Synthesis and Characterization of Cation-Exchange Membrane Based on Sulfonated Sty/HEA/LMA Terpolymer

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ABSTRACT: A cation-exchange membrane based on a styrene/hydroxyethyl acrylate/lauryl methacrylate (Sty/HEA/LMA) terpolymer was prepared via a postsulfonation reaction for various sulfonation times. Sulfonic groups were introduced into the membrane structure with sulfuric acid as the sulfonating agent and silver sulfate as an initiator in a nitrogen atmosphere. Sulfonated Sty/HEA/LMA terpolymer membranes were characterized by Fourier transform infrared (FTIR) spectrometry and nuclear magnetic resonance as well as by determining the degree of sulfonation (DS), ion-exchange capacity (IEC), water uptake (WU), and electrical property of the membranes. The presence of sulfonic groups in the sulfonated Sty/HEA/LMA terpolymer was confirmed by FTIR, and the resulting membrane showed an IEC of 1.29 meq/g and an electrical resistance of 0.1 Ω cm^2. The WU of the prepared membranes increased with the DS at the reaction time. The surface morphology obtained by atomic force microscopy clearly showed an increase of roughness with reaction time. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3180–3188, 2011

Key words: ion-exchange membrane; postsulfonation; polystyrene membrane; electrical property

INTRODUCTION

Ion-exchange membranes play an important role in an increasing number of processes in various industries because of their superior selectivity for specific ions and wide applicability in fuel cells, desalination of seawater, recovery of valuable metals from effluents diffusion dialysis, production of ultra-pure water, and other purposes.[1–7]

In general, an excellent ion-exchange membrane should have high chemical and mechanical stability with favorable electrochemical properties such as low electrical resistance (ER) and high ion-permselectivity. To obtain the desired properties of ion-exchange membranes, many preparation methods have been practiced. Currently, the most widely used materials for the preparation of high-performance proton ion-exchange membranes are PEEK, polystyrene (PS), polyimide, PES, polysulfone, and so on.[8–14] It is generally agreed that cation-exchange membranes should have high chemical and mechanical stability with favorable electrochemical properties.

Sulfonated aromatic polymers can provide the functionality of the ion-exchange material.

The material most widely used as ion-exchange resin in particle form is sulfonated PS; however, it is too brittle if used alone to make suitable polymer films for ion-exchange membranes, even when it is crosslinked with divinyl benzene (DVB) during polymerization. PS is the most frequently used polymer because of its good chemical stability and excellent characteristics for functionalization.[15] Also, a styrene (Sty)–DVB copolymer has been used; it is an attractive material because of its improved mechanical properties and decreased swelling compared with PS.[2,16] However, there is expensive and brittle requiring modification for use in membrane applications[17] if based on polystyrene; therefore, it is necessary to improve membranes to overcome these problems.

To improve the poor performance, a grafting has been suggested, for example, by introducing a high-strength polymer.[18–20] Another way to improve mechanical properties is to prepare a cation-exchange membrane by using a different polymer film.[21–23] These polymer films show good mechanical and dimensional stability because of their hydrophobic characterization.

In this study, an ion-exchange membranes based on styrene, hydroxyethyl acrylate, and lauryl methacrylate (Sty/HEA/LMA) were synthesized various monomer weight ratio by solution polymerization. The chemical structures of the membranes were characterized by their Fourier transform infrared (FTIR) spectrometry, nuclear magnetic resonance

Code	Monomer (wt %) Sty : HEA : LMA	t-Butyl peroxide (wt %)	Temperature (°C)	Reaction time (h)
SHL-1	70 : 10 : 20	0.45	80	10
SHL-2	70 : 15 : 15	0.45	80	10
SHL-3	70 : 20 : 10	0.45	80	10

(NMR) spectra, and the basic membrane properties such as degree of sulfonation (DS), ion-exchange capacity (IEC), water uptake (WU), and electrical property were investigated by chemical and electrical methods.

