Synthesis of Microphase-Separated Poly(styrene-*co*-sodium styrene sulfonate) Membranes Using Amphiphilic Urethane Acrylate Nonionomers as an Reactive Compatibilizer

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ABSTRACT: Microphase-separated poly(styrene-*co*-sodium styrene sulfonate) random copolymer (PSSU) membranes were fabricated through a new copolymerization process. Two immiscible monomers, styrene and sodium styrene sulfonate were dissolved in a single solvent and formed homogeneous solutions, which were directly converted to wall-to-wall membranes via radical copolymerization process with microphase separation. Since urethane acrylate nonionomer (UAN) chain has amphiphilicity as well as reactivity with vinyl monomers, UAN chain could act not only as compatibilizer for polystyrene and poly(sodium styrene sulfonate), but also as macrocrosslinker, which makes it possible for the formation of crosslinked copolymer of two immiscible polymers without macrophase separation. TEM image of the PSSU membranes showed that nanosized hydrophilic domains formed by hydrophilic/hydrophobic microphase separation were dispersed at hydrophobic matrix phase. PSSU membranes fabricated using UAN chain having longer chain length of polyethylene oxide showed bigger size of hydrophilic domains, which was also confirmed by TEM images. Fabricated PSSU membranes showed proton conductivity higher than 10^{-2} S/cm and methanol permeability lower than 10^{-7} cm^2/s of Nafion® 117 membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2150–2158, 2008

Key words: microphase separation; amphiphilic urethane acrylate; proton conducting polymer; methanol permeability

INTRODUCTION

The proton exchange membrane is the key component in solid polymer electrolyte fuel cells. The membrane acts as separator to prevent mixing of reactant gases and as an electrolyte for transporting protons from the anode to the cathode. Proton conductivity, mechanical strength, and chemical stability of the membrane are major factors that determine fuel cell performance. Nafion, perfluoropolymer having sulfonic acid groups at the terminal carbons of their branch chains, has been recognized as the best material for the proton conducting membrane. However, because of the relatively high cost of Nafion, a lot of researches have been carried out to develop alternatives.[1–3]

One of the representative alternative membranes is the proton exchange membrane based on hydrocarbon polymer. These membranes have been generally synthesized through (i) the sulfonation of aromatic polymer such as polystyrene, poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK), poly(1,4-phenylene), poly(oxy-1,4-phenylene), and poly(phenylene sulfide), (ii) the sulfonation of aromatic block copolymer ionomers, (iii) attaching ionic polymer graft to polymer backbone by grafting copolymerization, and (iv) copolymerization of ionic vinyl monomer having sulfonic group with hydrophobic vinyl monomers.[4–12]

In general, sulfonated aromatic polymers can be prepared through two kinds of methods. One is the sulfonation of aromatic polymer, and the other is copolymerization of nonsulfonated monomer and sulfonated monomer of aromatic polymers.[8–12] Unlike the sulfonation of aromatic polymers, the copolymerization of sulfonated monomer with nonsulfonated monomer can produce the sulfonated aromatic polymers containing well-defined degree of sulfonation. Styrene and sodium styrene sulfonate (NaSS) are representative nonsulfonated and sulfonated aromatic monomers, respectively. These monomers can be copolymerized only through heterogeneous polymerization processes such as emulsion polymerization, suspension polymerization, because their polymers cannot be dissolved using a single solvent.[13–16] In this study, we present the new

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synthetic process of poly(styrene-NaSS) copolymers using amphiphilic urethane acrylate precursor [urethane acrylate nonionomer (UAN)] as a reactive compatibilizer.

Conventionally, poly(styrene-NaSS) copolymers synthesized by emulsion polymerization process were hot-pressed or solvent-cast to fabricate proton exchange membranes. In our process, the solutions containing dissolved UAN, NaSS, and styrene in dimethyl sulfoxide (DMSO) at various compositions were directly converted to wall-to-wall sulfonate aromatic polymer membranes via a simple solution polymerization process where amphiphilic UAN chains acted not only as compatibilizer between polystyrene and poly(NaSS) but also as macromonomer copolymerized with styrene and NaSS. UAN has polypropylene-based hydrophobic segment and polyethylene oxide-based hydrophilic segment at the same backbone and can be copolymerized with several kinds of vinyl monomers because of reactive vinyl groups located at both ends of its polypropylene-based hydrophobic segment. We previously reported that this chain could form self-assembled nanostructure polymeric membranes through hydrophilic/hydrophobic microphase separation on external conditions.[17–19]

