Macromolecular Research, Vol. 13, No. 2, pp 135-140 (2005)

Aging Effect of Poly(vinyl alcohol) Membranes Crosslinked with Poly(acrylic acid-*co*-maleic acid)

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Received November 13, 2004; Revised March 4, 2005

Abstract: Poly(vinyl alcohol) (PVA) membranes crosslinked with poly(acrylic acid-*co*-maleic acid) (PAM) were prepared to investigate the effect of aging on their morphology by swelling them for up to 7 days. PAM was used both as a crosslinking agent and as a donor of the hydrophilic -COOH group. A 30 wt% weight loss of the dry membrane was observed in the swelling test after 6 days. The surface of the membrane was dramatically changed after the swelling test. The surface roughness of the PVA/PAM membrane was increased, as determined by atomic force microscopy (AFM). The swelling loosened the polymer structure, due to the release of the unreacted polymer and the decomposition of the ester bond, thereby resulting in an increase in the free volume capable of containing water molecules. The water molecules present in the form of free water were determined by differential scanning calorimetry (DSC). The fraction of free water increased with increasing swelling time. The swelling of the membrane may provide space for the transport of protons and increase the mobility of the protonic charge carriers. The proton conductivity of the membranes measured at $T = 30$ and 50 °C was in the range of 10^{-3} to 10^{-2} S/cm, and slightly increased with increasing swelling time and temperature.

Keywords: fuel cell, poly(vinyl alcohol), aging effect, crosslinking, membrane.

Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer that is used in practical applications because of its easy preparation, excellent chemical resistance, and physical properties.[1] In particular, PVA membrane has been used in ethanol dehydration to break the ethanol-water azeotrope because it selectively passes water molecule over ethanol or methanol.[2-4] Although PVA itself dose not have the fixed charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be used to impart hydrophilicity and/or ionic group.[5,6] Several crosslinking methods have been published for different use, since as a rule, all multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain three dimensional networks in PVA.[7] As reported earlier,[8] the poly(vinyl alcohol) (PVA)/poly(acrylic acid-*co*-maleic acid) (PAM) blended membrane was prepared and tested by pervaporation. Besides, very hydrophilic membranes for pervaporation were evaluated as polymer electrolyte membrane (PEM) in direct methanol fuel cells (DMFCs) application.[9]

Recently, DMFC using polymer electrolyte membranes have demonstrated improved performance.[10] The proton conduction through membrane is very closely associated with the water transport through the membranes. In the

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operation of PEM, membrane hydration is critical to the fuel cell performance and influences proton conductivity.[11]

The state of water in polymers such as nonfreezing bound water, freezing bound water, and free water previously suggested and was quantified by both pressure differential scanning calorimetry (DSC) and ^{1}H pulse NMR techniques.[11] In the presence of excess water, a polymer may become swollen, exhibiting major changes in its structure and mechanical properties. Yoshida *et al.*[12] reported that the structure of nonfreezing bound water changed according to the surroundings. Therefore, it is important to know the state of water in the membrane.

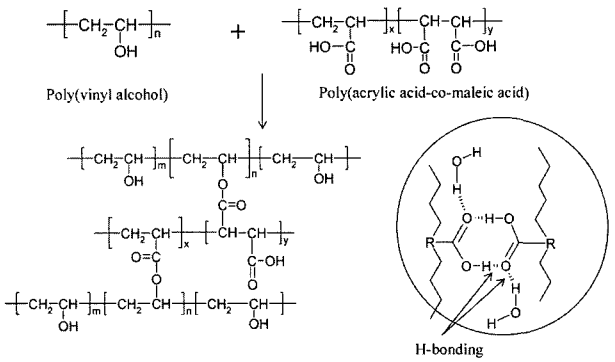
In our previous study, the crosslinked PVA/PAM membrane was prepared to investigate the pervaporation performance, and analyzed by FT-IR and water swelling test.[13] The main objective of this work was to investigate the aging effect of PVA/PAM membrane with swelling time. To do this, the introduction of carboxylic group into PVA matrix was achieved by the modification of PVA chemical structure through esterification with PAM containing carboxylic group, the PAM was used as a crosslinking agent and as a donor of the hydrophilic -COOH group. Here, we expect that the introduction of carboxylic acid group in the polymer chain helps to facilitate the conduction of proton. The structure of the membrane with swelling time is characterized by AFM, the water state and the performance of the membranes is determined by proton conductivity.

