped with a Porapak-Q column (at 180°C). Permselectivity of water was evaluated by a separation factor ($\alpha_{W/E}$), which is obtained by

$$\alpha_{W/E} = (X_W/X_E)/(Y_W/Y_E)$$

where X_W and X_E denote the concentrations of water and ethanol in permeate and Y_W and Y_E are those of feeds.

RESULTS AND DISCUSSION

### Plasma Graft Polymerization of DMAEMA

Plasma graft polymerization process which was applied for the preparation of pervaporation membranes in this work is composed of the two successive steps, i.e., plasma activation of the substrate materials and the followed graft polymerization by a monomer. Therefore, the grafting should be dependent on the various factors in these conditions. Some of the factors were selected and the effects on graft polymerization of DMAEMA was studied.

Plasma Pretreatment Condition

In the present study, the residual gas was used for the plasma source without supplying any special inorganic gases. Using such plasma, the effect of discharge power on the graft polymerization of DMAEMA was investigated at first.

Figure 1 shows the dependence of the grafting on discharge power of plasma for the activation of Celgard films. Here, the substrate films were treated for 2 min by plasma and the 10 wt % aqueous DMAEMA solution (40 mL) was reacted at 60°C for 2 h.

Grafting increased with the power at first to reached maxima at around 20 W, and the grafting gradually decreased beyond the power. Similar phenomena have been observed in the graft polymer-
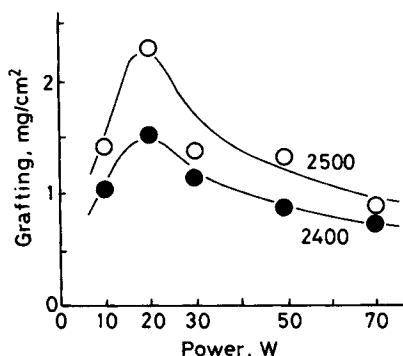
Figure 1 Dependence of grafted weight of poly-(DMAEMA) on the discharge power, respectively, onto polypropylene substrate films of Celgard 2400 and 2500; plasma = 60 s, grafting = 10 wt % aqueous DMAEMA solution, 60°C, 2 h.
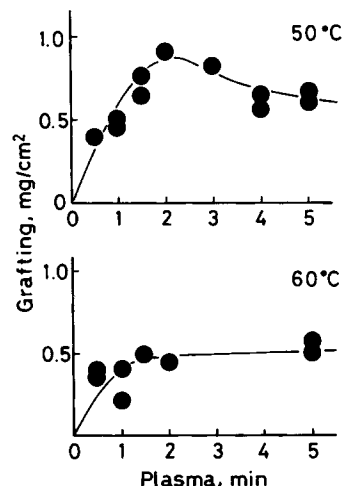
Figure 2 Dependence of grafted weight of poly-(DMAEMA) on the plasma discharge period onto Celgard 2400 film, respectively, at 50 and 60°C; plasma = 10 W, grafting = 5 wt % aqueous DMAEMA solution, 2 h.

ization of acrylamide onto the plasma activated surface of polyethylene films,[9] although the maxima have been observed much sharply in these cases. In any event, the appearance of such maxima of the grafted amount has been commonly observed in many cases of graft polymerization induced by glow discharge plasma.

For the decrease of grafting, the effect of temperature increase which should be caused during the prolonged plasma exposure must be taken into account. During the glow discharge exposure, the excess energy is converted into heat and the depression of the initiation of graft polymerization should result through the rise in temperature. (Decrease of grafting has been observed in the graft polymerization carried out at temperature higher than 60°C.[10])
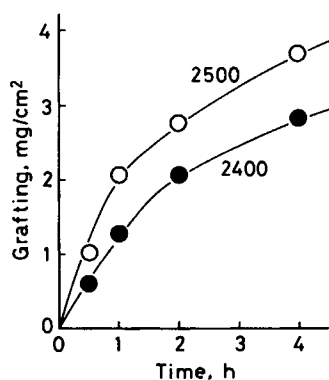
It also should be noticed from these results that the grafting amount is in general greater onto Celgard 2500 film than onto Celgard 2400 film. The difference in the reactivity is attributed to some effects related to the surface morphology generated during the finish of these substrate porous films.