EXPERIMENTAL

Materials

The monomers, including styrene, hydroxyethyl acrylate, and lauryl methacrylate, and the t-butyl peroxide (PO) used in the study were high-purity grades purchased from Aldrich (Seoul, Korea). The 1,2-dichloroethane (DCE, 99%) used as a solvent was obtained from Samchun (Seoul, Korea). The thermal initiator, benzoyl peroxide (BPO, 75%) from Lancaster, was purified by recrystallization from water. As a crosslinking agent, blocked isocyanate was purchased from Aekyung Chemical. Sulfuric acid and silver sulfate were from Duksan (Ansan, Korea).
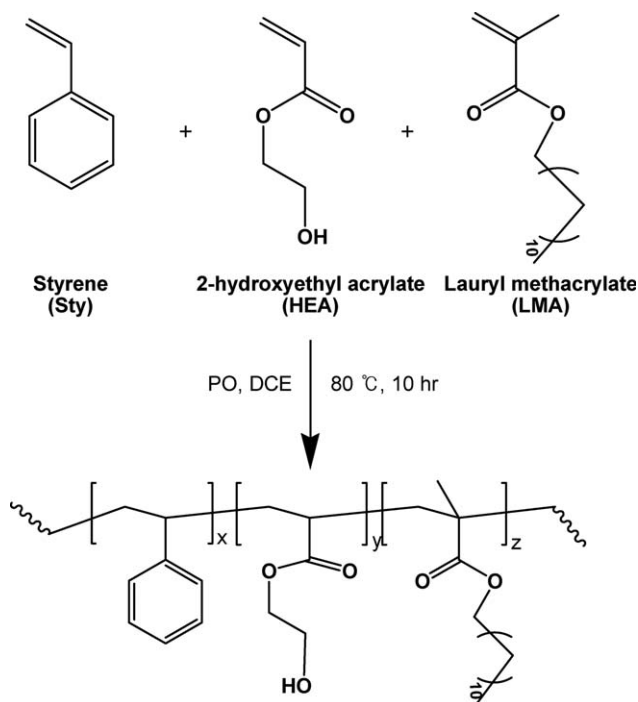
Figure 1 Synthetic scheme of Sty/HEA/LMA terpolymer.

Synthesis of Sty/HEA/LMA terpolymer

The synthetic conditions of copolymerization are summarized in Table I. Figure 1 shows the radical copolymerization procedure of Sty/HEA/LMA schematically. To synthesize the terpolymer, the reactant, a mixture of Sty, HEA, and LMA in DCE were synthesized by solution polymerization in various monomer weight ratio.

The solvent, 1,2-dichloroethane, was placed into a 1.0-L four-necked flask and heated to 80°C with reflux condensation. The reactant mixture and PO as an initiator were then added to the flask with a dropping funnel over 3 h, after which the reaction was continued with stirring for 7 h. After reaction, the unreacted monomers and solvent were removed from the flask using a vacuum pump.

Preparation of sulfonated membranes

The preparation conditions for the membranes are summarized in Table II. A solution consisting of Sty/HEA/LMA, blocked isocyanate, and BPO was dissolved in DCE. The 30 wt % solution was cast onto a teflon plate with a bar coater using the solvent-casting method[24] and dried overnight at room temperature. The dried membrane was crosslinked in a vacuum oven at 170°C for 1 h. Figure 2 shows the crosslinking mechanism of the Sty/HEA/LMA terpolymer.

To introduce sulfonic groups into the Sty/HEA/LMA membranes, a sulfonation reaction was carried out under the conditions shown in Table III. The membranes were immersed in a sulfuric acid solution with silver sulfate added as a catalyst. The sulfonation reactions were performed at different sulfonation times. After sulfonation reaction, the membranes were washed with diluted sulfuric acid with 70, 50, and 30% of deionized water. We treated

