Ion-exchange Membrane based on Poly(styrene sulfonic acid-*co*-N-(2-hydroxyethyl) acrylamide)

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ABSTRACT: A new ion-exchange membrane was prepared by blending a copolymer of poly(styrene sulfonic acid-*co*-N-(2-hydroxyethyl) acrylamide) with poly(vinylidene fluoride). The dissolution of the copolymer into water was prevented by the crosslinked network formed by condensation reaction between *N*-(2-hydoroxyethyl) acrylamide (HEAA) units. The reaction was caused after film-forming the blend. Swellability in water, ion-exchange capacity, ion conductivity, and mechanical properties of the membrane were investigated and compared with those of a well-known ion-exchange membrane, Nafion 117. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2788–2796, 2007

Key words: copolymerization; blends; crosslinking; membranes; swelling

INTRODUCTION

The aim of our research is to produce a cost-effective cation-exchange polymer membrane. The performance of the membrane we aimed is the level of a DuPont perfluorosulfonate ionomer membrane, Nafion 117, with respect to ion exchange capacity, the proton conductivity, and the mechanical properties. The Nafion membrane is a copolymer having a hydrophobic ($-CF_2-CF_2-$) skeleton and hydrophilic ($-SO_3H$) groups at the end of the long perfluoroether side chains.[1] In the water-swollen perfluorosulfonate ionomer membranes, the sulfonic acid groups cluster together and make ion channels by which ions can be diffuse through the membrane.[2–6] As the matrix surrounding the cluster regions are made of hydrophobic tetrafluoroethylene chains, the degree of swelling can be moderately restrained, and the mechanical properties do not decline on swelling. The Nafion membrane is appraised as the first-class ion-exchange membrane among the commercially available membranes. The Nafion membrane has also been used as the most valuable membrane for the polymer-electrolyte type fuel cell.[7,8]

However, the expensiveness of the Nafion membrane is unfavorable. So, we have attempted to prepare a more inexpensive ion-exchange membrane that has the same level of performance as that of the Nafion membrane. Our basic concept of designing the membrane does not significantly deviate from that of the Nafion membrane. The comparison between our concept and the Nafion membrane is shown in Figure 1. The definite difference between the two concepts is that our membrane comprises two types of polymers, whereas the Nafion comprises one copolymer. Our two component polymers are blended into one membrane. Because of our choice of this blending method, we could produce a cheaper membrane. Our main part of the polymer electrolyte is composed of poly(styrene sulfonic acid) (PSSH), which corresponds to the electrolyte component of the Nafion copolymer. A copolymer unit of *N*-(2-hydroxyethyl) acrylamide (HEAA) is copolymerized with PSSH as a crosslinker. PSSH is a polymer highly soluble in water, and so, the crosslinking method is indispensable for converting the film to an insoluble one in water. Further, as P(HEAA-SSH) is an amorphous and glassy polymer, it is very fragile. Blending of P(HEAA-SSH) with another tough polymer is our choice to improve the mechanical properties of our copolymer. Poly(vinylidene fluoride) (PVDF) is suitable blending, because it has a common solvent, dimethyl sulfoxide (DMSO), with our copolymer.[9] Another important reason for our choice of PVDF is that a flexible film can be obtained through blending with PVDF. Crosslinked polymers generally cannot be blended with other polymers by solution mixing methods. However, the crosslinking reaction of the crosslinker HEAA can be started not only by using acid, but also by heating. So, we crosslinked the copolymer by heating the film, after the blending and the subsequent film-forming processes. We call it the film crosslinking method.
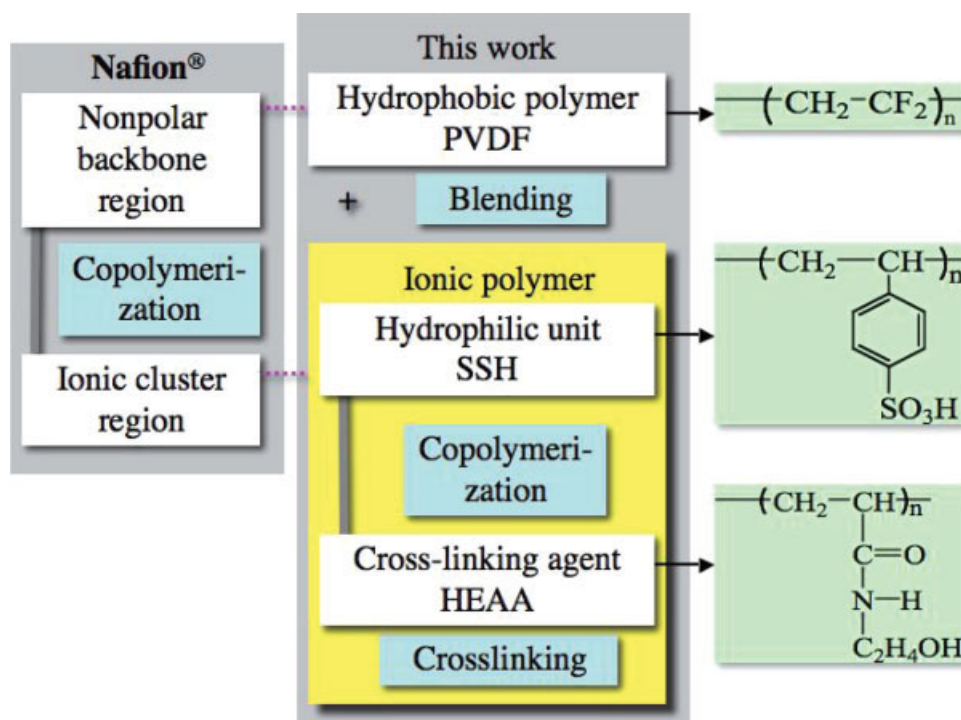
Figure 1 Comparison of material designing concepts for the ion-exchange membrane between ours and Nafion 117. The Nafion membrane was based on a simple concept of copolymerization of a hydrophobic monomer of tetrafluoroethylene (TFE) and an ionic monomer. On the other hand a hydrophobic polymer of PVDF and the ionic polymer (copolymer of SSH and HEAA monomers) are blended in our material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