In this article, we first describe the synthesis of poly(styrene-co-NaSS) random copolymers having microphase-separated structure which will be confirmed by transmission electron microscopy (TEM) measurement. Three kinds of UAN chains having different chain length of polyethylene oxide segments were synthesized and used to investigate the effect of size of hydrophilic segments on the morphology of nanostructure of the membrane. Proton conductivity, ion exchange capacity (IEC), water-uptake behavior of the membranes synthesized at different compositions, and type of UAN chains will be also presented.

EXPERIMENTAL

Materials

In the synthesis of amphiphilic UAN precursor chains, poly(propylene oxide triol) (PPO triol, M_W = 1000, Aldrich Chemical, Milwaukee, WI), 2,4-toluene diisocyanate (TDI, Aldrich Chemical, Milwaukee, WI), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical, Milwaukee, WI), and polyethylene glycol (PEG, M_W = 200, 600, and 1500, Aldrich Chemical, Milwaukee, WI) were used. PPO triol and PEG were dried and degassed at 80°C and 3–5 mmHg for 2 days. Styrene, NaSS, 2,2′-azobisiso-butyronitrile (AIBN), and DMSO were purchased from Aldrich Chemical (Milwaukee, WI) and used as received.
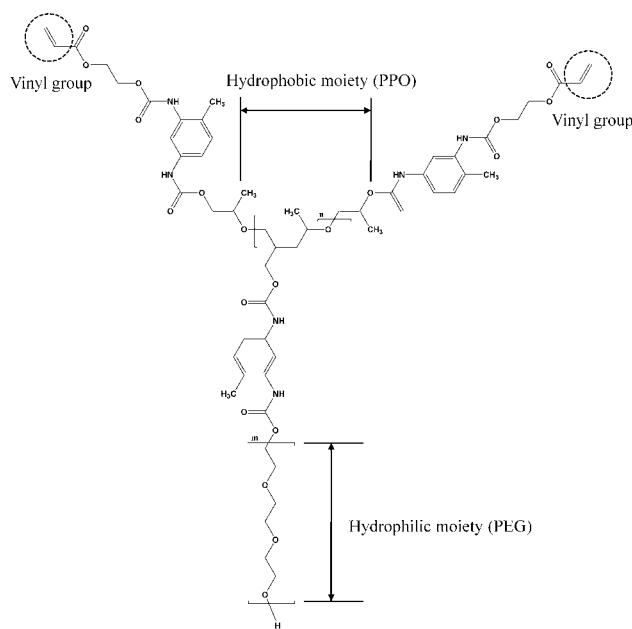

Figure 1 Schematic presentation for chemical structure of UAN.

Synthesis of UAN chain

Amphiphilic UAN precursor chains were synthesized by using an established three-step process as described in previous publication.[17–19] For the synthesis of UAN chain, molar ratio of TDI/PPO triol/2-HEMA/PEG was fixed as 3/1/2/1, and the detail synthetic procedure was illustrated in our previous articles.[17–19] At the same molar ratio, molecular weight of PEG used was varied from 200 to 1500 to control hydrophilicity of UAN chains. The Arabic numerals of UAN 200, UAN 600, and UAN 1500 indicate the molecular weight of PEG used in the synthesis of UAN chain. The molecular weight of UAN precursor chains were measured by Model 410 GPC equipped with Styragel HR1-4 column (Waters Associates) at 25°C. Average molecular weight of synthesized UAN chains is 4300–6700 (g/mol) with a polydispersity of 2.01. Expected molecular structure of UAN chain was schematically illustrated in Figure 1.