Experimental

Materials. PVA (99% hydrolyzed, average M_w = 89,000 ~98,000; Aldrich) and PAM (50 wt% solution in water, M_w = 3,000; Aldrich) used in this study were purchased from the Aldrich Chemical Co., Milwaukee, WI, USA. The water used was distilled and deionized water.

Membrane Preparation. The crosslinked PVA/PAM membranes were prepared with the following two steps. First, aqueous 10 wt% PVA solutions were prepared by dissolving pre-weighed quantities of dry PVA in water and then refluxing at 90 °C for 6 h and aqueous PAM was dissolved in water at room temperature. Then PVA solutions were mixed together with PAM solution until forming a homogeneous solution for 1 day at room temperature. The amount of PAM solution was 7% by weight to PVA solution. The mixed solution was poured onto a Plexiglass plate, and cast using the casting knife. The cast polymer solutions were allowed to dry in oven at 30 °C. The dried membranes were peeled off away from the glass plate, and then heated in a thermosetting oven at 140 °C for 1 h to induce crosslinking reaction. The membranes were immersed in water at 100 °C from 1day to 7days. The postulated reaction mechanism of PAV and PAM is illustrated in Scheme I.

Membrane Characterization. Differential scanning calorimeter (DSC) measurement was carried out using a DSC



Scheme I. Structure model of the PVA/PAM membrane and PAM cyclic dimer-water H-bonds.

2010 thermal analyzer (TA Instrument, New Castle, DE, USA) equipped with a cooling apparatus. The bound water and free water of wet sample was determined form DSC measurement. After cooling the sample with liquid nitrogen, the experiment began by heating the sample from -50 to 50 °C using a heating rate of 5 °C /min. Nitrogen was used as a carrier gas with a flow rate of 200 mL/min.

Atomic force microscopy (AFM) images were obtained in air using a Digital Instruments Nanoscope II.

Weight Change. Weight change of the membranes were carried out to investigate the aging effect of the membranes. The weight of the dry membranes was measured (W_{d1}). The membranes were immersed in water at 100 °C from 1day to 7days. The weight of dry membrane measured after drying the water immersed membrane in an oven at 90 °C (W_{d2}). The weight change of the membranes was calculated as follow:

$$\text{Weight change (\%)} = [(W_{d1} - W_{d2})/W_{d1}] \times 100 \quad (1)$$

The total water content (%) was determined by;

$$\text{Total water content (\%)} = [(W_{wet} - W_{dry})/W_{dry}] \times 100 \quad (2)$$

where W_{wet} and W_{dry} are wet and dried membrane weight after immersing in water, respectively.

IEC Value and Proton Conductivity. The ion exchange capacity (also known as IEC value) was measured using the classical titration. After immersing samples in distilled water, they were soaked in a large volume of 0.1 mol/L HCl solution to change them into the H^+ form. They were washed with distilled water to remove excess HCl, and then equilibrated with 100 mL of 0.1 mol/L NaOH solutions for 24 h. The IEC values were determined from the reduction in alkalinity measured using a back titration method. The IEC values (in meq/g) were obtained from the following equation:

$$\text{IEC} = \frac{M_{O,NaOH} - M_{E,NaOH}}{W_{dry}} \quad (3)$$

where $M_{O,NaOH}$ is milli-equivalent (meq) of NaOH in the flask before titration, $M_{E,NaOH}$ is meq of NaOH after equilibrium, and W_{dry} is the weight of dried membrane (g). The reported values were the mean of at least five measurements.

The proton conductivity of membranes was measured using the normal four-point probe technique at RH 95%. The impedance of membrane was determined using Full Material Impedance System 12608 W consisted of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 (Solatron analytical). The impedance analyzer was worked in galvanostatic mode with AC current amplitude of 0.1 mA over frequency range form 100 kHz to 0.1 Hz by Nyquist method. Each sample was cut in 4×1 cm^2 prior to mounting on the cell. The proton conductivity (σ) was obtained as follows;

$$\sigma = \frac{l}{R \cdot S} \tag{4}$$

where σ is the proton conductivity (in S/cm), l is the distance between the electrodes used to measure the potential (cm). R is the impedance of the membrane (in Ω) and S is the surface area for ion to penetrate the membrane (in cm^2). The impedance of each sample was measured five times to ensure good data reproducibility.