If styrene sulfonic acid (SSH) is chosen as the starting monomer unit, another monomer unit of HEAA can be crosslinked by reaction with protons emitted from the SSH units. So, we used sodium styrene sulfonic acid (SSNa) instead of SSH. Thus, we have to exchange the Na ion with proton after cross-linking the blended film. This protonation was done by soaking the film in a HCl solution. When the content of the copolymer in the blend film is high, the copolymer film was cracked on contacting with water. However, the copolymer blended with PVDF did not cause solvent cracking. PVDF is used not only to suppress the swelling degree of the film, but also to keep the film shape during the film-forming processes.

EXPERIMENTAL

Materials

N-(2-Hydroxyethyl) acrylamide (HEAA) was provided by Kohjin, Japan. Sodium p-styrene sulfonate (SSNa) and 2,2′-azobis[2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044) were products of Wako Pure Chemical Industries, Japan. Poly(vinylidene fluoride) (PVDF) (MW 530,000) was a product of Scientific Polymer Products, NY.

Polymerization of HEAA

A 1.0 mol L^{-1} solution of the HEAA monomer in water was prepared. Then, the initiator VA-044 (0.1 mol L^{-1}) was added to the monomer solution. The solution (10 mL) thus prepared was sealed in a test tube of 18 mm diameter after flushing by nitrogen gas. The tube was kept at 60°C for 12 h to yield a polymer product with conversions around 84% (Scheme 1). The polymer product was dissolved in water and then precipitated in an excess volume of acetone. This purification cycle was repeated three times. The limiting viscosity number [η] of this polymer (PHEAA) at 30°C in water was 6.0 dL g^{-1}.
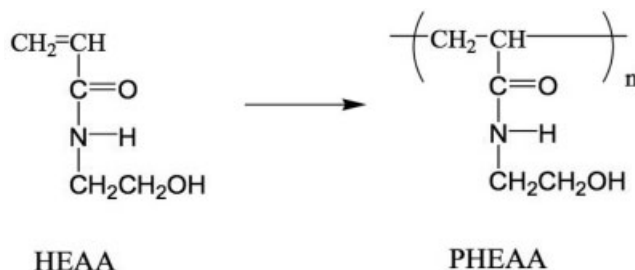
Scheme 1 Polymerization of HEAA.
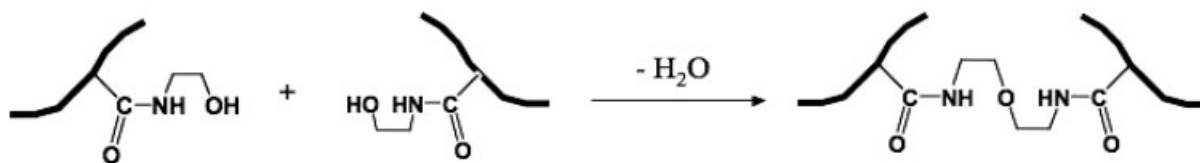
Scheme 2 Interchain crosslinking reaction of PHEAA.

Preparation of crosslinked PHEAA

A 3 wt % solution of PHEAA in water (20 mL) was cast at 40°C in a Teflon dish with 84 mm diameter and then kept for 12 h to yield a film sample. A test strip of 20 mm × 20 mm from the cast film was sealed in a test tube with nitrogen gas. The sample was then annealed for 10 min at a given annealing temperature (100–300°C) to cause a crosslinking reaction in the film as shown in Scheme 2. ^{1}H-NMR of P(HEAA) in D_2O (δ, ppm): 1.5–2.3 (CH, CH_2, backbone), 3.2–3.4 (CH_2), 3.7–3.8 (CH_2O).

