

# Characterization of Semi-Interpenetrating Polymer Network Polystyrene Cation-Exchange Membranes

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**ABSTRACT:** Polystyrene cation exchange membranes were prepared by a PVC-based semi-interpenetrating polymer network (IPN) method. The reaction behaviors during polymerization and sulfonation in the preparation method were investigated. The prepared membranes were characterized in terms of the physical and electrochemical properties. The membranes exhibited reasonable mechanical properties (tensile strength, 13 MPa, and elongation at break, 52%) for an ion-exchange membrane with the ratio of polystyrene-divinylbenzene (DVB)/poly(vinyl chloride) (PVC) ( $R_{\text{St-DVB/PVC}}$ ) of below 0.9. Fourier transform infrared/attenuated total reflectance, differential scanning calorimetry, and scanning electron microscopy studies revealed the for-

mation of a homogeneous membrane. The resulting membrane showed membrane electrical resistance of  $2.0 \Omega \text{ cm}^2$  and ion-exchange capacity of 3.0 meq/g dry membrane. The current-voltage (I-V) curves of the membrane show that the semi-IPN polystyrene membranes can be properly used at a high current density, and that the distribution of cation-exchange sites in the membrane was more homogenous than that in commercial membranes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1488–1496, 2003

**Key words:** polystyrene; cation-exchange membrane; characterization; interpenetrating network

## INTRODUCTION

Ion exchange membranes have been widely used in electrodialysis for desalination of brackish water, production of table salt, recovery of valuable metals from effluents in the metal-plating industry, and other purposes.<sup>1–7</sup> Since Juda reported a synthetic ion-exchange membrane,<sup>8</sup> a number of studies have been carried out on synthesis of ion-exchange membranes.<sup>1–7</sup> In general, an excellent ion-exchange membrane should have high chemical and mechanical stability with favorable electrochemical properties such as low electrical resistance and high ion-permselectivity.<sup>9</sup> To obtain the desired properties of ion-exchange membranes, many preparation methods have been practiced.

To date, styrene (St)-divinylbenzene (DVB) copolymer and its derivatives have been used as base materials in the preparation of ion-exchange membranes because of their good workability and mechanical strength.<sup>10–15</sup> Styrene-based preparation methods are typically grouped into four categories: bulk polymerization,<sup>15</sup> latex,<sup>16</sup> polymer blending,<sup>17</sup> and paste methods.<sup>18</sup> Among these, the polymer blending and paste

methods have been frequently applied to academic research and commercial production because the processes are relatively simple, and the resulting membranes exhibit good permselectivity and mechanical strength.<sup>14</sup>

Even though the polymer blending has been of considerable interest as a simple route for attaining the properties required, the challenge confronting their development has been related to the thermodynamics of the system, including immiscibility. Studies have been performed to enhance the miscibility of polymer blends through the incorporation of local centers capable of participating in strong interaction such as hydrogen bonding, dipole-dipole interaction, ion-dipole interaction, and charge-transfer complexation.<sup>17</sup> In spite of such efforts, the polymer blending is applied to a limited number of ion-exchange membranes because the properties of ion exchange membranes depend considerably on the miscibility.

Meanwhile, the paste method has been more popularly applied to the preparation of ion-exchange membranes because the resulting membrane exhibits high permselectivity and good mechanical strength.<sup>14</sup> However, the paste method is somewhat complicated because the poly(vinyl chloride) (PVC) powder is used during the preparation process, resulting in increased processing cost. To overcome the drawbacks of the preparation method described above, we proposed the sorption method with a concept of interpenetrating polymer network (IPN) for preparing a cation-

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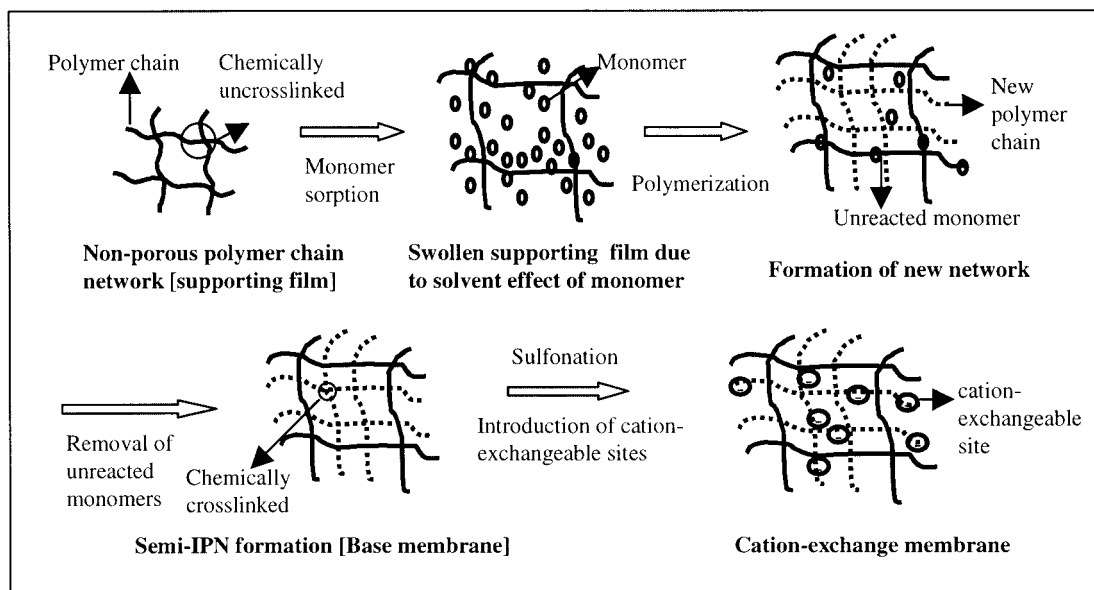