Results and Discussion

Swelling Test of the Membranes. Figure 1(a) shows the weight change ratio of the membranes with swelling time. As shown in Figure 1(a), the weight change ratio of the membrane increased with the swelling time. The 30 wt% weight loss of the dry membrane was observed in the swelling test for 6 days. The total water content increases with swelling time as shown in Figure 1(b). This result suggested that the unreacted polymer was released from the membrane with swelling time, and the ester bond between -OH and -COOH was partially decomposed at experimental condition such as boiling water swelling test. This made the polymer structure more loosely, and resulted in an increase in the free volume capable of containing water molecules. This behavior was confirmed with the state of water using DSC experiment, and IEC value. The prepared proton exchange membranes at each swelling test condition possessed IEC values in the range of 0.85~1.59 meq/g-dry membrane as shown in Table I. We expected that the IEC value would decrease with swelling time due to the degradation of polymer. In addition, these expectations were based on the weight change ratio of dry membrane. However, this expectation was somewhat different when compared to the results of IEC value before and after boiling water test.

The IEC value increases with swelling time up to 3day. Up to the swelling time about 3day, the IEC value maintains. This behavior was attributed to increase the ionic site due to re-forming carboxylic acid group derived from decomposing ester bond between -OH and -COOH.

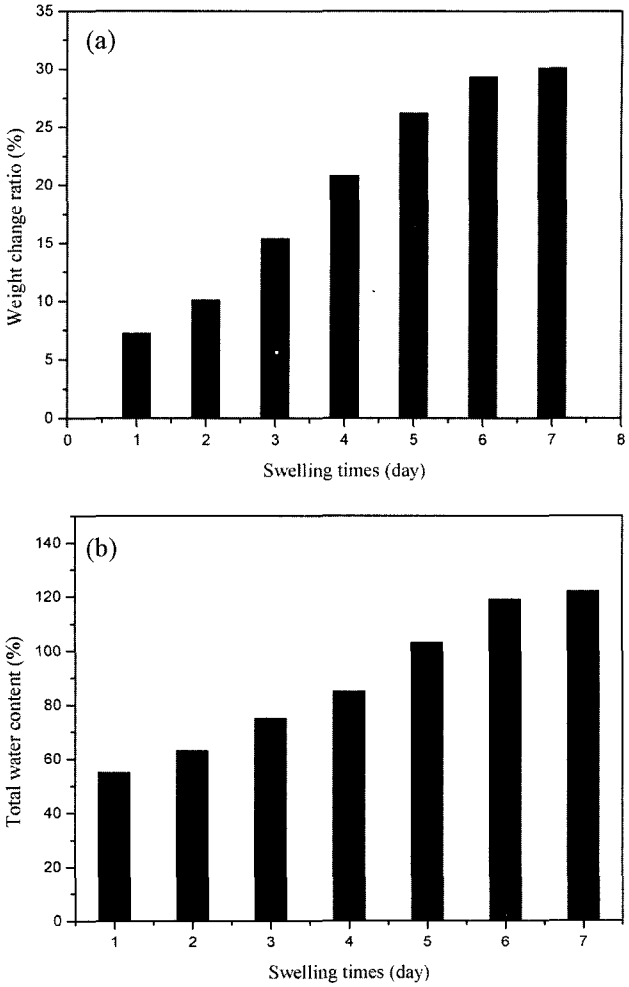


Figure 1. (a) weight change ratio and (b) total water content of the membranes with swelling time.

The states of water in the membrane can be categorized as free water, freezing bound water, and non-freezing bound water. Free water is the water that has the same phase transition temperature as bulk water (0 °C).[14] Freezing bound water is defined as the water that has phase transition temperature lower than 0 °C due to weak interaction with the polymer. Non-freezing bound water is the water that has no detectable phase transition from -73 to 0 °C due to strong interaction with the polymer.[14] The maximum volume of bound water is typically dependent on the polarity and the content of ionic group in the polymer.

In this study, DSC measurement was used to determine the amount of free water that is not bound by hydrogen bonding. Figure 2 shows the DSC curve of the water-swollen membrane. As shown in Figure 2, two melting peaks can be seen in the DSC curves for the swollen membranes up to the