Plasma exposure period also affected the graft polymerization of DMAEMA. Figure 2 shows the dependence of graft polymerization on the plasma pretreatment period (0–5 min). The results presented here are for the substrate film of Celgard 2400, which was pretreated by the residual gas plasma at 10 W. Graft polymerization was made with the 5 wt % aqueous DMAEMA solution at 60°C for 2 h. Under such a reaction condition, the grafting increased at first with the increase of pretreatment period and reached maximum around at 2 min. As
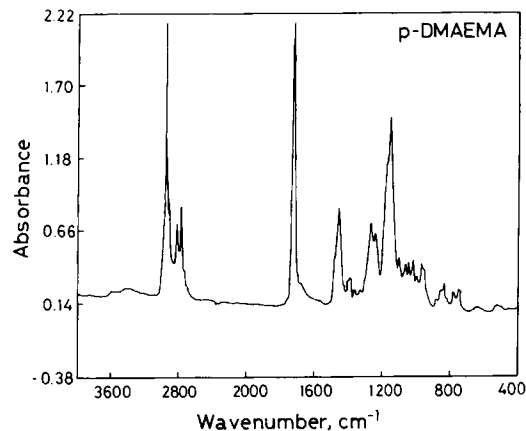
the plasma pretreatment was continued further, the grafted amount decreased slightly and leveled off after 4–5 min.

Post-Polymerization Condition

Effects of post-polymerization condition were investigated from the aspects of monomer concentration, reaction temperature, reaction period, etc. The graft polymerization of DMAEMA was generally made with the aqueous monomer solution at the concentration of 5 wt %, and the reactivity was compared. When grafting was carried out with the 3 wt % solution, the graft polymerizability was much smaller. In contrast, when the reaction was made with the 10 wt % solution, homopolymerization rather prevailed. The grafted amount of DMAEMA of course increased with the reaction period. Figure 3 shows a result of the dependence on the graft polymerization period, respectively, onto Celgard 2400 and 2500 treated with the residual gas plasma at 10 W for 2 min. It should be noticed here that the increasing ratio of the grafted amount against the reaction period suppressed gradually after 2 h. The similar reaction dependences have been observed in some other monomers like 2-hydroxyethyl methacrylate. On the basis of the relationship between the grafted amount of the polymer and the reaction period, the polymerizability of a monomer was evaluated from the slope, i.e., the reactivity can be judged higher in the case that the slope is more steep. The plasma graft polymerizability was thus compared under certain conditions. Among the monomers so far investigated, DMAEMA was not so reactive, and 2-hydroxyethyl methacrylate which is also a methacrylate derivative was the best polymerizable to give

Figure 4 Infrared spectra of the grafted poly-(DMAEMA) on Celgard 2400 film.

the greater amount of graft polymers onto the same polypropylene substrates. However, DMAEMA was more graft-polymerizable than some other N,N-dimethylamino group containing monomers such as N,N-dimethylaminoethyl acrylate (DMAEA) or N,N-dimethylaminopropyl acrylamide (DMA-PAAm), i.e., the reactivity was in the order of

$$DMAEMA > DMAEA > DMAPAAm$$

It should be noticed that DMAEMA was more reactive than the acrylate derivative of DMAEA in spite of the steric hinderance by methyl group. The exact reason for such a difference in monomer reactivity in graft polymerization onto the plasma surface-activated Celgard films cannot be given at present. However, one of the factors that should af-