Figure 1 Concept of the proposed preparation method.

exchange membrane by absorbing monomer solution into supporting material (i.e., PVC film).<sup>19</sup>

The concept of the sorption method is schematically illustrated in Figure 1. The nonporous supporting material is swollen while the monomers are absorbed in the base material. The monomer-absorbed PVC film permits enlarged free volume due to the solvent effect. When the temperature is increased to the decomposition temperature of initiator [e.g., benzoyl peroxide (BPO)], the monomers can be polymerized in the free volume of PVC film. Physical network structures are formed between the propagated St-DVB polymer chains and the polymer chains of the supporting material, as St-DVB monomers are polymerized. Two polymers—poly(styrene-DVB) and PVC—become miscible according to the concept of a semi-IPN.<sup>20</sup> Here, the membrane morphology and mechanical property can be controlled by the polymerization time and cation-exchangeable sites introduced to the base membrane by a general sulfonation process. The re-

sulting membrane exhibited reasonable mechanical and chemical properties. The sorption method includes polymerization within the PVC matrix followed by functionalization and electrochemical characterization of the resulting membrane is needed to be used as ion exchange membrane.

This article presents reaction behaviors during polymerization and sulfonation in the sorption method, and physical and electrochemical characteristics of the membrane prepared accordingly.

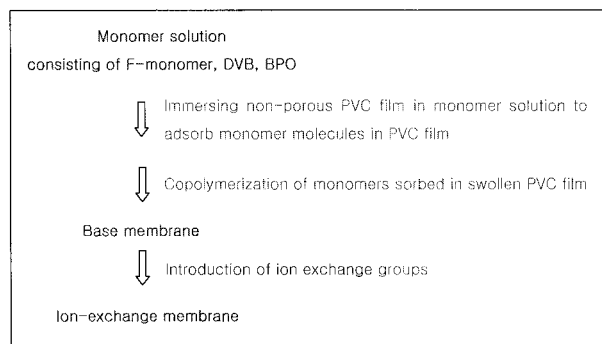
## EXPERIMENTAL

### Materials

PVC film supplied by LG Chem. Co. (Seoul, Korea) with a thickness of 100  $\mu\text{m}$  was used as supporting material. Styrene (St, Kanto Chem., Tokyo, Japan) and DVB (Aldrich, Milwaukee, WI) were purified to remove inhibitors by treating with 10 wt % of aqueous

TABLE I  
Specification of Selected Commercial Membranes<sup>21,22</sup>

Membrane	CMX	CMB	HQC
Type	Strongly acidic cation permeable (sulfonic acid group)	Strongly acidic cation permeable (sulfonic acid group)	Strongly acidic cation permeable (sulfonic acid group)
Characteristics	High mechanical strength Reinforcing material	High mechanical strength Excellent chemical resistance	Heterogeneous type Polyethylene (Reinforcing material)
Electric resistance ( $\Omega \text{ cm}^2$ )	2.5–3.5	3.0–5.0	4.0–5.0
Ion-exchange capacity (meq/g)	1.5–1.8	1.4–1.7	2.0 $\leq$
Transport number for $\text{Na}^+$ (—)	0.98<	0.98<	0.90 $\leq$
Manufacturer	Tokuyama Corp. (Japan)	Tokuyama Corp. (Japan)	Hangzhou Qianqiu Chemical (China)



**Figure 2** Procedure of membrane preparation.

sodium hydroxide and then washed with water. After drying with anhydrous calcium sulfate overnight, they were fractionally vaporized under vacuum condition. BPO (Fluka, Buchs, Switzerland) was purified by recrystallizing in a methanol/water mixture at  $-5^{\circ}\text{C}$ . Chlorosulfonic acid (98%, Across Organics, Geel, Belgium) and concentrated sulfuric acid were used as sulfonation reagents as received.

Three commercial cation-exchange membranes, Neosepta<sup>®</sup> CMX and CMB membranes (Tokuyama Co., Tokuyama, Japan), and a heterogeneous type of cation exchange membrane, code-named HQC (Hagzhou Qianqiu Chemical, Hagzhou, China), were examined to compare with the membrane prepared in this study. The properties of these membranes are listed in Table I.

### Membrane preparation

The preparation procedure is summarized in Figure 2. Monomer solutions consisting of St, DVB, and BPO were prepared with various contents of DVB and BPO. Membranes prepared are listed in Table II with their composition and given individual names. PVC film was immersed in monomer solution and maintained at room temperature for 3 h for the monomers to be absorbed into the PVC film. After the PVC film was

swollen, it was placed between glass plates and sealed with aluminum foil and polypropylene tape to prevent evaporation of the monomer. Polymerization was carried out in an oven at  $80^{\circ}\text{C}$  for 0.5–10 h. The film was then dried at room temperature for 24 h to evaporate unreacted monomers. The resulting membrane was immersed in a 1:1 mixture of concentrated sulfuric and chlorosulfonic acids for 5–100 min at  $50^{\circ}\text{C}$  for sulfonation, followed by sequential treatments in 98% sulfuric acid, 80% sulfuric acid, 40% sulfuric acid, and pure water. The membrane was then immersed in aqueous 2.5N sodium hydroxide for 2 h at room temperature to hydrolyze the remaining sulfonyl chloride to sulfonate groups.