**TABLE II
Crosslinking Conditions of Sty/HEA/LMA Terpolymer**

Parameters	Values
Blocked isocyanate (wt %)	20.0
Benzoyl peroxide (wt %)	1.0
Crosslinking temperature (°C)	170.0
Crosslinking time (h)	1.0
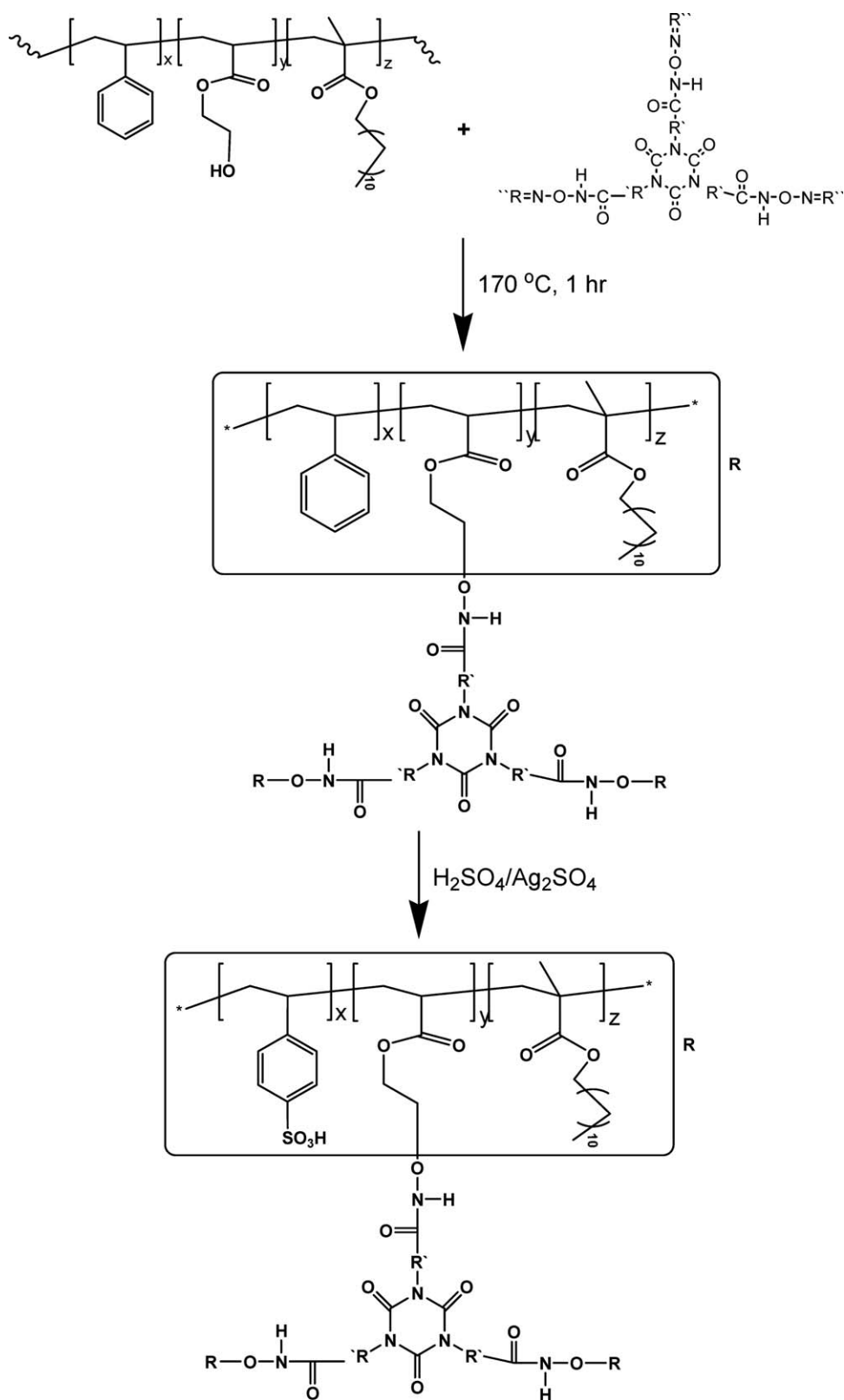
Figure 2 Crosslinking and Sulfonation scheme of Sty/HEA/LMA terpolymer.

TABLE III
Sulfonation Conditions of Sty/HEA/LMA Membrane

Sulfuric acid (mL)	Silver sulfate (g)	Temperature (°C)	Reaction time (min)
200	0.4	20	15
200	0.4	20	30
200	0.4	20	45
200	0.4	20	60
200	0.4	20	75

the membranes for 1 h with the above solution and finally with deionized water to remove the excess sulfuric acid, washed, and dried at 50°C for 24 h in a vacuum oven.

## Membrane characterization

FTIR spectroscopy

The chemical structures of Sty/HEA/LMA cation-exchange membrane were characterized by Fourier transform infrared spectrometry/attenuated total reflectance (FTIR/ATR). Infrared spectra were recorded in transmittance mode on a FTIR spectrometer (Shimatzu Model IR Prestige-21) in the range of waver numbers from 4000 to 600 cm^{-1}. The resolution and number of scans in all spectra were 4 cm^{-1} and 20, respectively.