Synthesis of proton conducting membranes

Styrene, NaSS, and UAN were dissolved in DMSO to form homogeneous solution at various weight ratios. And then, radical initiator, AIBN was added to the mixtures and poured into a silicone-packed mold to carry out crosslinking copolymerization for 3–4 h at 70°C to obtain wall-to-wall membranes with 150-μm thickness. Obtained membranes were immersed in water–acetone mixture for 24 h for purification and then dried for 2 days. Before proton

TABLE I
Recipe for Fabrication of PSSU Membranes

Membranes	Ingredients (g)					
	UAN200	UAN600	UAN1500	Styrene	NaSS	DMSO
PSSU 200-1	1 (16.00 wt %)	–	–	4	1.25	15
PSSU200-2	2 (27.58 wt %)	–	–	4	1.25	15
PSSU200-3	3 (36.36 wt %)	–	–	4	1.25	15
PSSU200-4	4 (43.24 wt %)	–	–	4	1.25	15
PSSU600-1	–	1 (16.00 wt %)	–	4	1.25	15
PSSU600-2	–	2 (27.58 wt %)	–	4	1.25	15
PSSU600-3	–	3 (36.36 wt %)	–	4	1.25	15
PSSU600-4	–	4 (43.24 wt %)	–	4	1.25	15
PSSU1500-1	–	–	1 (16.00 wt %)	4	1.25	15
PSSU1500-2-1	–	–	2 (27.58 wt %)	4	1.00 *(14.29 wt %)	15
PSSU1500-2-2	–	–	2 (27.58 wt %)	4	1.25 (17.24 wt %)	15
PSSU1500-2-3	–	–	2 (27.58 wt %)	4	1.50 (20.00 wt %)	15
PSSU1500-3	–	–	3 (36.36 wt %)	4	1.25	15
PSSU1500-4	–	–	4 (43.24 wt %)	4	1.25	15

conductivity, swelling ratio, and methanol permeability measurements, sodium ions of films were exchanged for protons by immersion in $0.5M$ H_2SO_4 for 2 days, followed by rinsing and washing with deionized water several times. Obtained poly(styrene-NaSS-UAN) random copolymer membranes were named as PSSU membranes. The membranes synthesized using UAN 200, UAN 600, and UAN 1500 were also named as PSSU 200, PSSU 600, and PSSU 1500, respectively. Recipes for the synthesis of various PSSU membranes were presented in Table I in detail. Weight percent of UAN and NaSS in the membrane fabrication correspond to weight percent of UAN and NaSS in reactants (UAN, styrene, and NaSS) used for membrane fabrication, which were also calculated and presented in Table I.

Measurements

Water sorption experiments were performed by immersing five sheets of PSSU membranes into deionized water at 30°C for 24 h. Then the membranes were taken out, wiped with tissue paper, and immediately weighed on a microbalance. Water uptake of the membranes, W_{H_2O}, was evaluated from

$$W_{H_2O} = (W_1 - W_0)/W_0 \times 100(\%)$$

where W_0 and W_1 are the weights of dry and corresponding water-absorbed membranes, respectively. Water uptake of a PSSU membrane was calculated from the average value of W_{H_2O} of five membrane sheets.

The IEC value was measured by the classical titration (ASTM 2187) of the released amount of H^+ of the preweighed polymer in an acid from $1M$ NaCl with $0.01M$ NaOH by using a phenolphthalein indicator. The IEC value was recorded as an average value for each sample in units of milliequivalents of NaOH per gram of the polymer (mequiv./g).

Proton conductivity was determined using a galvanostatic four-point probe electrochemical impedance spectroscopy technique.[20] Impedance system 12608W consists of a frequency response analyzer 1260 and electrochemical interface 1287 (Solatron analytical, UK). A four-point-probe cell with two platinum wire outer current-carry electrodes and two platinum wire inner potential-sensing electrodes was mounted on a Teflon plate. Membrane samples were cut into strips that were ~ 1.0-cm wide and 4.0-cm long before mounting in the cell. The cell was placed in a thermohumidity controlled chamber to measure both temperature and humidity dependence of proton conductivity. From this method, a fixed AC current is passed between two outer electrodes, and the conductance of the material is calculated from the AC potential difference observed between the two inner electrodes. This method is relatively insensitive to the contact impedance and interfacial resistance at the current-carry electrode and is therefore well suited for measuring proton conductance. The measurement was carried out in the sealed cell to maintain suitable thermal-hydrated condition at 60°C and the proton conductivity was calculated from the following equation:

$$\sigma = L/(R \times S)$$

where σ is the proton conductivity (S/cm), L is the membrane thickness (cm), R is the resistance (Ω), and S is the effective membrane surface area for proton to migrate (cm^2).