### Fourier transform infrared, gel permeation chromatography, differential scanning calorimeter, and scanning electron microscopy

The polymerized state of the prepared membrane was confirmed by Fourier transform infrared/attenuated total reflectance (FTIR/ATR) (460 plus, Jasco, Tokyo, Japan). For the samples without crosslinking—Mem.1, Mem.2, and Mem.4—the molecular weight of polystyrenes in all unsulfonated membranes were measured by using benzene as solvent. One gram of each membrane was immersed in 50 mL of benzene, and then it was stirred at room temperature for 24 h. Polystyrene was extracted from an unsulfonated membrane and dissolved in benzene. The benzene was removed from the polystyrene solution by suction overnight at room temperature. Twenty milligrams of polystyrene were dissolved in 10 mL of tetrahydrofuran (THF) and the molecular weight was measured by gel permeation chromatography (GPC).

The behavior of the glass transition temperature ( $T_g$ ) for the St-based PVC indicates the miscibility between the PVC and polystyrene.<sup>19</sup> The  $T_g$  values were calorimetrically determined by a Perkin-Elmer DSC-1B apparatus at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . Morphological observations of the prepared membranes were

**TABLE II**  
Semi-IPN Cation-Exchange Membranes Prepared in This Study

Unsulfonated membranes					
	St/DVB (wt %)	Polymerization time (h)	$R_{\text{St/PVC}}$ (—)		BPO addition
Mem.1	100/0	3	0.10		
Mem.2	100/0	5	0.40		0.01 part/one part of monomers
Mem.3	100/0	7	0.71		
Mem.4	100/0	8	0.83		
Sulfonated membranes (variation in DVB content)					
	St/DVB (wt %)	Polymerization time (h)	$R_{\text{St-DVB/PVC}}$ (—)	Sulfonation time (min)	BPO addition
Mem.5	99/1		0.70	60	
Mem.6	95/5	5–7	0.72	60	0.01 part/one part of monomers
Mem.7	90/10		0.69	60	

performed by a FE-SEM (field emission-scanning electron microscopy, S-4700, Hitachi, Tokyo, Japan) after the sample was mounted on a stub and coated with gold using an ion coater.

### Mechanical testing

The tensile strength and elongations at the break of wet membranes were measured according to ASTM method D-882-79 with the Instron model 5567 universal testing machine. A crosshead speed was 0.5 cm min<sup>-1</sup>, and 2 × 5 cm<sup>2</sup> dumbbells were tested in a flat-faced grip, set 2 cm apart initially.

### Measurement of water content

To measure the water-swelling properties, the samples were soaked in distilled water for 24 h, removed from the water with a filter paper, and immediately weighed. The samples were dried under vacuum at 60°C until a constant weight. The water content ( $W_C$ ) was calculated by the following equation:

$$W_C = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (1)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the wet and dried membrane weights, respectively.

### Measurement of ion-exchange capacity

After rinsing in pure water for one day, a membrane sample was soaked in a large volume of 1N HCl for one day to obtain the membrane in the H<sup>+</sup>-form. The excess HCl in the membrane was removed by washing with distilled water repeatedly. The membrane was then equilibrated with 50 mL of 0.01N NaOH for 24 h. The IEC was determined from the reduction in alkalinity determined by back titration. The alkalinity was measured by titration with 0.01N HCl. The membranes (of Na<sup>+</sup>-form) were dried at 60°C under vacuum until a constant weight was obtained. The ion-exchange capacity (IEC) of the cation exchange membrane was calculated from the following equation:

$$\text{IEC} = (M_{\text{O,NaOH}} - M_{\text{E,NaOH}}) / W \quad (2)$$

where  $M_{\text{O,NaOH}}$  is the initial milliequivalent of NaOH in the flask,  $M_{\text{E, NaOH}}$  the milliequivalent of NaOH after equilibrium, and  $W$  the weight of dry membrane in grams.

### Measurement of membrane electrical resistance

The membrane electrical resistances (MER) were determined using a lab-made clip cell and LCZ meter.

The samples were immersed in 0.5M NaCl solution at 25°C for one day to convert to the Na<sup>+</sup>-form completely. They were then inserted into the clip cell and alternating current was applied to the cell. A 2321 LCZ meter (NF Electronic Instruments, Yokohama, Japan) was used to measure the resistance at a frequency of 100 kHz. The magnitude of impedance,  $|Z|$ , and the phase angle of impedance ( $\theta$ ) were converted into the MER ( $\Omega$  cm<sup>2</sup>) by the following equation<sup>23</sup>:

$$\text{MER} = (|Z|_{\text{sample}} \cdot \cos \theta_{\text{sample}} - |Z|_{\text{blank}} \cdot \cos \theta_{\text{blank}}) \times \text{area} \quad (3)$$

### Measurement of transport numbers

The apparent transport number of the counter ion in the membranes was determined by the electromotive force (EMF) method using Ag/AgCl electrodes. To ignore the effects of ionic strength on the activity coefficient of the electrolyte, dilute solutions (0.001 and 0.005M) of NaCl were used. The transport number,  $\bar{t}_+$ , for each membrane was calculated by the following equation<sup>24</sup>:

$$E_m = \frac{RT}{F} (2\bar{t}_+ - 1) \ln \frac{C_1}{C_2} \quad (4)$$

where  $R$  is the universal gas constant,  $F$  the Faraday constant,  $T$  the absolute temperature,  $E_m$  the membrane potential, and  $C_1$  and  $C_2$  the electrolyte concentrations in both compartments. All the experiments were performed at room temperature.