Preparation of poly[*N*-(2-hydroxyethyl) acrylamide-*co*-sodium-*p*-styrene sulfonate]

Given molar fractions of SSNa and HEAA (totally 0.01 mol) were put into a test tube of 18 mm diameter with water (10 mL) and the initiator VA-044 (3.2 mg, 0.001 mol) and then dissolved. The concentrations of the monomers and the initiator were 1.0 and 0.1 mol L^{-1}, respectively. The tube was sealed after repeating three times of the evacuating and nitrogen gas flushing cycle and then kept at 60°C for 12 h to yield the polymer product. The product of poly[*N*-(2-hydroxyethyl) acrylamide-*co*-sodium-*p*-styrene sulfonate] [P(HEAA-SSNa)] thus obtained was precipitated into an excess amount of acetone. The precipitate was then dried at 60°C for 12 h. The dried product was further purified through totally three cycles of the dissolution in water and subsequent precipitation into acetone. Finally, the product was dried at 60°C for 24 h. The average conversion was 79%. The polymerization reaction scheme was shown in Scheme 3. The copolymer composition was analyzed by a ^{1}H-NMR method. ^{1}H-NMR of P[HEAA-SSNa] in D_2O (δ, ppm): 0.8–2.1 (CH, CH_2,

backbone), 2.9–3.1 (CH_2, HEAA), 3.4–3.6 (CH_2O, HEAA), 4.6 (D_2O), 6.0–7.8 (C_6H_4, SSNa).

Preparation and crosslinking of blend film of P(HEAA-SSNa)/PVDF and protonation

The copolymers of P(HEAA-SSNa) (P1–P9) with SSNa contents higher than 73 mol % were able to dissolve in DMSO as shown in Table I. So, only the soluble copolymers were blended with PVDF through the following blending method. A given blending ratio of SSNa and PVDF (totally 0.3 g) was put into a test tube of 18 mm diameter with DMSO (10 mL) and then heated at 120°C for 8 h to dissolve them. The solution thus prepared was cast in a glass dish of 59 mm in diameter. The glass dish was put on a hotplate kept at 130°C. The solvent (DMSO) was evaporated at 130°C for 1 h, and the blend film was obtained. The film was annealed at 240°C for 1 h to cause self-crosslinking reaction between the HEAA units. The bottom surface of the cast film was adhering to the bottom of the dish through the annealing process. The change in film volume observed was scarce. The annealed film was soaked in 0.1*M* HCl solution for 12 h to exchange sodium ion of the SSNa residue with proton. The protonated film was washed in water for 12 h and finally dried *in vacuo* at 150°C for 1 h. Average thickness of the films finally obtained was 98 μm.

Mearsurements

The ^{1}H-NMR spectra was recorded on a Bruker Avance 400 spectrometer using D_2O as a solvent. The spectra were referenced on internal tetramethylsilane.

For measuring the degree of swelling, a specimen, 2 cm ×2 cm of the film, dried at 100°C for 1 h just before use was immersed in water at 40°C, and then,
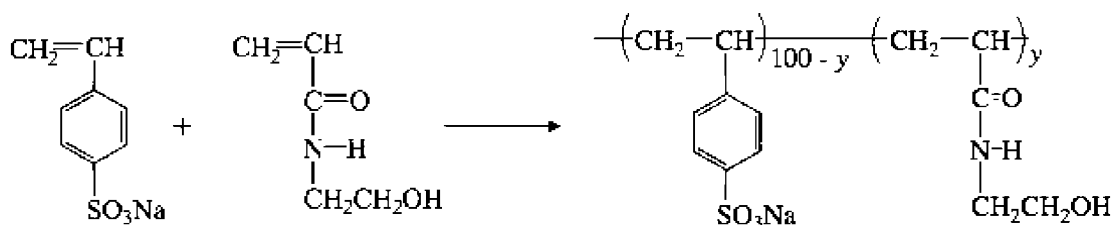
Scheme 3 Copolymerization of SSNa and HEAA.

TABLE I
Monomer Composition of our Copolymers of P[HEAA$_y$-SSNa$_{(100-y)}$]

| Polymer | Monomer composition (mol %) | | | | Solubility in DMSO |
| | In feed | | In copolymer | | |
	HEAA, y	SSNa $(100 - y)$	HEAA, y	SSNa $(100 - y)$	
P0 (PSSNa)	0	100	0	100	Soluble
P1	10	90	3	97	Soluble
P2	20	80	11	89	Soluble
P3	30	70	13	87	Soluble
P4	40	60	27	73	Soluble
P5	50	50	52	48	Unsoluble
P6	60	40	74	26	Unsoluble
P7	70	30	76	24	Unsoluble
P8	80	20	85	15	Unsoluble
P9	90	10	93	7	Unsoluble
P10 (PHEEA)	100	0	100	0	Unsoluble

it was repeatedly taken out for weighing. Before weighing, the wet specimen was lightly wiped with tissue paper. The degree of swelling was estimated by using the following equation:

$$\text{Degree of swelling (wt \%)} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are the weights of dry film and swelled one, respectively.

The ion change capacity (IEC) (with unit of mmol g^{-1} of dry polymer) of the sulfonated blend membrane was determined by measuring the concentration of H$^+$ that was exchanged with Na$^+$ when the film samples were equilibrated with a NaCl solution. The blend film (0.1 g) dried at 100°C for 30 min before use was immersed in a NaCl solution (1.0M) at 40°C for 10 min and subsequently kept at room temperature for 12 h. The NaCl solution (10 mL) after immersing was titrated with a NaOH solution (0.005M) to estimate the IEC of the film.