The diffusion cell was used to determine the methanol permeability of the PSSU membranes. This glass cell consisted of two chambers each ~ 35 mL, separated by a membrane. One compartment of the cell (V_A) was filled with a $2M$ solution of methanol

in deionized water. The other (V_B) was filled with pure ionized water. The membrane (effective area 7.02 cm^2) was clamped between the two compartments and was kept under stirring throughout the experiment. A flux of methanol penetrates across the membrane resulted from concentration difference between the two compartments. Under pseudosteady-state condition, which prevailed during the experiment and for $C_A \gg C_B$, the methanol concentration in the receiving compartment as a function of time is given by

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0)$$

where C is concentration, A (cm^2) and L (cm) the membrane area and thickness; D (cm^2/s) and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively.[21] The assumptions are made in this study that D inside the membrane is constant and K does not depend on concentration. The product DK is the membrane permeability (P).

$$P = DK = \frac{1}{A} \frac{C_B(t)}{C_A(t - t_0)} V_B L$$

C_B is measured with a constant interval of 15 min during the experiment and the permeability is calculated from the slope of the straight line. The methanol concentrations were measured by gas chromatography with a thermal conductivity detector (Shimadtzu, model 14B, Tokyo, Japan). During permeability tests the temperature was controlled in a thermostatic water bath.

Transmission electron microscope (TEM, JEM 2020CX, JEOL), applying an acceleration voltage of 200 kV, was used to clarify the nanostructure of membranes. The membranes were embedded in an epoxy resin of Epon-812 supplied by SPI. Ultra-thin sections of the membranes with thickness of $\sim$70 nm were prepared at -60°C by a ultramicrotome of Ultracut R made by Leica. Carbon was vacuum-evaporated on the thin sections to prevent accumulation of electrons during TEM observation. The membranes were immersed in OsO$_4$ (2 wt %) aqueous solution for 1 day and rinsed with water to stain the hydrophilic domains of the membranes.

RESULTS AND DISCUSSION

Synthesis of poly(styrene-NaSS-UAN) (PSSU) membrane and their microstructure

Because of the immiscibility between polystyrene and poly(NaSS), poly(styrene-NaSS) copolymers can be synthesized only through emulsion copolymeriza-tion or graft copolymerization process. In this study, styrene and NaSS were copolymerized via a solution polymerization process in the presence of amphiphilic UAN acting as reactive compatibilizer.

Two kinds of solutions were first prepared to synthesize poly(styrene-NaSS) copolymers. One is prepared by dissolving styrene and NaSS in DMSO. The other is prepared by dissolving styrene, NaSS, and UAN in DMSO. These two solutions were poured in silicone-packed mold and placed at 70°C for 3 h like curing process of thermosetting plastic such as epoxy or phenol resin. After curing process, the solution without UAN chains was changed to opaque liquid and did not form solid film. This result can be interpreted as due to the insolubility of polystyrene in DMSO and incompatibility between polystyrene with poly(NaSS). That is, even though styrene and NaSS could be completely dissolved in DMSO and form homogeneous solution, polystyrene formed in the course of polymerization was precipitated from the solution because of the insolubility of polystyrene in DMSO, as a consequence, styrene and NaSS could not be copolymerized in DMSO solution.

However, the solution containing UAN chains was converted to wall-to-wall semitransparent membrane after curing process, which can be explained by amphiphilic property and vinyl group reactivity of UAN chains. Since UAN chain has hydrophobic PPO segment and hydrophilic polyethylene oxide segment at the same backbone, UAN chain can act as compatibilizer for hydrophobic polystyrene and hydrophilic poly(NaSS). In addition, because of reactive vinyl groups of UAN chains, UAN chains can be copolymerized with NaSS and styrene and act as macrocrosslinker. Consequently, the solutions containing styrene, NaSS, UAN, and DMSO were directly converted to wall-to-wall membranes (PSSU membrane) without macrophase separation. Figure 2 shows photographs of dried (a) and water-swollen (b) PSSU random copolymer membranes. As seen, dried membrane is transparent and freestanding film and swollen membrane is little opaque.