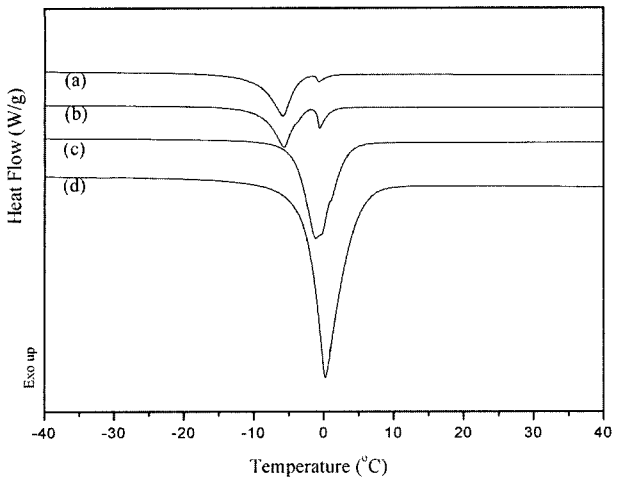


Figure 2. DSC melting curve of (a) PVA/PAM, (b) after the membrane was swelling for 3 day, (c) 4day, and (d) 7day.

swelling time of 3day. However, only one melting enthalpy peak was observed in the membrane after swelling for 4 and 7day. Therefore, in this case, we consider this peak to arise from free water. The amount of bound water was calculated as the difference between the total water content and the amount of free water.

Before a trial for the water state, we expected that the non-freezing bound water might exist because the amount of ionic group (-COOH) increased due to decomposing ester bond. In addition, these expectations were based on IEC values. However, these -COOH groups turned out to be quite insensitive to the water state. There is the H-bonding self-association in -COOH group of PAM, and cyclic dimer-water H-bonds as shown in Scheme I.[15] This result suggested that this water absorbed due to the cyclic dimer-water H-bond was detected as overlapping melting peaks due to weak interaction of H-bond, showing the melting of bulk water by DSC. Therefore, the freezing bound water peak shown in 3 day was shown in overlapping melting peak combined with free water peak after 4 days.

Table I shows the total water and the fraction of water state. The amounts of free water, freezing bound water, and non-freezing bound water were estimated using the following equation:

$$W_{free} = (\Delta H_{free}/Q_{melting}) \times W_{total,}$$
$$W_{freezing} = (\Delta H_{freezingboud}/Q_{melting}) \times W_{total} \quad (5)$$

The free water content (%) in total water was estimated as the ratio of endothermic peak area at around 0 °C for water swollen membrane to melting endothermic heat of fusion ($Q_{melting}$ = 334 J/g) for pure water.[14] Non-freezing bound water is determined by subtracting the freezing water and free water from the total water absorbed in the membrane. As shown in Table I, the non-freezing bound water increased with swelling time up to 4 day, and above this day the non-freezing bound water decreased. However, the fraction of free water dramatically increased with swelling time. This result suggests that the free volume derived from releasing unreacted polymer, and decompose ester bond was capable of containing water molecules, and these water molecules was regarded as free water.

AFM Images. Figure 3 show the surface AFM images of the PVA/PAM membranes before and after swelling test. The area of the image is 3 μm × 3 μm in the x,y-plane with an expanded z-axis. The membrane surface was dramatically changed after swelling. The swelling test increased the surface roughness from 7.41 to 15.31 Å, respectively. The different depth profile before and after swelling test was shown in Figure 3. These results suggest that the swelling test affects the surface morphology.

Proton Conductivity. To use as polymer electrolyte membrane (PEM), it is necessary to provide the facilitated channel for proton transport by providing ion exchange sites

Table I. Characterization of IEC Value and Fraction of Water State

Aging Time (day)	Iec Value (meq/g)	Total Water Content (%)	Free Water (%)	Freezing Bound Water (%)	Non-Freezing Bound Water(%)
0	0.85	55 (1)[a]	17.4 (0.32)[b]	29.4 (0.53)[c]	8.2 (0.15)[d]
1	1.45	63 (1)	21.4 (0.34)	32.9 (0.52)	8.7 (0.14)
2	1.59	75 (1)	28.2 (0.38)	37.3 (0.50)	9.5 (0.13)
3	1.54	85 (1)	32.0 (0.38)	44.2 (0.52)	8.9 (0.10)
4	1.55	103 (1)	65.8 (0.64)	-	37.2 (0.36)
5	1.57	119 (1)	88.1 (0.74)	-	30.9 (0.26)
6	1.55	122 (1)	103.0 (0.84)	-	19.0 (0.16)
7	1.57	123 (1)	103.9 (0.84)	-	19.1 (0.16)

[a-d]Fraction of water state. [a](total water,%)/(total water,%). [b](free water,%)/(total water,%). [c](freezing bound water,%)/(total water,%). [d](non-freezing bound water, %)/(total water, %).