The proton conductivity of membranes was measured by the ac impedance analyzer over a frequency range of 10^2–10^6 Hz with 50 mV. A system of a Solartron 1260 frequency response analyzer configured with a Solartron 1296 dielectric interface was used to measure the proton conductivity of membranes with a two-point probe cell. The conductivity of the sample was obtained from complex impedance analysis. The real and imaginary parts of the complex impedance were plotted, and the proton conductivity was obtained from the bulk resistance found in complex impedance diagram. The proton conductivity σ can be calculated by using the equation $\sigma = L/RA$, where L is the thickness of the sample, A is the surface area of the electrode, and R is the resistance from the impedance data.

Dynamic mechanical analysis (DMA) was performed using a IT Keisoku Seigyo DVA-225 dynamic mechanical analyzer with a tension film clamp installed. The film samples were cut to be 5 mm in width and 15 mm in length to conform to the dimensional limits required for the tension film clamp. The gauge length of the sample film was 10 mm. After mounting the sample, it was heated from room temperature to 200°C at 10°C min^{-1} under a prestrain of 0.1%. The samples were tested, using a dynamic force with single frequency oscillation of 10 Hz and strain amplitude of 0.05%. The storage modulus E' and tan δ for each run were calculated as a function of increasing temperature, using thermal analysis software included as part of the DMA.

The surface and the crosssection view of the blend film was examined by a Hitachi scanning electron microscopy, S-3000N.

RESULTS AND DISCUSSION

As the cast film of PHEAA was very tough, its mechanical properties could be measured in the form of film by a dynamic mechanical analyzer. The storage modulus E' versus temperature curve of the uncrosslinked PHEAA film is shown in Figure 2. Three orders of the magnitude of abrupt decrease in modulus at 120°C indicate the presence of the glass transition. The PHEAA film uncrosslinked is tough one at room temperature in spite of its amorphous nature and high glass transition temperature. Another important information for the purpose of our research is that the annealing temperature of the PHEAA-polymer film or the HEAA-monomer-containing copolymer film should be set at temperatures higher than 120°C to cause self-crosslinking reaction between the HEAA units. The reaction is condensation between the two hydroxy ethyl acrylamide groups accompanying dehydration. Annealing at lower temperatures than its glass transition temperature caused no crosslinking. No crosslinking was confirmed by its retaining solubility in water at room temperature.
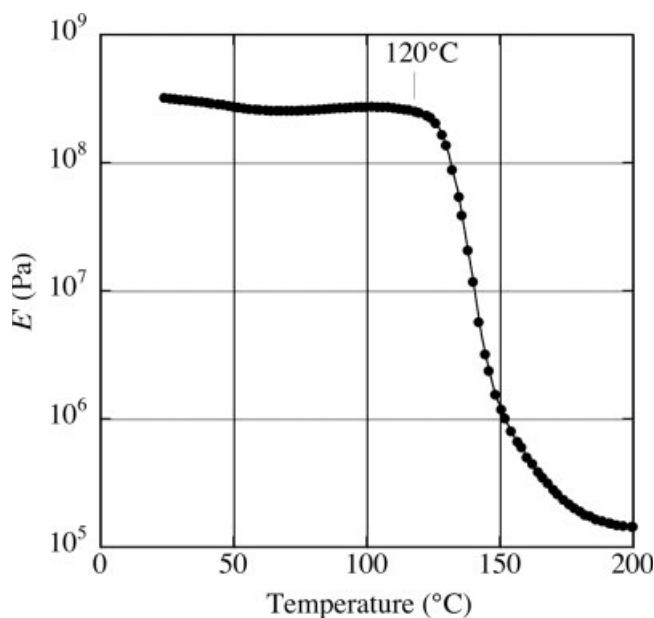
Figure 2 The storage modulus E' of the PHEAA film as a function of temperature. The heating rate was $10°C \ min^{-1}$.

However, the film crosslinked through annealing at higher than the glass transition temperature became insoluble on soaking in water. Poly (vinyl alcohol) (PVA) can be crosslinked by the reaction with organic compounds.[10] Difunctional aldehydes such as glyoxal or glutaraldehyde are used as the crosslinkers for PVAs. They are similar to HEAA, because the crosslinking reaction of these aldehydes with the polymer can be caused by heating or addition of acid. However, the HEAA is more excellent crosslinker, because the reaction of the HEAA does not occur at temperatures lower than its glass transition temperature. In case of aldehydes, the reaction with PVAs occurs gradually at room temperatures, although the glass transition temperature of PVA is higher than room temperature.