NMR spectroscopy

The chemical structures of Sty/HEA/LMA membrane were characterized by NMR (JNM-AL400 NMR spectrometer). Using CDCl$_3$ as a solvent, ^{1}H-NMR and ^{13}C-NMR were measured, and tetramethyl silane was used as reference materials.

Water uptake

The WU of the cation-exchange membranes was determined by measuring the change in weight
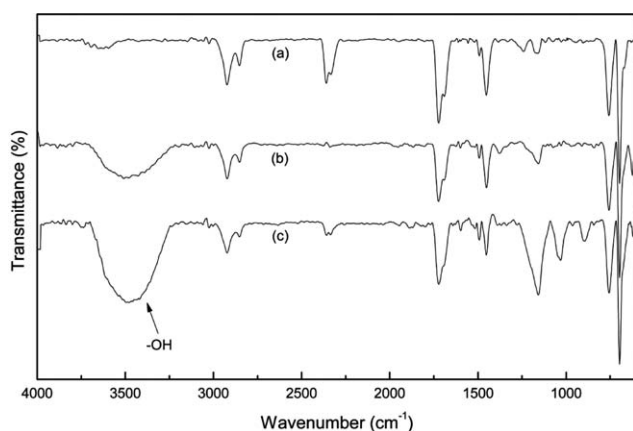
Figure 3 FTIR spectra of synthetic Sty/HEA/LMA membranes at different ratio: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.
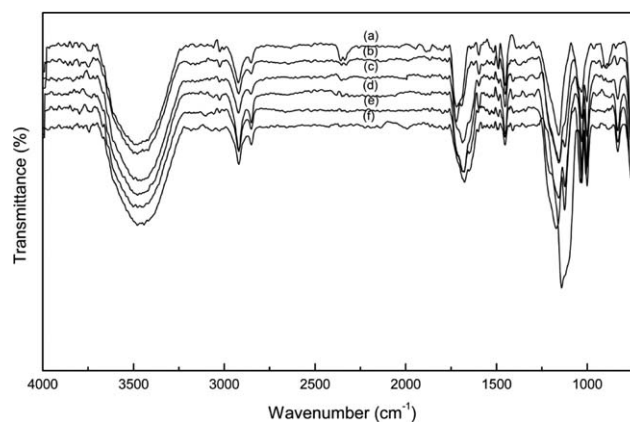
Figure 4 FTIR spectra of Sty/HEA/LMA = 70/20/10 membranes: (a) Sty/HEA/LMA membrane, sulfonation time (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, and (f) 75 min.

between the wet and dry membrane. The samples were soaked in distilled water for 24 h, removed from the water with filter paper, and immediately weighed; the samples were then dried in vacuum oven at 50°C to a constant weight.

The WU was calculated using the following equation:[25]

$$\text{WU} (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100, \tag{1}$$

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

Ion-exchange capacity

After rinsing in pure water for 1 day, a cation-exchange membrane sample was soaked in a large volume of 1N HCl solution for 1 day to obtain the membrane in the H$^+$ form. The excess HCl in the membrane was removed by repeated washing with pure water. The membrane in the H$^+$ form was then soaked in 1N NaOH solution at room temperature for 1 day. The membrane was then taken out, and the NaOH solution was titrated with 0.1N HCl solution with a drop of phenolphthalein solution (0.1% in ethanol) as a pH indicator. The sample was dried at 50°C under vacuum and weighed.

The IEC was calculated according to the following equation:[26]

$$\text{IEC (meq/g.dry)}$$
$$= \frac{(V_{\text{H}_2\text{OH}} \times N_{\text{H}_2\text{OH}}) - (V_{\text{HCl}} \times N_{\text{HCl}})}{\text{Weight of sample}}, \tag{2}$$