In addition, there was a critical concentration of UAN for formation of wall-to-wall membrane. For fabrication of PSSU 200 and 600 membranes, weight percent of UAN 200 and UAN 600 in reactants, as presented in Table I, should be higher than 36.63 and 43.24%, respectively to obtain wall-to-wall membrane. That is, only PSSU 200-4, PSSU 600-3, and 600-4 could be fabricated among various compositions presented in Table I. For UAN 1500, PSSU membrane could be formed at the lower weight percent (28.57%) compared with UAN 200 and UAN 600, so it can be thought that UAN 1500 is a better compatibilizer for polystyrene and poly(NaSS) compared with UAN 200 and UAN 600.
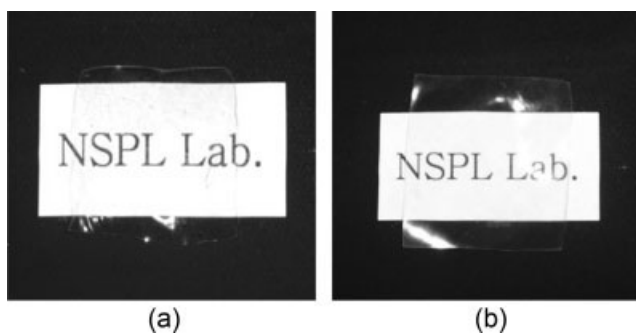
Figure 2 Photographs of (a) dried PSSU membrane and (b) water-swollen membrane.

Figure 3(a–c) shows the TEM images of the PSSU membranes fabricated using different UAN chains, which was stained by OsO$_4$ aqueous solution before measurement.[22] These pictures show that dark spots were dispersed within whole matrix. Since OsO$_4$ aqueous solution is absorbed only by hydrophilic moieties (PEO segments of UAN and sulfonate groups of NaSS), it can be thought that the dark spots dispersed within matrix represent the hydro-

philic domains of PSSU membranes. So, it can be confirmed by these pictures that PSSU membranes have microphase-separated structure where hydrophilic domains are dispersed within hydrophobic matrix. That is, in the course of copolymerization, hydrophilic moiety (PEO segments of UAN and sulfonic groups of NaSS) and hydrophobic moiety (PPO-based hydrophobic segment of UAN and styrene) are microphase-separated from each other and form hydrophilic domains and hydrophobic domains, respectively. This is because amphiphilic UAN chains prevent macrophase separation between two immiscible polymers [polystyrene and poly(NaSS)] in the course of copolymerization, which is schematically presented in Figure 4. In the absence of UAN at styrene/NaSS/DMSO solution, polystyrene and poly(NaSS) are macrophase separated in the course of copolymerization, which made it impossible to fabricate poly(styrene-NaSS) copolymer membranes.

As seen in TEM images of Figure 3(a–c), PSSU membranes, synthesized using UAN 200, UAN 600, and UAN 1500, respectively, showed different sizes
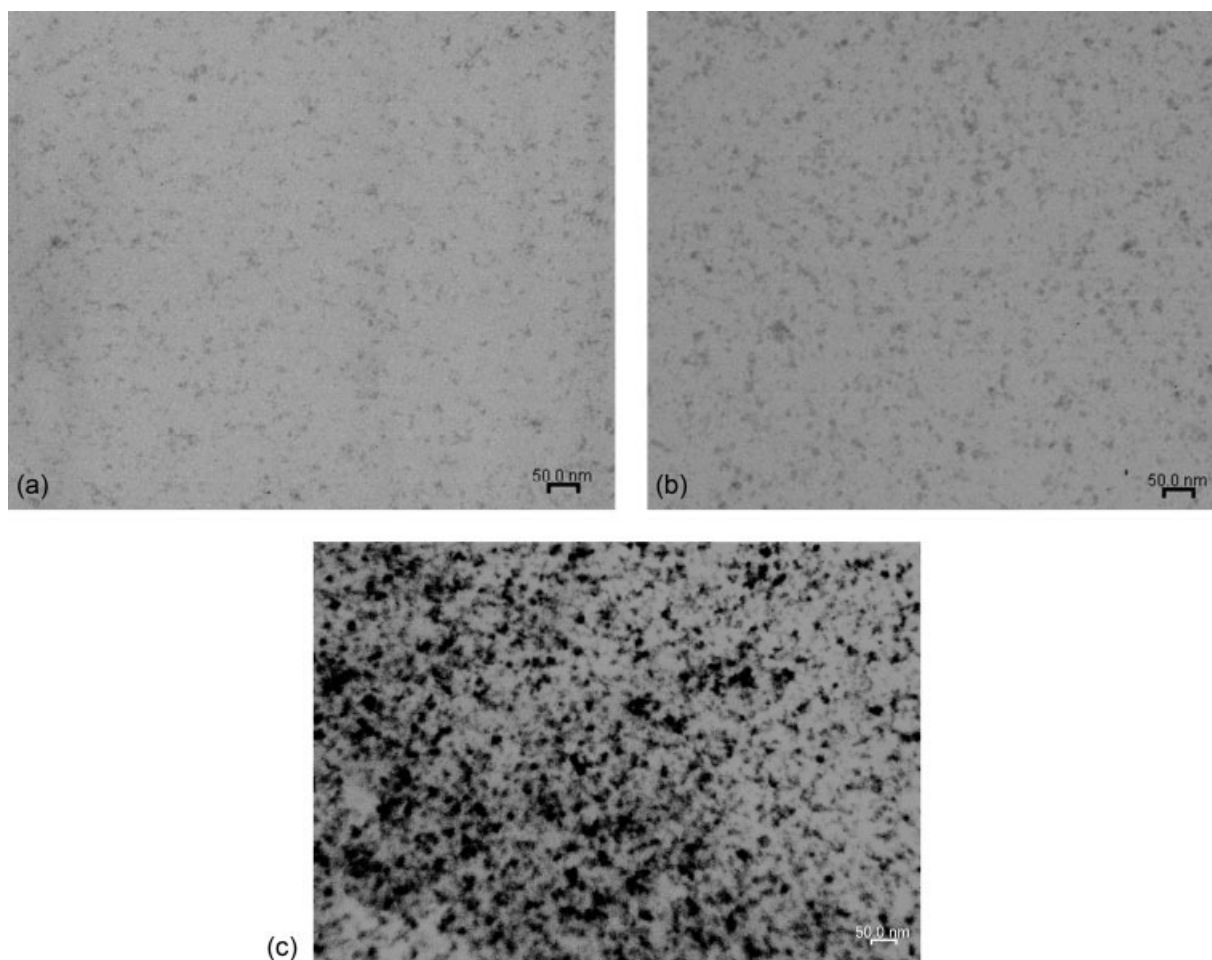