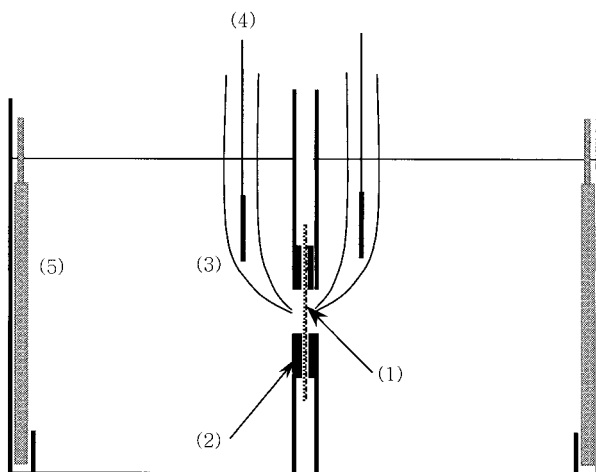
### Current-voltage experiments

Current-voltage (I-V) experiments were performed in a conventional two-compartment cell as shown in Figure 3. The electro-dialytic cell was composed of two compartments of equal volume (230 cm<sup>3</sup>). The membrane was placed in a circular hole between the compartments. The effective area of the membrane was 0.785 cm<sup>2</sup>. The potential difference across the membrane was measured as a function of current density by using two Ag/AgCl electrodes immersed into Luggin capillaries. The electrical current was supplied by a potentiostat/galvanostat (PGSTAT 30, AutoLab, Utrecht, Netherlands) connected to a pair of Ag/AgCl electrode plates at a current scanning rate of 1  $\mu\text{A s}^{-1}$ . To minimize the water dissociation reactions at the electrodes, which may change the composition of electrolytes in the compartment, two Ag/AgCl electrodes were used. All the experiments were repeated several times to ensure the reproducibility.

## RESULTS AND DISCUSSION

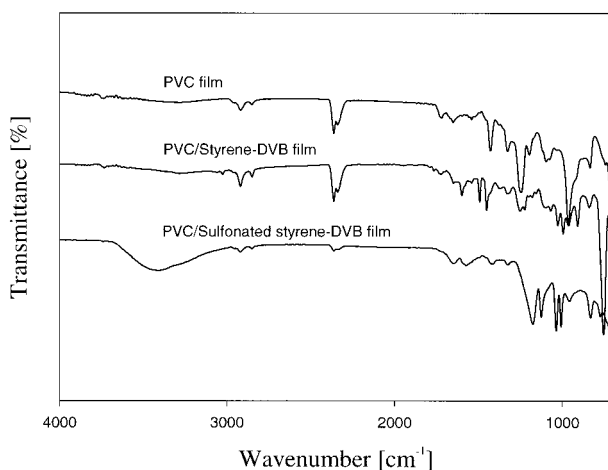
### Fourier transform infrared

Membranes with a thickness of 120–200  $\mu\text{m}$  were prepared, showing reasonable flexibility and strength.

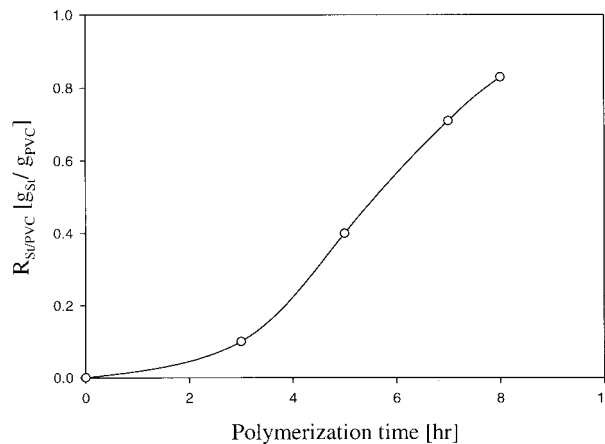


**Figure 3** Schematic diagram of two-compartment electrolytic cell used in the I-V experiment: (1) membrane (effective area: 0.785 cm<sup>2</sup>); (2) gasket (silicon rubber); (3) Luggin capillary (filled with concentrated KCl); (4) Ag/AgCl wire; (5) Ag/AgCl plate (cathode/anode).

The FTIR spectra of the cation-exchange membranes are presented in Figure 4. In the base membrane, the absorption band assigned to the aromatic group was observed at 1600 and 1490 cm<sup>-1</sup>. It indicates that styrene and DVB were introduced to the PVC film. In the sulfonated membrane, the absorption band assigned to sulfonic acid groups were observed at 1123 and 1003 cm<sup>-1</sup>, and the spectra for S=O stretching vibration was observed at 1369 and 1163 cm<sup>-1</sup>. They also indicate that the sulfonic group was introduced into the base membrane through the sulfonation reaction. All FTIR/ATR spectra show that the cation exchange membrane was successfully prepared according to the sorption method.