Figure 3 Dependence of grafted weight of poly-(DMAEMA) on the grafting period, respectively, onto Celgard 2400 and 2500 films; plasma = 10 W, 60 s, grafting = 10 wt % aqueous DMAEMA solution, 50°C.
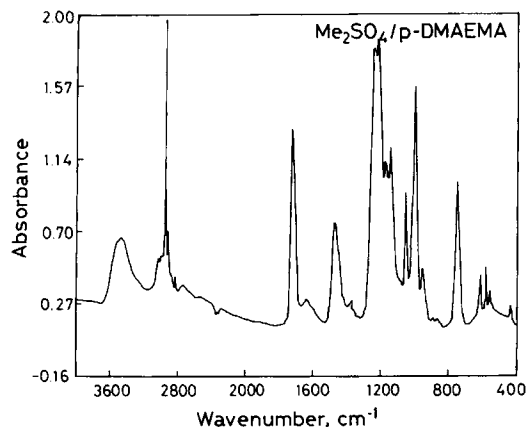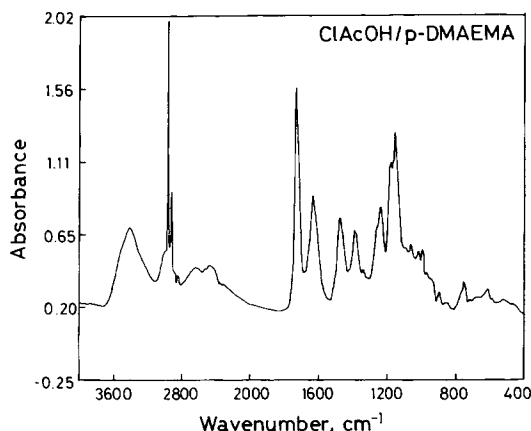

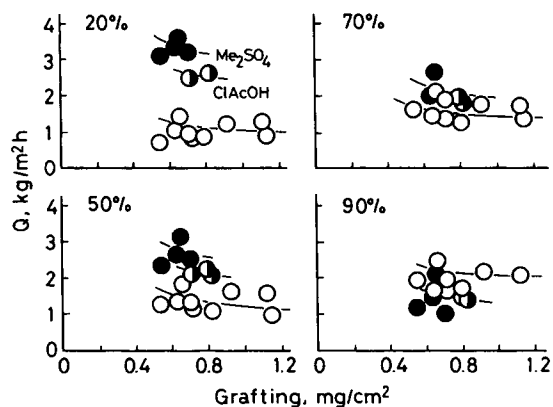**Figure 5** Infrared spectra of the grafted poly-(DMAEMA) on Celgard 2400 film treated with dimethyl sulfate.

Figure 6 Infrared spectra of the grafted poly-(DMAEMA) on Celgard 2400 film treated with chloro-acetic acid.

Figure 8 Dependence of separation factor of water ($\alpha_{W/E}$) on the grafting amount of DMAEMA onto Celgard 2400 (at 40°C).

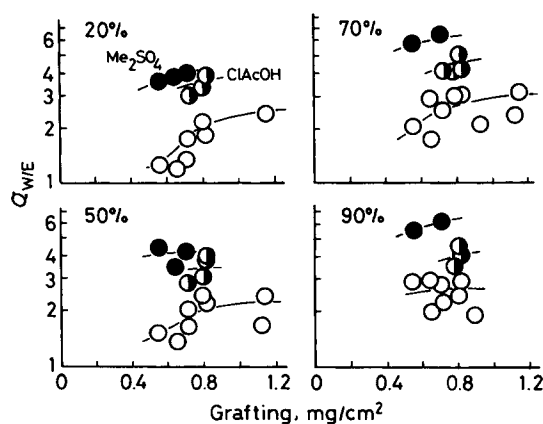fect the reactivity may be the hydrophobicity affecting the monomer interaction to the surface of the substrate film.