Figure 3 TEM image of microstructure of (a) PSSU 200, (b) PSSU 600, and (c) PSSU 1500 membranes.
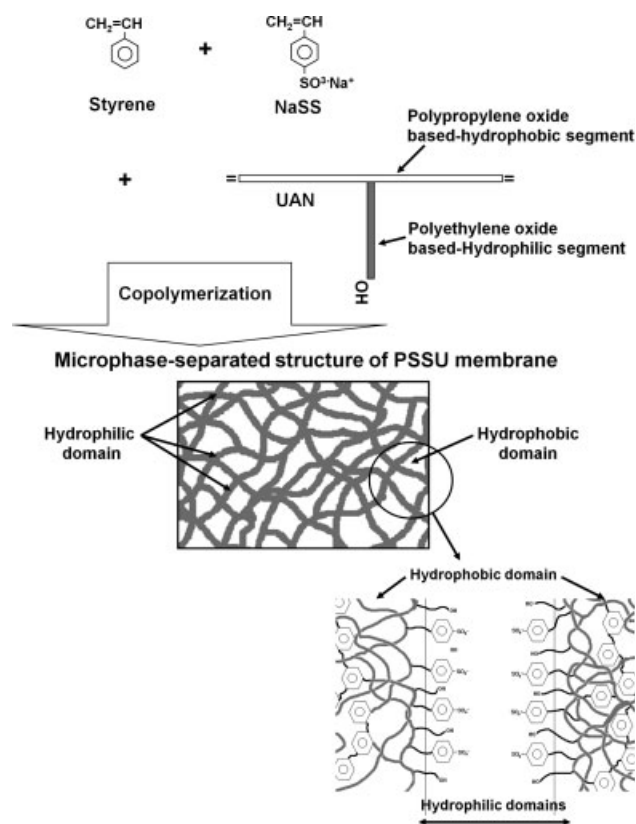
Figure 4 Schematic presentation of formation of PSSU membranes.

of hydrophilic domains dispersed within whole matrix. PSSU 1500 synthesized using UAN 1500 showed the bigger size of hydrophilic domains (average size is about 33.97 nm) compared with PSSU 600 (17.45 nm) and PSSU 200 (11.24 nm). This result can also be explained as due to the longer chain length of PEO segment at UAN 1500 chains used for the synthesis of PSSU 1500 membranes. That is, UAN 1500 chains having the longest chain length of PEO segment form the biggest hydrophilic domains through hydrophilic/hydrophobic microphase separation in the course of copolymerization.