**Figure 4** FTIR spectrum of PVC, St-DVB/PVC membrane, and sulfonated St-DVB/PVC membranes.



**Figure 5** Relationship between  $R_{St/PVC}$  and reaction time in the preparation of styrene-based membrane.

#### Behaviors of $R_{St/PVC}$ and $T_g$ as a function of time

Figure 5 shows the ratio of polystyrene to PVC ( $R_{St/PVC}$ ) as a function of reaction time.  $R_{St/PVC}$  was defined as follows:

$$R_{St/PVC} = g_{st} (\text{gram of styrene}) / g_{pvc} (\text{gram of PVC film}) \quad (5)$$

The  $R_{St/PVC}$  increased with increasing reaction time. Meanwhile, it was confirmed in a previous study through differential scanning calorimetry (DSC) that the resulting membrane was homogeneously manufactured according to the sorption method.<sup>19</sup> In this study, the relationship between  $R_{St/PVC}$  and  $T_g$  was examined from theoretical and experimental  $T_g$  values. Theoretical  $T_g$  values were calculated by the plasticizer equation of the polymer. The glass transition temperature of the plasticized polymer is given by

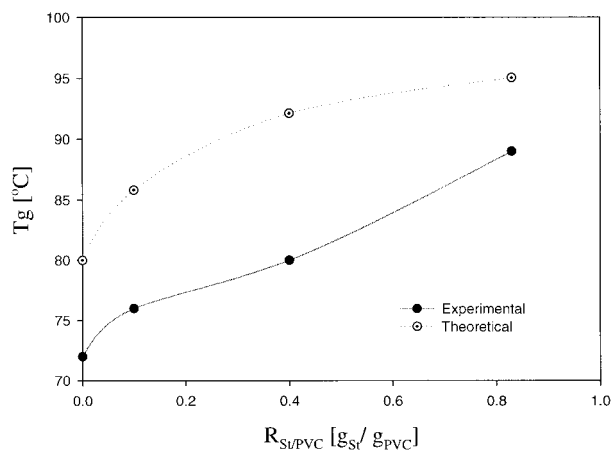
$$T_g = (Kw_{st}T_{g,st} + w_{pvc}T_{g,pvc}) / (Kw_{st} + w_{pvc}) \quad (6)$$

where  $T_{g,st}$  and  $T_{g,pvc}$  are the glass transition temperatures of styrene polymer and PVC polymer, respectively, and  $w_{st}$  and  $w_{pvc}$  are the weight fractions of styrene polymer and PVC polymer, respectively ( $w_{st} + w_{pvc} = 1$ ).  $K$  is a constant given by

$$K = (\alpha_r - \alpha_g)_{pvc} / (\alpha_r - \alpha_g)_{st} \quad (7)$$

where  $\alpha_{st}$  and  $\alpha_{pvc}$  are the thermal expansion coefficients of the styrene polymer and PVC polymer, respectively. The subscript,  $r$ , and the subscript,  $g$ , refer to the rubbery and the glass states, respectively. In this study  $w_{st}$  and  $w_{pvc}$  were calculated from the  $R_{St/PVC}$  obtained in this study and the  $K$  value was obtained from the literature.<sup>25</sup>

Figure 6 shows that the increase in  $R_{St/PVC}$  led to an increase in  $T_g$ . Increasing  $R_{St/PVC}$  implies increasing



**Figure 6** Relationship between  $R_{St/PVC}$  and  $T_g$ .

polystyrene according to the definition of  $R_{St/PVC}$ . Accordingly, the  $T_g$  of the prepared membrane approached that of the styrene polymer as the weight fraction of the styrene polymer increased. Hence, the increase in  $R_{St/PVC}$  resulted in an increased  $T_g$  because the  $T_g$  of the styrene polymer (around 100°C) was higher than that of PVC (around 80°C).<sup>26</sup> However, the experimental value was somewhat lower than the theoretical value because the plasticizer included in the PVC film decreased the  $T_g$  of the prepared membranes.

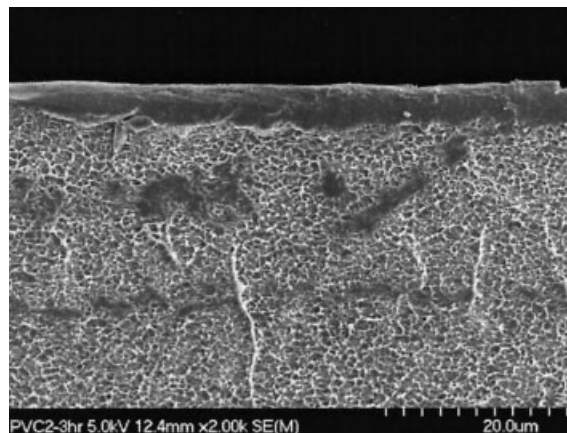
#### Field emission-scanning electron microscopy

Morphology of the prepared membrane was examined by FE-SEM. Figure 7 shows the FE-SEM image of the prepared membrane in cross-section at different reaction times. The membrane morphology gradually changed to a more dense structure with the reaction time. Droplets that indicate the presence of semi-compatible polymer blends and copolymers were not found in the FE-SEM image, whereas droplets were found in the ion-exchange membrane prepared by the paste method.<sup>14</sup> This result indicates that the membrane prepared in this study was more homogeneous than that manufactured by the paste method. The result agreed well with DSC result of the previous study.<sup>19</sup>