Figure 3 shows the degree of swelling in water at 40°C versus annealing temperature curve of the PHEAA film that was annealed at various temperatures higher than the glass transition temperature. Two characteristic annealing temperatures are observed: the decreasing rate of the degree of swelling with increasing annealing temperature slows down at 190°C, and the degree shows a small step down from 40 to 10% at 280°C. Here, we will not discuss the origins of these two characteristic annealing temperatures observed in Figure 3. The observed decreasing trend with increasing annealing temperature indicates that the interchain crosslinking of PHEAA caused by film annealing decreases the degree of swelling and that the degree of crosslinking can be precisely controlled by annealing temperature. The way of causing crosslinking by such

annealing method has a big advantage for keeping the film shape even after crosslinking, because the timing of causing crosslinking can be set after the film-forming process. If the crosslinking agent functioned during the copolymer preparation process, the crosslinked copolymer could not be blended with other polymers because of insoluble nature of the crosslinked copolymer. On the basis of the data in Figure 3, we selected 240°C as the annealing temperature for the P(HEAA-SSNa)/PVDF blend film. No significant chemical reaction except crosslinking was observed through the annealing at 240°C. The degree of swelling of the PHEAA film annealed at 240°C is almost at the same level as that of PVA films with relatively lower crystallinity than 30 wt %.[11] Another merit of our crosslinking method is that the film shape is almost kept through the crosslinking. This can be understood by scanning electronic microscopic observation of the blend film of the copolymer and PVDF, which is discussed later. The partner polymer of PVDF is also a thermally stable polymer. This is one merit that we choose PVDF. The thermal stability of PVDF is due to its relatively high melting temperature, about 170–180°C.[12]

The HEAA unit fraction in the copolymer of P(HEAA-SSNa) is plotted against the HEAA monomer fraction in feed in Figure 4, indicating that the monomer reactivity of both monomers are good and the copolymers of the required copolymer composition can be prepared in the whole copolymer composition range. The copolymers of P(HEAA-SSNa) with various monomer compositions are named as shown in Table I. The solubility in DMSO at room tempera-
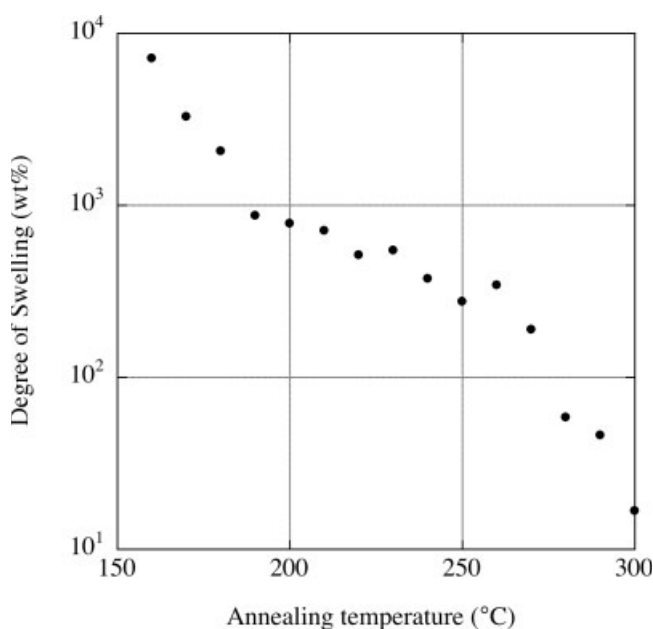

Figure 3 Dependence of the degree of swelling of the PHEAA film in water at 40°C on the annealing temperature.
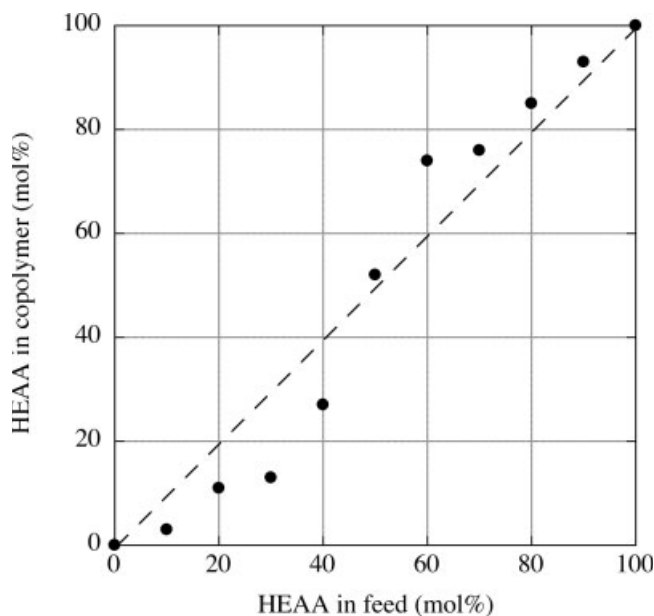
Figure 4 Relation between HEAA fraction in monomer feed and HEAA in the copolymer.

Figure 5 The degree of swelling of the blend films in water at 40°C are plotted against the —SO$_3$H content: (○) PVDF$_x$/P1$_{100-x}$, (□) PVDF$_x$/P2$_{100-x}$, (◇) PVDF$_x$/P3$_{100-x}$, and (△) PVDF$_x$/P4$_{100-x}$.

ture is also shown for the copolymers in Table I. In our blend sample preparation method, the solubility in DMSO is the crucial factor (for determining whether the copolymer can be blended with another polymer component of PVDF or not), because the two polymer components are dissolved in a common solvent of DMSO in our method. The copolymers of P(HEAA-SSNa) with a higher monomer content of SSNa than 73 mol % (P1–P4) could be blended with PVDF, while those with the lower fractions than 48 mol % (P5–P9) could not be blended because of their insolubility in DMSO.