Quaternary-Ammonium Ionization

Graft-polymerized membranes of DMAEMA were quaternary-ammonium-ionized by the reaction with the solution of Me_2SO_4 or ClAcOH, and pervaporation through these membranes was investigated for the separation of water–ethanol. The ionized states of the graft polymers were analyzed spectroscopically by FT-IR and ESCA, using the instruments of 1720-X (Perkin-Elmer) and ESCA-760 (Shimadzu).

Figures 4–6 show the IR spectra of the grafted poly(DMAEMA) and the ones reacted with Me_2SO_4 and ClAcOH, respectively, formed on Celgard 2400 film. These spectra were obtained by subtracting the

spectrum of the substrate polypropylene film from that of the products. In the grafted membranes treated with Me_2SO_4, several characteristic peaks that indicate the ammonium-ionized form appeared, i.e., the peaks located at 1227 ($\nu_s SO_2$),[11] 1150, 1008, and 749 cm^{-1} were observed. These peaks were not observed at all in the original untreated polymer, and were suggested to be derived from the counterion of $CH_3SO_4^-$. In the adduct with ClAcOH, the moderately intensive absorbance peak appeared at the much lower field of 1632 cm^{-1}, which should be assigned to either $-N(CH_3)_2(CH_2COOH)^+Cl^-$ or $-N(CH_3)_2H^+ClCH_2COO^-$.

In the IR spectra of the DMAEMA graft polymer, the peak of the carbonyl group in ester was observed at 1729 cm^{-1}, and the position did not change after

Figure 7 Dependence of flux (Q) on the grafting amount of DMAEMA onto Celgard 2400 (at 40°C).
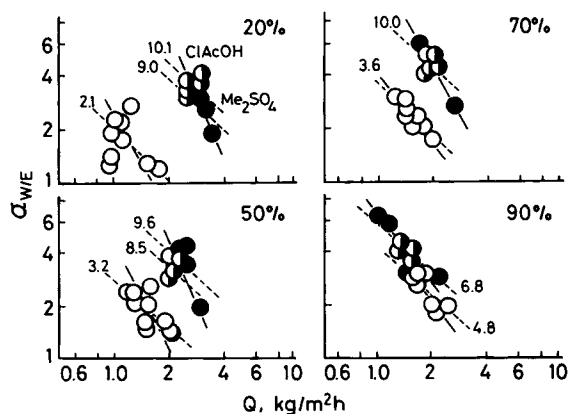
Figure 9 Relationship between the separation factor of water ($\alpha_{W/E}$) and flux (Q) by pervaporation through the DMAEMA-grafted membranes and the ammonium-ionized membranes.

Table I   Water–Ethanol Separation Characteristics by Pervaporation Evaluated by the Product Values of $\alpha_{W/E} \times Q$ (kg/m² h)

| Membrane | Treatment | $\alpha_{W/E} \times Q$ (kg/m² h) | | | | Ref. |
		20 wt %	50 wt %	70 wt %	90 wt %	
DMAEMA	—	2.1	3.2	3.6	4.8	This work
DMAEMA	Me₂SO₄	9.0	9.6	10.0	6.8	This work
DMAEMA	ClAcOH	10.1	8.5	10.0	6.8	This work
AAm[a]	—	5.4	8.5	7.2	4.6	7
AA[b]	—	7.2	6.2	6.8	5.5	7
AA	NaOH	56.3	94.4	75.7	4.4	7
AA–AAm (0.4)[c]	—	8.2	6.3	3.1	1.3	7
AA–AAm (0.4)	NaOH	18.6	45.7	45.4	2.6	7

[a] AAm = acrylamide.
[b] AA = acrylic acid.
[c] AA–AAm (0.4) = AA/(AA + AAm) = 0.4.

the ammonium ionization of the terminal N,N-dimethylamino group by Me₂SO₄ or ClAcOH.