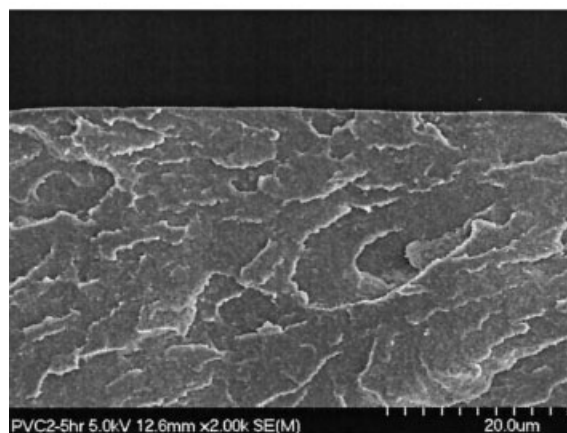
#### Mechanical property

Figure 8 shows the mechanical behavior of the unsulfonated membranes (i.e., Mem.1, Mem.2, and Mem.4) as a function of polymerization time. Elongation of the PVC film was improved with the increasing polystyrene content, although tensile strength decreased. Considering that the ion-exchange membrane processes are driven by electrochemical driving force rather than mechanical pressure, the elongation property might be more important than the tensile

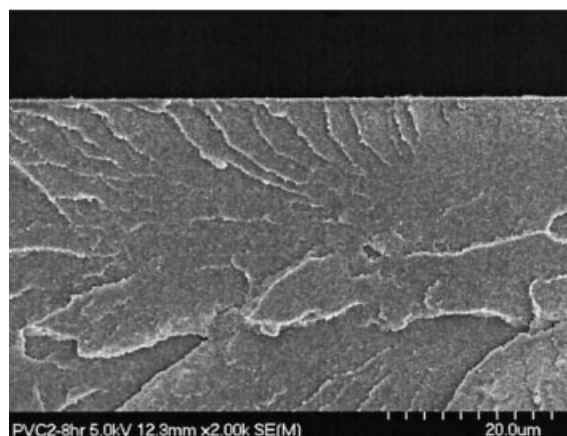
strength. Table III shows the comparison of commercial membrane, CMX, with the cation-exchange membrane prepared in this study. The elongation of the membrane was improved significantly compared to



(a)

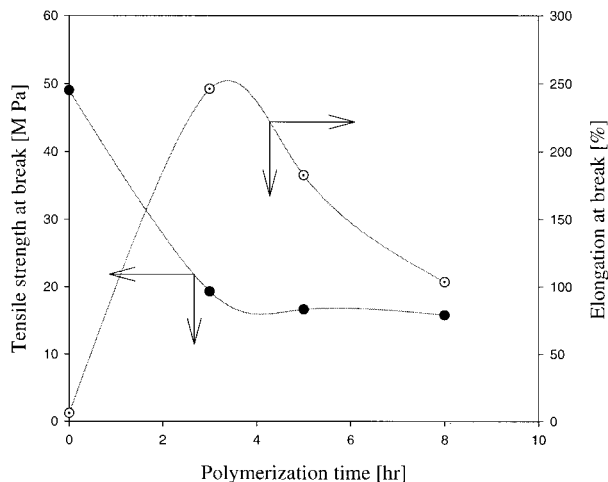


(b)

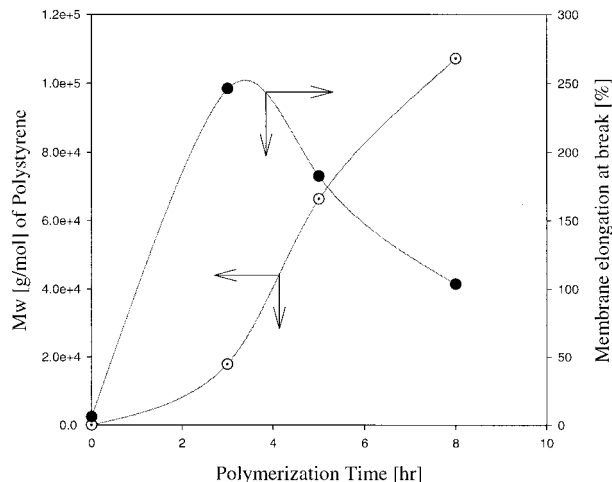


(c)

**Figure 7** FE-SEM image of the styrene-based membranes—Mem.1, Mem.2, and Mem.4—on cross-section: (a) reaction time 3 h; (b) reaction time 5 h; (c) reaction time 8 h.



**Figure 8** Mechanical behaviors of the styrene-based membranes—Mem.1, Mem.2, and Mem.4—as a function of polymerization time.



**Figure 9** Relationship between the molecular weight and elongation in the styrene-based membranes—Mem.1, Mem.2, and Mem.4—as a function of reaction time.

the commercial membrane, although the tensile strength of the membrane was lower than a commercial membrane.

**Relationship between molecular weight of polystyrene and membrane elongation**

Figure 9 shows the molecular weight and elongation of Mem.1, Mem.2, and Mem.4 as a function of reaction time. The increasing polystyrene molecular weight in the membrane caused to decrease elongation of the membrane. An explanation for this would be that the low molecular weight polystyrene acted as a plasticizer in the PVC film.