The blend films were then thermally crosslinked and subsequently protonated. To keep the film shape, the film was crosslinked before protonation. If the uncrosslinked blend film was soaked in an acid solution for protonation, the part of the film dissolved in water.

The crosslinked and protonated blend films thus obtained were flexible and transparent. The water swellability of the blend films at 40°C is shown as a function of the total content of the sulfonic acid group contained in the film in Figure 5. Four series of data for the four kinds of based copolymers (P1–P4) can be fitted to one curve, indicating that the swellability of the blend mainly depends on the total content of sulfonic acid group. This is very reasonable result because the component copolymers are pair of an unswellable polymer (PVDF) and the swellable amorphous copolymer. The degree of swelling of the Nafion 117 film was 20.8%. Our blends with lower —SO$_3$H contents than 1.5 mmol g^{-1} had lower swellability than the Nafion 117.
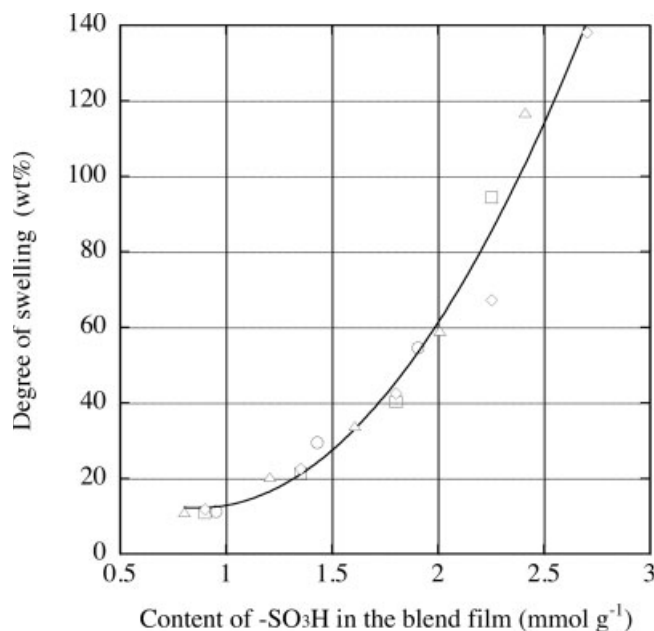
Figure 6 shows the IEC versus the total content of sulfonic acid group in the blend films for four kinds of based copolymers. These IEC data can be fitted to one curve, indicating that the IEC also depend mainly on the total content of the sulfonic acid group. The IEC of the Nafion 117 film was 0.87 mmol g^{-1}. Our blends
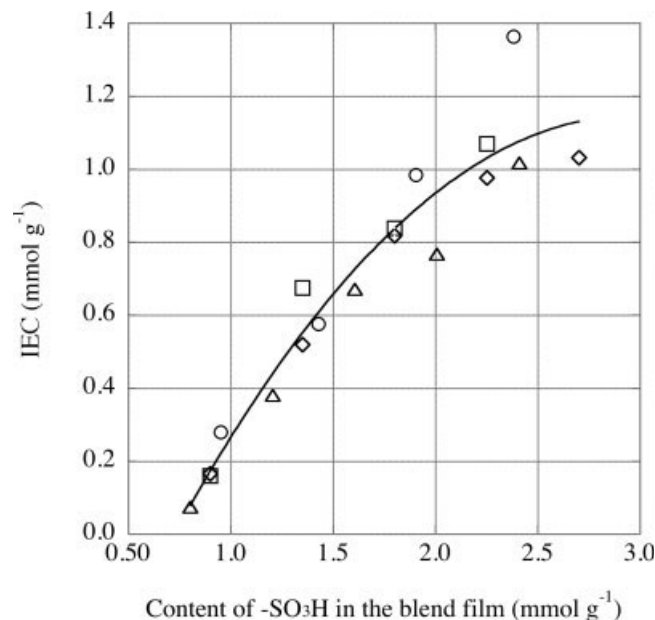