where N_{NaOH} and N_{HCl} are the concentrations of the NaOH and HCl solutions, respectively, and V_{HCl} and V_{NaOH} are the volumes of HCl and NaOH solutions, respectively.
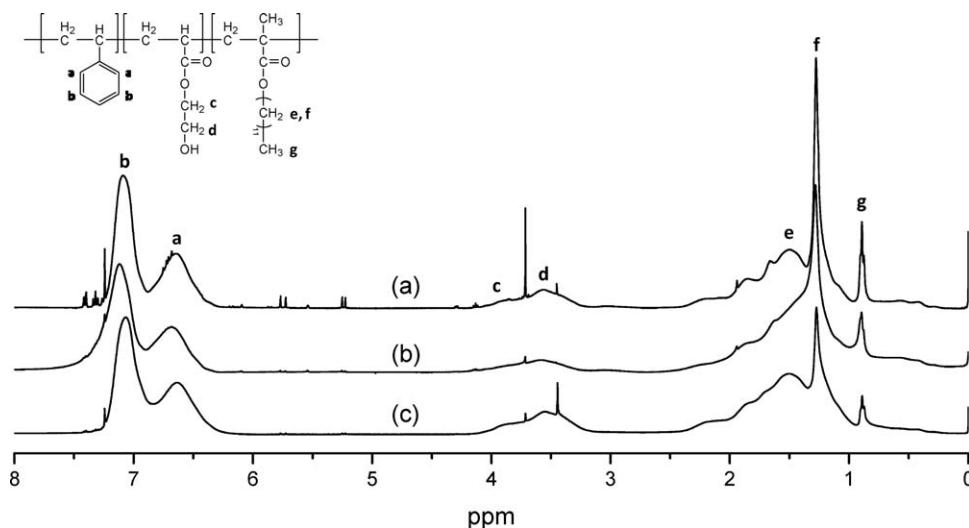
Figure 5 ^{1}H-NMR spectra of Sty/HEA/LMA membranes: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.

Electrical resistance

The electrical properties of the cation-exchange membranes were measured using a clip cell and LCR meter (HIOKI 3522-50 LCR HiTESTER, Japan). Before the measurement, the membrane samples were immersed in 0.5M NaCl solution for 1 day at room temperature. The sample was then inserted into the platinum clip cell, and current was applied to the cell, and then electrolyte resistance was measured after removing the membrane.

The ER and membrane conductivity were calculated according to the following expressions.[26,27]

$$\text{Electrical resistance}(\Omega \cdot cm^2) = (R_1 - R_2) \times A, \quad (3)$$

where R_1 is the resistance of membrane and electrolyte, R_2 is the resistance of electrolyte alone, and A is the effective membrane area.

$$\text{Membrane conductivity}(S/cm) = \frac{L}{R \times A}, \quad (4)$$

where R is the obtained membrane resistance and L is the membrane thickness.

Ion transport numbers

The ion transport number (ITN) of the counter ion in the cation-exchange membranes was determined by the electromotive force 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, tm, for each membrane was calculated by the following equation:

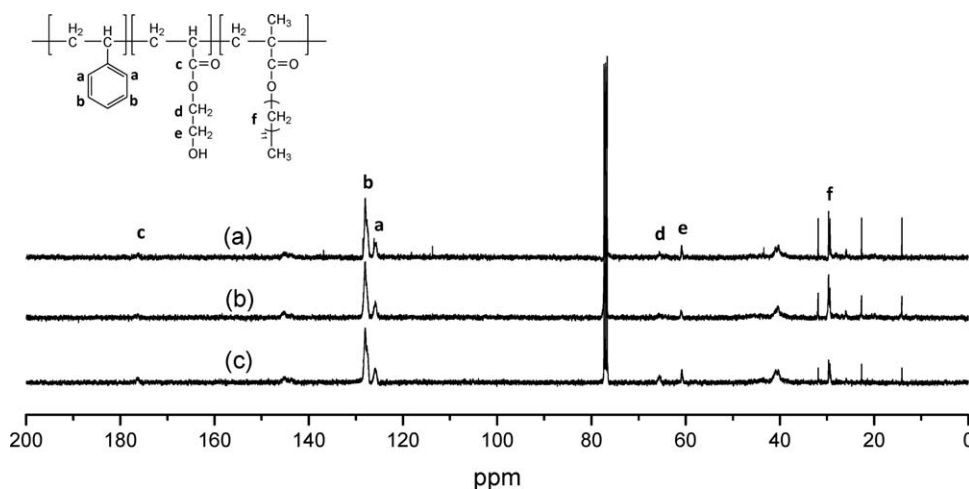$$E_m = \frac{RT}{F}(2t_m - 1)\ln\frac{C_1}{C_2}. \quad (5)$$

Figure 6 ^{13}C-NMR spectra of Sty/HEA/LMA membranes: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.