**Estimation of sulfonation conversion through IEC**

Sulfonation conversion was estimated by comparing the theoretical IEC with the experimental IEC as a function of time. Sulfonation conversion was defined as follows:

$$\text{Conversion [\%]} = [\text{Experimental IEC} / \text{Theoretical IEC}] \times 100 \quad (8)$$

$$\text{Theoretical IEC} = A[R_{\text{St/PVC}}M_{w,\text{sst}}/M_{w,\text{st}}] / [1 + (R_{\text{St/PVC}}M_{w,\text{sst}}/M_{w,\text{st}})] \quad (9)$$

**TABLE III**  
Comparison of Commercial Membrane with Cation-Exchange Membrane Prepared on the Mechanical Properties

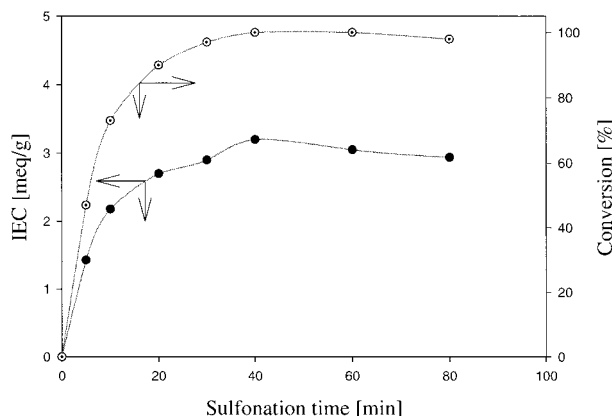
Membrane	Tensile strength (MPa)	Elongation at break (%)
CMX	29	15
Mem.5	13	52

where *A* is the maximum theoretical IEC (5.43 meq/g), *R<sub>St/PVC</sub>* the ratio of polystyrene to PVC (grams of styrene polymer/grams of PVC), *M<sub>w,sst</sub>* the molecular weight of sulfonated styrene, and *M<sub>w,st</sub>* the molecular weight of styrene.

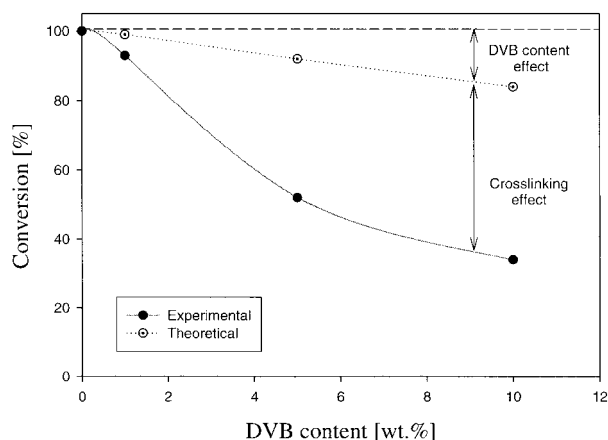
Figure 10 shows the IEC and the conversion as a function of a sulfonation time for Mem.3. The IEC and conversion increased as the sulfonation reaction proceeded. Complete sulfonation conversion was achieved at 40 min, demonstrating that the IEC could be easily controlled by the sulfonation time.

**Effect of crosslinking during the sulfonation reaction**

To investigate the effect of crosslinking on the sulfonation reaction, membranes were prepared by varying the content of DVB. Unsulfonated membranes having a *R<sub>St-DVB/PVC</sub>* of 0.7 were sulfonated for 60 min. Since the increasing DVB content increases the crosslinking



**Figure 10** Change in IEC and conversion (in the case of *R<sub>St/PVC</sub>* = 0.7) as a function of sulfonation time.



**Figure 11** Relationship between the content of DVB and conversion rate.

degree during the membrane preparation, the efficiency of conversion might be affected by two factors: nonsulfonated DVB and the crosslinking degree. To explain the effects of the two factors separately, theoretical conversion rates were estimated with two assumptions: (1) the composition ratio (St/DVB) before polymerization is equal to that after polymerization. (2) DVB is not sulfonated by the sulfonation reagent. The sulfonation conversion is defined as follows:

$$\begin{aligned} \text{Theoretical sulfonation conversion with DBV [\%]} \\ = [\text{Theoretical IEC with DBV} \div \\ \text{Theoretical IEC without DBV}] \times 100 \quad (10) \end{aligned}$$

$$\begin{aligned} \text{Theoretical IEC without DVB} \\ = \frac{A[R_{\text{St/PVC}}M_{w,\text{sst}}/M_{w,\text{st}}]}{[1 + (R_{\text{St/PVC}}M_{w,\text{sst}}/M_{w,\text{st}})]} \quad (11) \end{aligned}$$

$$\begin{aligned} \text{Theoretical IEC with DVB} \\ = \frac{A[R_{\text{St-DVB/PVC}}M_{w,\text{sst}}/M_{w,\text{st}}]}{[1 + (R_{\text{St-DVB/PVC}}w_{\text{st}}(M_{w,\text{sst}}/M_{w,\text{st}}) + R_{\text{St-DVB/PVC}}w_{\text{DVB}})]} \quad (12) \end{aligned}$$

$$\begin{aligned} \text{Experimental sulfonation conversion with DVB [\%]} \\ = [\text{Experimental IEC with DVB} \div \\ \text{Theoretical IEC without DVB}] \times 100 \quad (13) \end{aligned}$$

where  $A$  is the theoretical IEC (5.43 meq/g),  $R_{\text{St-DVB/PVC}}$  is the ratio of polystyrene–DVB to PVC (grams of styrene–DVB polymer/grams of PVC),  $M_{w,\text{sst}}$  is the molecular weight of sulfonated styrene,  $M_{w,\text{st}}$  is the molecular weight of styrene, and  $w_{\text{st}}$  and  $w_{\text{DVB}}$  are the weight fractions of styrene and DVB before polymerization, respectively.