Surface states of these graft polymers were also analyzed with ESCA, especially from the aspects of elemental composition. In the spectra of the Me₂SO₄-treated polymer, the peak of S_{2p} newly appeared at 170 eV. The relative composition of sulfur was estimated to be ca. 40% by the analyses using the relative intensity factor of 1.7 for S_{2p}/C_{1s}. Thus, the incorporation of sulfur was much smaller than that expected by the stoichiometric 1 : 1 complex.

Water–Ethanol Separation by Pervaporation

Pervaporation of water–ethanol mixture solution through these grafted membranes was made at 40°C. These graft polymerized membranes were hydrophilic, and water permselectivity resulted with the membranes grafted beyond the certain amount of poly(DMAEMA).

Figures 7 and 8 show the dependence of flux (Q, kg/m² h) and separation factor of water ($\alpha_{W/E}$) on

the weight of the grafted poly(DMAEMA) on Celgard 2400 film. The results of pervaporation were compared to those by the ammonium-ionized membranes by Me₂SO₄ and ClAcOH, respectively. Pervaporation functioned with the membranes grafted more than 0.5–0.6 mg/cm² on the substrate film of Celgard 2400 film. Water separation by pervaporation was improved when the grafted membranes were ammonium-ionized by Me₂SO₄ or ClAcOH, i.e., separation factor increased generally, and flux also increased except to the feed of 90 wt % ethanol.

The pervaporation characteristics of these membranes were compared by the relationship of $\alpha_{W/E}$ and Q, and the results are shown in Figure 9, respectively, for the feeds of 20, 50, 70, and 90 wt % ethanol. The greater product values of $\alpha_{W/E}$ and Q (i.e., $\alpha_{W/E} \times Q$) indicate the better performance of pervaporation. The product value increased from 2–4 to 7–10 by the treatments of the grafted membranes with Me₂SO₄ and ClAcOH, and the increase was greater toward the feeds with lower ethanol concentration. The increase was mainly due to the

Table II   Activation Energy of Permeation by Pervaporation Obtained from the Arrhenius Plots

| Membrane | Grafting (mg/cm²) | Treatment | Activation Energy (kcal/mol) | | | | |
			0 wt %	20 wt %	50 wt %	70 wt %	90 wt %
DMAEMA	1.13	—	3.1	6.4	7.8	7.4	6.6
DMAEMA	1.13	Me₂SO₄	5.6	6.4	6.4	6.6	—
DMAEMA	0.93	—	4.3	6.8	8.1	7.0	7.1
DMAEMA	0.93	ClAcOH	6.2	6.6	7.2	6.9	—
AA	1.26	—	6.2	8.7	5.7	4.3	4.6
AA	1.26	NaOH	4.9	4.8	3.8	2.5	4.4

higher flux of permeates. However, the increase in the water permselectivity in these quaternary-ammonium-ionized membranes was not so much as those observed previously in the anionic membranes derived from the graft polymers of acrylic acid[5] and acrylamide–acrylic acid.[7]

In Table I, the product values are summarized and the effects of ionization on the pervaporation are compared. Increase of the $\alpha_{W/E} \times Q$ values is shown in both types of cationic and anionic membranes, but improvement in the pervaporation performance is much prominent in the latter membranes generally. The less increase in these ammonium-ionized membranes should be related with the smaller incorporation of ions as suggested by the ESCA analyses.

It has been observed previously that the activation energy of permeation became generally smaller by the anionic ionization of the grafted poly (acrylic acid) membranes, and the similar phenomena were also observed in the pervaporation through these ammonium-ionized membranes. The energy was calculated from the Arrhenius plots in the temperature range of 40–70°C, and the results are summarized in Table II with the data of the membranes grafted with poly (acrylic acid). In the poly (sodium acrylate)-type membranes, the energy lay in the range of 2.5–4.9 kcal/mol, and much decreased from the energy in the untreated membranes. The decrease of energy was also observed in the pervapor-

ation through the trimethylammonium-ionized membranes, but the change was much smaller.

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