TABLE IV
Membrane Characteristics of the Sulfonated Sty/HEA/LMA Membrane

Code	Sulfonation time (min)	WU (%)	IEC (meq/g)	ER (Ω cm^2)	Conductivity (S/cm)	ITN
	15	20.6	0.610	533.5	3.75E-05	0.72
	30	53.2	0.916	226.2	8.84E-05	0.79
SHL-1	45	84.0	1.137	2.2	8.64E-03	0.91
	60	120.8	1.220	0.8	2.75E-02	0.92
	75	320.8	1.290	0.1	2.25E-01	0.96
	15	8.0	0.550	607.3	2.80E-05	0.73
SHL-2	30	33.0	0.823	372.2	4.57E-05	0.75
	45	78.1	0.971	1.5	1.03E-02	0.89
	60	145.7	1.156	1.4	1.50E-02	0.90
	75	351.4	1.173	0.9	2.06E-02	0.94
	15	16.2	0.394	643.7	2.87E-05	0.69
SHL-3	30	59.6	0.461	38.1	4.86E-04	0.71
	45	108.3	0.560	1.4	1.61E-02	0.84
	60	160.0	0.592	1.1	2.09E-02	0.88
	75	412.1	0.910	0.4	3.75E-02	0.89

Surface morphology

The surface morphology of the Sty/HEA/LMA cation-exchange membranes was measured using an atomic force microscope (AFM, Nanoscope-IV Veeco Instruments, USA). The surface morphology was analyzed over 25 μm^2 of the membrane surface in tapping mode.[28]

RESULTS AND DISCUSSION

FTIR spectroscopy

To confirm the changes in the chemical structure of polymer at each preparation step, FTIR spectra were analyzed and are presented in Figures 3 and 4.

Figure 3 shows the spectra of the Sty/HEA/LMA terpolymer. We were able to confirm synthesized terpolymer; the —OH characteristic peak from HEA, which occurs at near 3500 cm^{-1}, has increased with increasing the amount of HEA contents. Absorption bands attributed to the aromatic group were observed at 2900 and 1450 cm^{-1}, which are assigned to the stretching vibrations of C—H and C=C double bonds, respectively. Thus, it was confirmed that the Sty-HEA-LMA terpolymer was synthesized.

Figure 4 represents the characteristics of the peak depending on the sulfonation time that the Sty content is 70 wt % of HEA/LMA copolymer content changes. Figure 4(a) shows the characteristic peak of before sulfonation; Figure 4(b–f) represents the spectrum on the increasing sulfonation time. Comparing peak of introduced before and after of sulfonic groups, absorption bands assigned to sulfonic acid groups were observed at 1250–1150 cm^{-1}, which are assigned to the stretching vibration of S=O and 1060–1030 cm^{-1}, which are represented to the symmetric characteristic peak (O=S=O). This indicates that the sulfonic groups were introduced into the

membrane through the sulfonation reaction. And, increasing the reaction sulfonation time, we confirmed the increasing intensity of characteristic peak. These results seemed that sulfonation reaction is increased with growing sulfonation time.

NMR spectroscopy

To confirm the changes in the chemical structure of polymer at synthesis conditions, ^{1}H- and ^{13}C-NMR spectra were analyzed and are presented in Figures 5 and 6. Figures 5 and 6 represent the characteristics of the peak that the Sty content is 70% where HEA/LMA content changes.

In the ^{1}H-NMR spectra, we were able to confirmed aromatic C—H peak of Sty at 7.3 ppm and CH$_2$ peak of HEA at 4.3 and 3.8 ppm. The peaks at 0.86 and 1.93 ppm were CH$_3$ peaks of LMA.