Figure 6 The ion exchange capacity (IEC) of the blend films are plotted against the —SO$_3$H content: (○) PVDF$_x$/P1$_{100-x}$, (□) PVDF$_x$/P2$_{100-x}$, (◇) PVDF$_x$/P3$_{100-x}$, and (△) PVDF$_x$/P4$_{100-x}$.
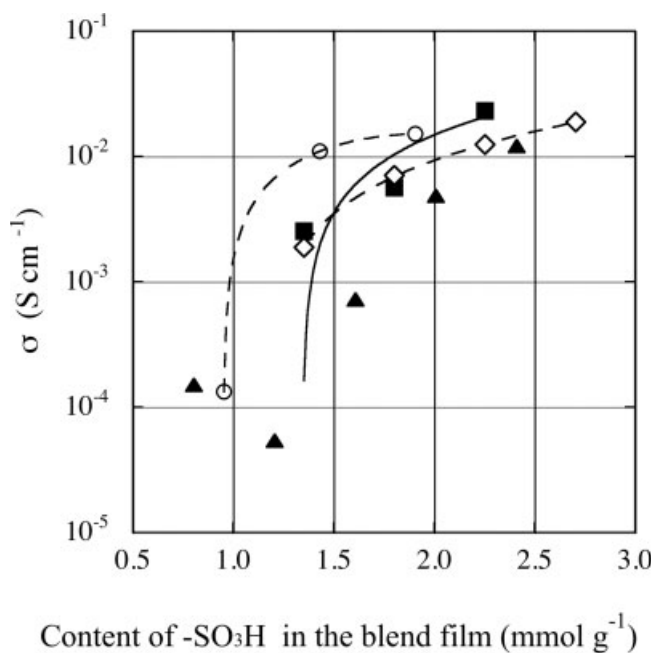
Figure 7 The ion conductivity σ of the blend films are plotted against the $-SO_3H$ content: ($\bigcirc$) $PVDF_x/P1_{100-x}$, ($\square$) $PVDF_x/P2_{100-x}$, ($\diamondsuit$) $PVDF_x/P3_{100-x}$, and ($\triangle$) $PVDF_x/P4_{100-x}$.

with higher $-SO_3H$ contents than 2.0 mmol g^{-1} had rather higher IEC values ($\sim$0.1 mmol g^{-1}) than that of Nafion 117.

The ion-conductivity data versus the total content of sulfonic acid group in the blend films for four kinds of the copolymers cannot be represented by one curve as shown in Figure 7. Contrary to the data of the swellability and the IEC, the data of the ion-conductivity does not depend only on the total content of sulfonic acid group. The inner structure of the film may be different depending on the copolymer composition. The ion channel passing through the film thickness direction is influenced by phase-separation process of the film. However, all data show that the conductivity increases with increasing content of the sulfonic acid group and that the highest achievable values are in the same level of 10^{-2} S cm^{-1}, which is also same as that of Nafion 117. It should be noticed that the our blend films used for conductivity measurements had the equilibrium water content, while the Nafion film used for conductivity measurement had a lower water content (5 wt %) than its equilibrium.

The characteristics of the blend films are listed in Table II. The mark α indicates the case that our film has the same or higher level of the ion conductivity compared with that of Nafion 117 (data in Fig. 7). The mark β indicates the case that our film has the same or lower level of the swellability in water compared with that of Nafion 117. There is one compara-

TABLE II
Characteristics of the Blend Films of
$PVDF_x/P[HEAA_y\text{-}SSNa_{(100-y)}]_{(100-x)}$

Copolymer	PVDF, x (wt %)								
	10	20	30	40	50	60	70	80	90
P1	C	C	C	C	C	α	α, β	β	
P2	C	C	C	C	α		β	β	
P3	C	C	C	α	α		β	β	
P4	C	C	C	α			β	β	

C, the film of $PVDF_x/P[HEAA_y\text{-}SSNa_{(100-y)}]_{(100-x)}$ cracked on contacting with water; α, β, the film of $PVDFx/P[HEAA_y\text{-}SSH_{(100-y)}]_{(100-x)}$ had a higher value than that of Nafion in proton conductivity (α) and a lower value than that of Nafion in swelling ratio in water (β).

ble film on these two properties with Nafion 117, that is $PVDF_{70}/P[HEAA_3\text{-}SSH_{97}]_{30}$. This result comes from the quantity balance of hydrophobic part of the PVDF blend component and the polymer electrolyte part of the SSH sequence. The third component of the crosslinking agent HEAA should be minimized.

The tensile storage modulus is shown as a function of temperature for PVDF, $PVDF_{70}/P[HEAA_3\text{-}SSH_{97}]_{30}$, and Nafion 117 in Figure 8. The PVDF film was dried one. The Nafion 117 film used here contained 5.0 $\pm$ 0.5 wt % of water. Our blend film used here contained about 5 $\pm$ 3 wt % of water. The retention of high E' value up to 100 °C of the Nafion film is one of the remarkable properties as a fuel cell membrane. Although the water content is different
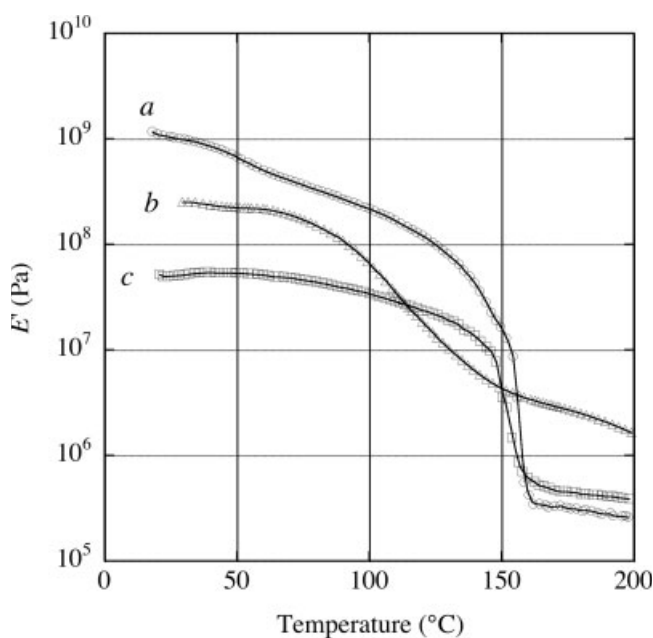