Figure 11 shows the relationship between the DVB

**TABLE IV**  
Comparison Between Prepared (Mem.5) and Several Commercial Cation-Exchange Membranes on the General Properties

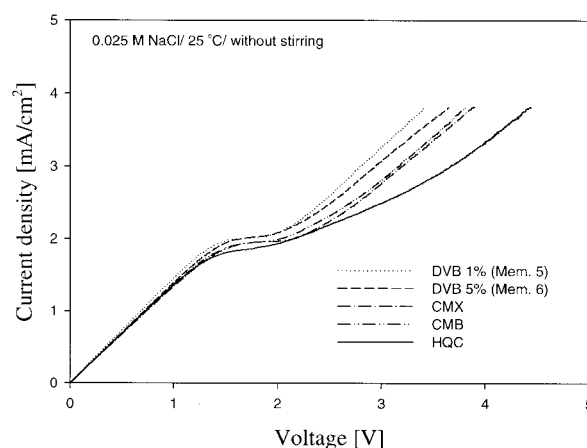
Membranes	Mem.5	CMX	CMB	HQC
Water content, $W_c$ (—)	0.38	0.27	0.43	0.45
Ion exchange capacity (meq/g)	2.44	1.67	3.11	1.79
Electrical resistance ( $\Omega \text{ cm}^2$ )	2.11	2.98	3.42	4.69
Transport no. (—)	0.998	0.987	0.980	0.915

content and the sulfonation conversion. The experimental values were much lower than the theoretical values. It could be interpreted that the sulfonation conversion was governed more dominantly by crosslinking than by the DVB content itself. Such phenomenon indicates that crosslinked polystyrene prevent sulfonation reagents from penetrating into the base membrane because of its dense structure.

#### Electrochemical characterization

Table IV shows the properties for the sulfonated membrane (i.e. Mem.5) and commercial membranes, i.e., CMX, CMB, and HQC. The polystyrene membrane with 1% DVB exhibited the ion-exchange capacity, electrical resistance, and transport number, comparable to those of commercial membranes.

Figure 12 shows the I–V characteristics of the membranes prepared in this study, i.e., Mem.5 and Mem.6, and commercial membrane, i.e., CMX, CMB, and HQC. As shown in the figure, all the curves show the typical three characteristic regions. The slopes in the I–V curve give useful information on the ion transport under and over the limiting current density (LCD). The characteristic values of the curves are summarized in Table V. The electrical resistances of the first region ( $R_{1st}$ ) are strongly dependent on the intrinsic membrane resistance. The  $R_{1st}$  values of the mem-



**Figure 12** I–V curves of Mem.5, Mem.6, CMX, XMB, and HQC.



TABLE V  
Characteristic Values of I-V Curves

Membranes	Mem.5	Mem.6	CMX	CMB	HQC
$R_{1st} \times 10^{-3}$ ( $\Omega \text{ cm}^2$ )	694.93	719.99	732.89	733.25	733.43
$R_{3rd} \times 10^{-3}$ ( $\Omega \text{ cm}^2$ )	754.15	807.75	824.14	825.01	875.12
$R_{3rd}/R_{1st}$ (—)	1.09	1.12	1.12	1.13	1.19
$\Delta V$ (V)	0.73	0.74	0.89	0.95	0.95
LCD ( $\text{mA cm}^{-2}$ )	1.97	1.97	1.94	1.91	1.70

branes prepared were somewhat lower than those of the commercial membranes and this is in accordance with the result of MERs. Choi et al. analyzed the I-V curves of cation-exchange membranes in various electrolyte solutions.<sup>27</sup> They suggested that the  $R_{3rd}/R_{1st}$  (the resistance ratio) and  $\Delta V$  (the plateau length) values of I-V curves result from the electroconvective effects over the LCD. Namely, the lower  $R_{3rd}/R_{1st}$  and the shorter  $\Delta V$  indicate the more active electroconvective effect. Since these parameters are directly related to the power consumption in operation at a current density over the LCD, they are important electrochemical properties of the ion-exchange membrane. The prepared membranes exhibited lower  $R_{3rd}/R_{1st}$  and  $\Delta V$  values than the commercial membranes. This result implies that the present membranes can be properly used at a high current density. In addition, the superficial LCD values of the present membranes were slightly higher than those of the commercial membranes. The result indicates that the higher portion of nonconducting area exists in the commercial membranes.<sup>24</sup> Namely, it seems that the addition of PVC powder increases the fraction of nonconducting region in the paste method. These results suggest that the distribution of cation-exchange sites of the membrane prepared in this study was more homogenous than those of the commercial membranes prepared by paste methods.

## CONCLUSIONS

Polystyrene cation exchange membranes were prepared by a PVC-based semi-IPN method. Within the PVC polymer network, polymerization and sulfonation reactions occurred to form an ion exchange membrane. The membranes prepared were characterized in terms of physical and electrochemical properties. The membranes exhibited reasonable mechanical properties for an ion-exchange membrane. FTIR/ATR, DSC, and SEM studies revealed the formation of a homogeneous membrane. The resulting membrane exhibited a low membrane electrical resistance ( $<2.0 \Omega \text{ cm}^2$ ) and a reasonable ion-exchange capacity (3.0 meq/g dry membrane). The I-V curves of the membrane indicate that the semi-IPN polystyrene membranes can properly be used at a high current density. This study demonstrates that a semi-IPN method can

be used to prepare a homogenous ion-exchange membrane with high compatibility between PVC and polystyrene.

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