In the ^{13}C-NMR spectra, we confirmed aromatic C—H peak of Sty at 125 ppm and aliphatic CH$_2$
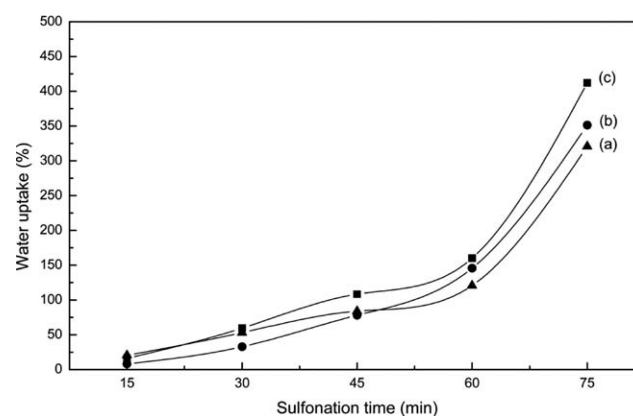
Figure 7 Effect of sulfonation time on the water uptake of the Sty/HEA/LMA membrane: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.

peak of HEA and LMA at near 60 and 29 ppm. The peak at 78 ppm is due to the CDCl$_3$ as the solvent used for the analysis.

As shown in Figure 6, with increasing HEA contents, the CH$_2$ peak of HEA was increased, and the CH$_2$ peak of LMA was reduced at 60 and 29 ppm.
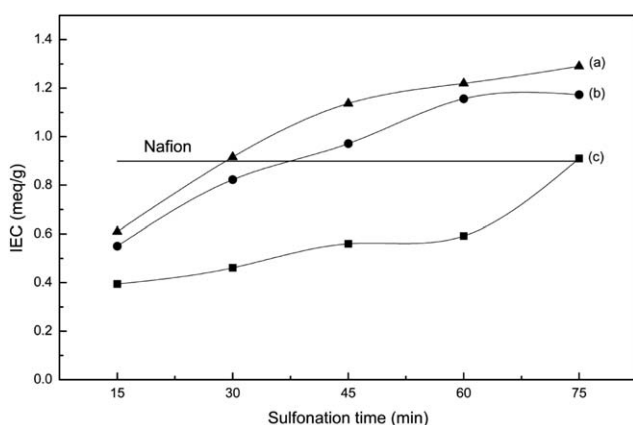
Characterization of cation-exchange membrane properties

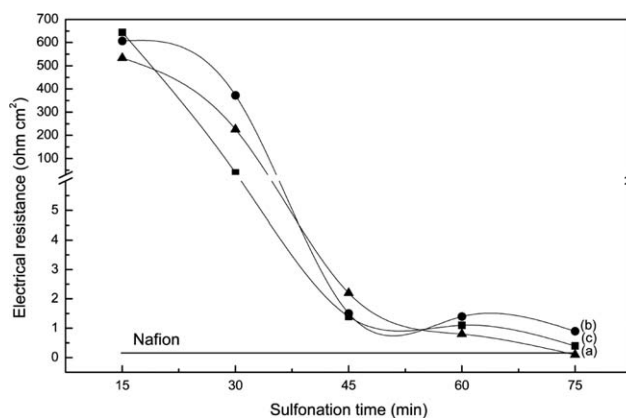The basic properties of membranes are represented in Table IV.

Figure 7 shows the WU of the cation-exchange membranes. As the sulfonation time increased, water uptake also increased. The maximum value was about 412% for the membrane prepared for weight ratio 70/20/10 at 75 min sulfonation time. The membranes prepared at longer reaction time took up more water than those prepared at shorter reaction time; this can be ascribed to the increased hydrophilicity because of the greater number of sulfonic groups introduced into the membrane.

The IEC was measured for the sulfonated membranes prepared at different sulfonation times, and the results are shown in Figure 8. As expected, the ion-exchange capacities increased according to the sulfonation time because of the increased content of sulfonic groups in the membranes, with a maximum value of 1.29 meq/g obtained at weight ratio 70/10/20.