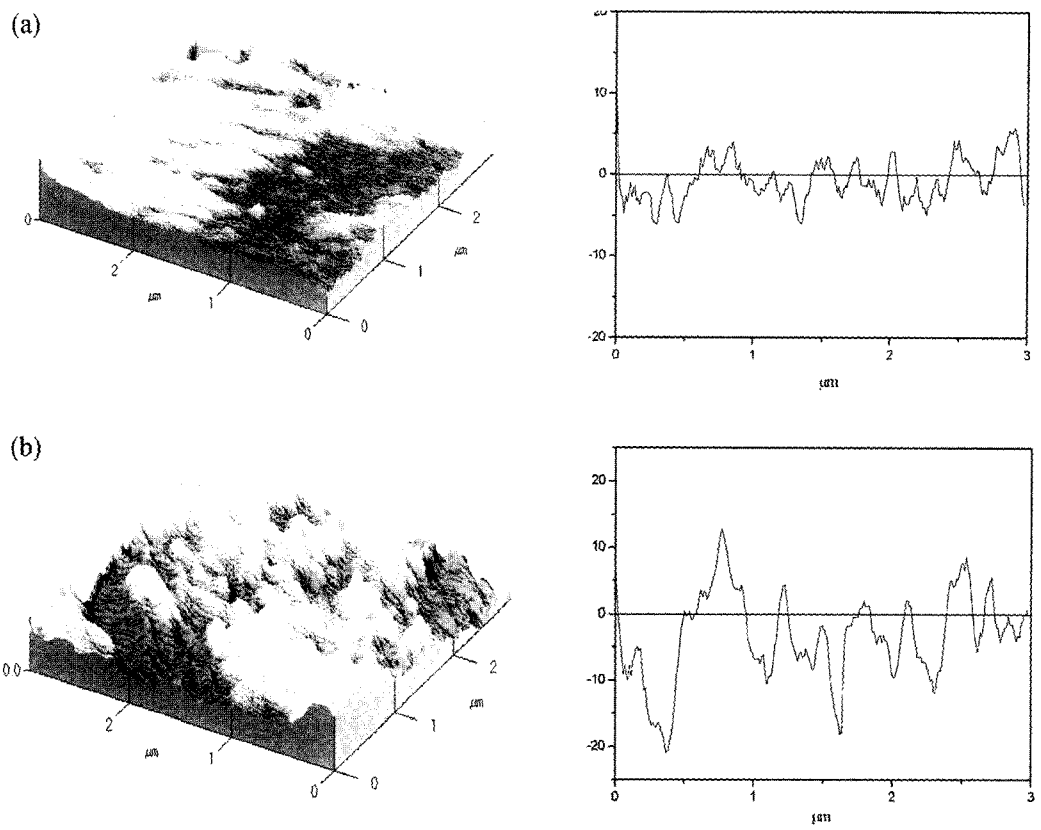


Figure 3. AFM image of (a) PVA/PAM and (b)after the membrane was swelling for 7 day.

such as sulfonic acid or carboxylic acid. In this study, the carboxylic acid groups derived from PAM were used as an ion exchange sites.

Proton conductive mechanism through these membranes is well-known to occur by two routes.[9] First of these routes is Grotthus mechanism (proton hopping) that a proton is passed down a chain of water molecules. Second of these routes is vehicle mechanism that a proton combines with solvent molecules, producing a complex like H_3O^+ or $CH_3OH_2^+$.

Generally, the proton conductivity is dependent on the state of hydration of the membrane. In a water swollen membrane, the protons are solvated and enabled to be transported through the membrane.[16] Since the conductivity in the membrane is dependent on the water content of the membrane, it is necessary to understand the water state in the membrane and how it is related to the mobility of water in the membrane.

Figure 4 shows a plot of the proton conductivity of the membranes as a function of the swelling time. The proton conductivity of the membranes measured at $T = 30$, and 50 °C was in the range of 10^{-3} - 10^{-2} S/cm, and slightly increased with swelling time, and temperature. This behavior was attributed to increase the ionic site due to decomposing ester bond, and hydration state.