Figure 5 shows biphasic swelling behavior of PSSU membranes. Three kinds of membranes were prepared at the same weight ratio of UAN/styrene/NaSS (4/4/1.25). When PSSU membranes fully swollen in water were transferred into toluene, the membranes were swollen again by absorbing toluene. Unlike conventional polymer network, PSSU membranes can absorb two immiscible solvents at the same time within the same network. We previously reported that crosslinked polymer films having microphase-separated structure formed by hydrophilic/hydrophobic microphase separation could absorb two immiscible solvents at the same time and same networks (biphasic swelling behavior). So, this interesting swelling behavior could be used as a

proof for formation of microphase-separated structure in polymer films.[23,24]

When PSSU membranes were immersed in water, only hydrophilic domains absorbed water and were swollen but its hydrophobic domains remained intact. When swollen membranes by water were transferred into toluene, hydrophobic domains absorbed toluene and were reswollen while its hydrophilic domains remained as swollen by water. This result also indicates that the PSSU membranes have nanoscaled heterogeneous biphasic structure formed by hydrophilic/hydrophobic microphase separation.

In addition, interesting swelling behavior is that PSSU 1500 membranes showed different swelling ratio in water but almost same swelling ratio in toluene. That is, even though PSSU 1500 showed higher water-swelling ratio than PSSU 600 and PSSU 200, these membranes showed almost same reswelling ratio in toluene. These membranes have the same content of sulfonic group in the networks, because all PSSU membranes were prepared with the same weight ratio of UAN/styrene/NaSS (4/4/1.25). So, higher water-swelling ratio of PSSU 1500 can be attributed to longer chain length of polyethylene oxide of UAN 1500 used in the membranes fabrication. In other words, as seen in Figure 3(a–c), PSSU 1500 has the biggest hydrophilic domains, resulting in the highest swelling ratio in water.

Proton conductivity and methanol permeability

Figure 6 shows proton conductivity of PSSU membranes fabricated using various amounts and type of UAN chain at the same composition of styrene and NaSS. As earlier mentioned, PSSU 200 and PSSU 600 membranes could be fabricated at only single (43.24%) and two compositions (36.63 and 43.24%), respectively (See Table I). So, proton conductivity of PSSU 200 and 600 membranes were measured at
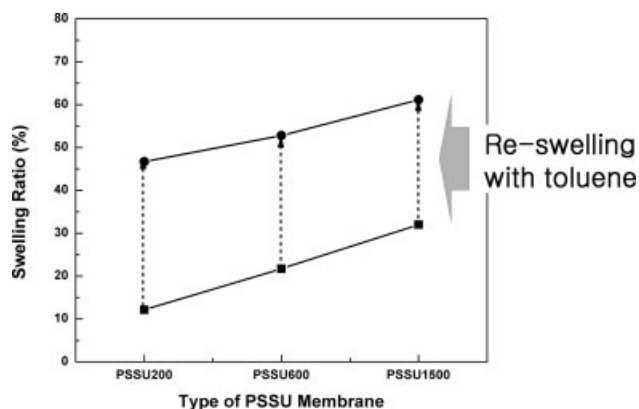