Figures 9 and 10 show the ER and conductivity of the sulfonated membranes. The average thickness of the membranes was 170 μm. The ERs decreased with increasing reaction time. These results are well matched with the ion-exchange capacity results, as the electrical resistance of an ion-exchange membrane is proportional to its ion-exchange capacity. The optimum values of ER and conductivity among the membranes prepared in this study are 0.1 Ω cm^2
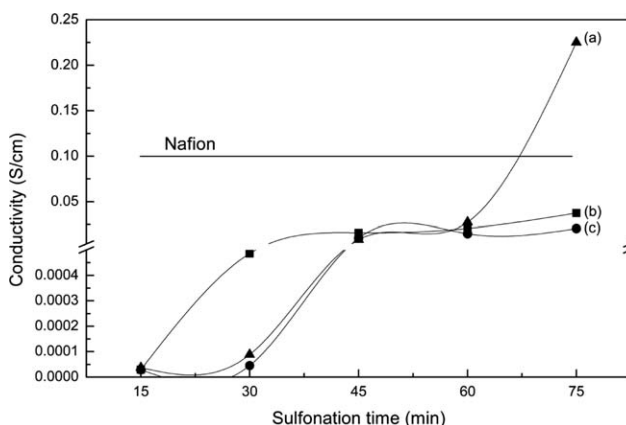
Figure 9 Effect of sulfonation time on the electrical resistance of the Sty/HEA /LMA membrane: (a) 70:10:20, (b) 70:15:15, and (c) 70:20:10.

and 0.225 S/cm for weight ratio 70/10/20 at 75 min sulfonation time.

The ITN of the Sty/HEA/LMA cation-exchange membranes prepared at different sulfonation times and amount of Sty/HEA/LMA ratio are shown in Figure 11. As shown in Figure 11, the ITN of the sulfonated membranes ranged from 0.69 to 0.96. The ion transport number was significantly dependent upon the sulfonation time, i.e., the contents of acidic SO$_3^-$ groups and the degree of crosslinking. Decreasing the HEA content, the ITN reached a maximum about 0.96.

Surface morphology

The microscopic morphology of the prepared membranes was examined by AFM, and the covering area of Figure 12 was 5 μm × 5 μm. Figure 12 shows the AFM image of the membranes prepared at different sulfonation time. As can be seen in Figure 12, the surface of the membrane was uniform and

Figure 8 Effect of sulfonation time on the ion-exchange capacity of the Sty/HEA/LMA membrane: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.

Figure 10 Effect of sulfonation time on the conductivity of the Sty/HEA/ LMA membrane: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.
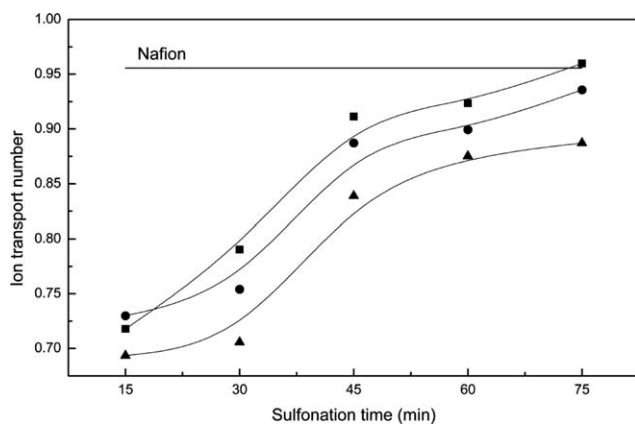
Figure 11 Effect of sulfonation time on the ion transport number of the Sty/HEA/LMA membrane: (a) 70/10/20, (b) 70/15/15, and (c) 70/20/10.

smooth when sulfonic groups were not introduced. However, it was observed that the surface of the membrane became rougher as the sulfonation reaction proceeded. As the DS increased, a broader size distribution was also observed.

CONCLUSIONS

In this study, a novel cation-exchange membrane based on a Sty/HEA/LMA terpolymer was synthesized. Cation-exchange membranes were prepared by heat crosslinking followed by sulfonation reaction for various times. The characterization of the Sty/HEA/LMA cation-exchange membrane properties provided the following results:

The synthesis of the Sty/HEA/LMA terpolymer and the presence of sulfonic groups after sulfonation reaction were confirmed by the FTIR spectra and ^{1}H- and ^{13}C-NMR spectra. Ion-exchange capacities

of the membranes increased as the sulfonation time was increased. The maximum value of the IEC was 1.29 meq/g. The WU of the cation-exchange membrane was increased with the sulfonation time. When the sulfonation reaction was carried out at 75 min, the membrane showed a good ER of 0.1 $\Omega \cdot cm^2$, a conductivity of 0.225 S/cm, and an ITN of 0.96. The surface morphology of the membranes depended on the sulfonyl groups introduced onto the membrane surface; it was observed that the surface of the membrane became rougher as the sulfonation reaction proceeded.

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