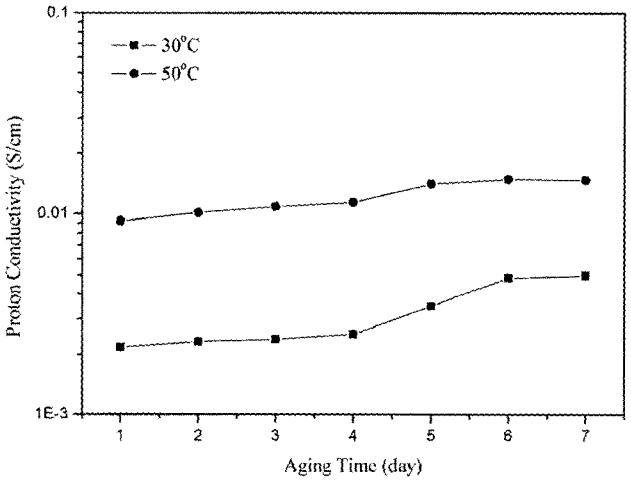


Figure 4. Proton conductivity of the PVA/PAM membranes at RH 95%.

As shown in Figure 4, the highly increase of the proton conductivity was observed from immersing in 4 days, although the IEC value didn't increase. This behavior was associated with the morphology of the membrane. We confirmed that the fraction of free water dramatically increased after 4 days of the swelling time. Therefore, the proton con-

ductivity of the PVA/PAM membrane increases with the fraction of the free water. The swelling of the membrane may provide the facilitated channel for proton transport and increase the mobility of protonic charge carriers due to remove unreacted polymer.

Therefore, it could be said that the swelling test affects the morphology, water state and proton conductivity of the membranes.

Conclusions

Crosslinked PVA/PAM membranes were prepared to investigate the aging effect with swelling time. The PAM was used as a crosslinking agent and as a donor of the hydrophilic -COOH group. The surface of the membrane was dramatically changed after swelling test. The surface roughness of the PVA/PAM membrane increased from 7.41 to 15.31 Å, as determined by AFM technique. The swelling made the polymer structure more loosely, and resulted in an increase in the free volume capable of containing free water molecules. The fraction of free water and the proton conductivity increased with swelling time. The swelling of the membrane may provide space for the transport proton and increase the mobility of protonic charge carriers. The proton conductivity of the membranes measured at $T = 30$, and 50 °C was in the range of 10^{-3} - 10^{-2} S/cm, and slightly increased with swelling time, and temperature.

Acknowldgements. This work was supported by Korea Science and Engineering Foundation (KOSEF) (No: R05-2004-000-10494-0).

References

(1) S. J. Kim, C. K. Lee, and S. I. Kim, *J. Appl. Polym. Sci.*, **92**, 1467 (2004).
(2) J. W. Rhim, S. W. Lee, and Y. K. Kim, *J. Appl. Polym. Sci.*, **85**, 1867 (2002).
(3) J. W. Rhim, C. K. Yeom, and S. W. Kim, *J. Appl. Polym. Sci.*, **68**, 1717 (1998).
(4) J. W. Rhim and Y. K. Kim, *J. Appl. Polym. Sci.*, **75**, 1699 (2000).
(5) J. F. Blanco, Q. T. Nguyen, and P. Schaetzel, *J. Membr. Sci.*, **186**, 267 (2001).
(6) H. B. Park, S. Y. Nam, J. W. Rhim, J. M. Lee, S. E. Kim, J. R. Kim, and Y. M. Lee, *J. Appl. Polym. Sci.*, **86**, 2611 (2002).
(7) M. Krumova, D. Lopez, R. Benavente, C. Mijangos, and J. M. Perena, *Polymer*, **41**, 9265 (2000).
(8) C. Vauclair, P. Schaetzel, R. Nobrega, and C. Habert, *J. Appl. Polym. Sci.*, **86**, 1709 (2002).
(9) B. S. Pivovar, Y. Wang, and E. L. Cussler, *J. Membr. Sci.*, **154**, 155 (1999).
(10) X. Ren, T. E. Springer, and S. Gottesfeld, *J. The Electro. Soci.*, **147**, 92 (2000).
(11) Y. S. Kim, L. Dong, M. A. Hickner, T. E. Glass, V. Webb, and J. E. McGrath, *Macromolecules*, **36**, 6281 (2003).
(12) T. Yoshida, M. Takahashi, T. Hatakeyama, and H. Hatakeyama, *Polymer*, **39**, 1119 (1998).
(13) S. Y. Nam, K. S. Sung, S. W. Chon, and J. W. Rhim, *Membr. J.*, **12**, 255 (2002).
(14) A. Higuchi and T. Iijima, *Polymer*, **26**, 1207 (1985).
(15) L. Daniliuc and C. David, *Polymer*, **37**, 5219 (1996).
(16) S. Hietala, S. L. Maunu, F. Sundholm, T. Lehtinen, and G. Sundholm, *J. Polym. Sci. Part B.*, **37**, 2893 (1999).