Figure 8 The storage modulus E' as a function of temperature. The heating rate was 10°C min^{-1}: (a) the dried PVDF film, (b) the Nafion 117 film with 5 wt % of water content, and (c) the mildly dried blend film of $PVDF_{70}/P1_{30}$.
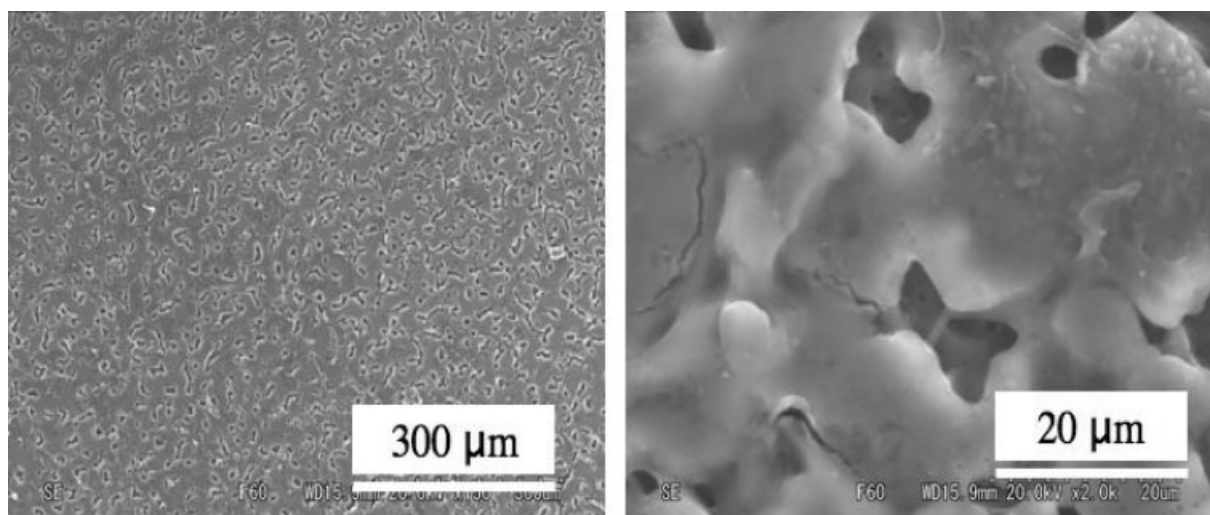
Figure 9 Scanning electron microscopic photos of the $PVDF_{60}/P1_{40}$ film with different magnifications show that the film is very porous one, so that the film swells well and the ion channel may be easily formed.

between our blend film and the Nafion film, the modulus of our blend film is somewhat lower than the Nafion film below 110 °C. This relationship reversed in a narrow temperature range between 110 and 150°C. The curve figure of our blend film was similar to that of the PVDF film especially at high temperatures above 150°C, where the PVDF is in the melt state. Since our copolymer is glassy amorphous material, it is very brittle regardless of crosslinking. So, the mechanical properties of our copolymers were difficult to measure. However, once the copolymer is blended with PVDF, the film blended becomes very tough film, because the PVDF material has a low glass transition temperature around −40°C and a high degree of crystallinity around 50 wt %.[13,14] This crystal nature raised and kept the modulus of our blend at a high level up to 160°C.

Figure 9 shows SEM photos of the film surface of $PVDF_{60}/P[HEAA_3\text{-}SSH_{97}]_{40}$. The most striking feature of the figure is the porous structure. This is the result of the shrinking of the film induced in the crosslinking process. The crosslinking is the dehydration process, and so, the porosity is due to the loss of the mass. The appearing of a number of porosity prevents the macroscopic change in film size. As the uncrosslinked film was stuck to the base of the Petri dish throughout the heating process for crosslinking, contraction of the film did not occur. This is the reason for making the film porous after the crosslinking.

CONCLUSIONS

A new type of ion-exchange membrane was produced by blending PVDF with our copolymer of poly (styrene sulfonic acid-*co*-N-(2-hydroxyethyl) acrylamide). The key material was a crosslinking agent of HEAA, which was previously copolymerized with sodium styrene sulfonic acid (the precursor of styrene sulfonic acid). Crosslinking reaction occurs by heating, after the precursor copolymer was blended with PVDF and formed to be a film shape. The crosslinked blend film of PVDF/copolymer was then cation-exchanged with proton. Only one of our membranes, $PVDF_{70}/P[HEAA_3\text{-}SSH_{97}]_{30}$, had the same level of performance with respect to ion-exchange capacity, ion-conductivity, and the degree of swellability. But, mechanical properties of our swollen membrane, which has comparable performance with the Nafion 117 membrane, were one order of magnitude smaller than the Nafion membrane. It was concluded that the excellency of Nafion 117 is high performance at low content of water, which may be due to the phase-separated structure having the very effective ion-channel.

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