Figure 5 Biphasic swelling ratio of PSSU membranes (■- swelling at water, ●- reswelling with toluene).
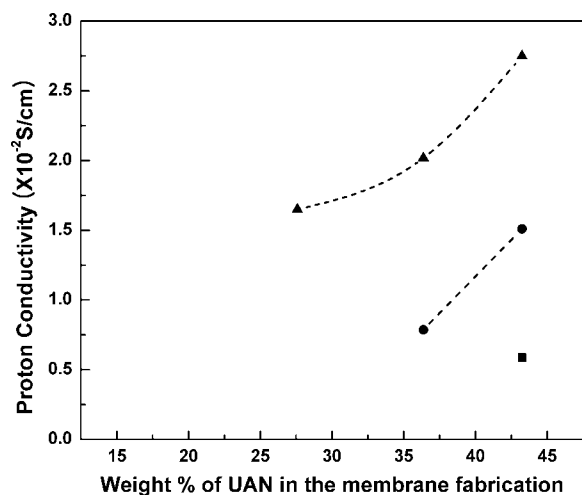
Figure 6 Proton conductivity of PSSU membranes as a function of weight percent of UAN in the fabrication composition (■- PSSU 200, ●- PSSU 600, and ▲- PSSU 1500).
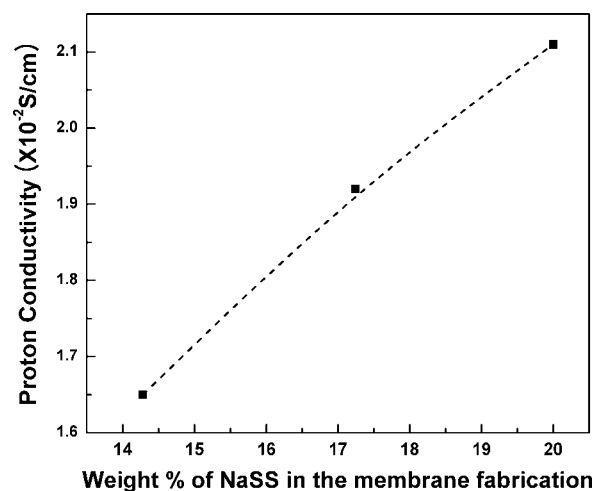

Figure 7 Proton conductivity of PSSU 1500 membranes as a function of weight percent of NaSS in the fabrication composition.

single composition (PSSU 200-4) and two compositions (PSSU 600-3 and 600-4) and presented as a single point and two points in Figure 6. PSSU 1500 membranes could be prepared at relatively lower amount of UAN (27.58 and 36.36 wt %) in the compositions, so that their conductivity was presented as three different points in Figure 6.

At the same composition of UAN/styrene/NaSS, PSSU 1500 membrane showed higher proton conductivity than PSSU 200 and 600 membranes. This can be interpreted as being due to the bigger size of hydrophilic domains formed at PSSU 1500 membrane, as presented in Figure 3(c). PSSU 1500 also showed higher water uptake compared to PSSU 200 and PSSU 600 (See Fig. 5). This result also indicates that PSSU 1500 membrane has bigger hydrophilic domains than PSSU 200 and 600 membranes. The proton transport mechanism in the sulfonated polymer membranes is complicated, but the vehicle mechanism and the hopping mechanism could be used for explaining the proton conduction of the sulfonated membrane in the hydrate state.[24–26] According to the vehicle mechanism, a proton can combine with molecules such as water and methanol, and form complex ions including H_3O^+ and $CH_3OH_2^+$, and then the proton can be transported along with the complex ions. So, degree of water uptake of a membrane is a critical factor in determining its proton conductivity. High water content in the sulfonated polymers generally guarantees excellent proton conductivity. Therefore, sulfonated polymers with a high water uptake can be desirable for proton conductivity.[25–27] So, it can be thought that the bigger hydrophilic domains formed at PSSU 1500 could absorb larger amount of water, resulting in higher conductivity of PSSU 1500 membranes.

Figure 7 shows the proton conductivity of the PSSU 1500 membranes synthesized at various weight percents of NaSS in reactants for membrane fabrication (See Table I). The proton conductivity of the membranes increased with the increase of weight percent of NaSS in the preparation composition. This result can be explained in terms of increased sulfonic acid group content of membranes at the greater weight percent of NaSS in the preparation composition. As presented in Figure 5, water-swelling ratio of PSSU 1500 membranes increased from 20 to 30% with the increase of weight percent of NaSS from 14.29 to 20 wt %. So, it can be thought that bigger hydrophilic domains formed at the greater weight percent of NaSS caused the higher conductivity of membranes.

Methanol permeability of PSSU membranes was also measured and presented in Table II. Even though high water content in the sulfonated polymers generally guarantees excellent proton conductivity, high water uptake can induce undesired side

TABLE II
Methanol Permeability, Water-Swelling Ratio, Methanol-Swelling Ratio and Methanol, and IEC Value

Membranes	IEC values (mequiv./g)	Methanol permeability (cm^2/s)	Swelling ratio at methanol (%)
PSSU200-4	0.62	2.33×10^{-7}	38.60
PSSU600-3	0.69	4.83×10^{-7}	39.06
PSSU600-4	0.78	6.07×10^{-7}	40.89
PSSU1500-2-1	0.81	2.01×10^{-7}	26.70
PSSU1500-2-2	1.14	3.38×10^{-7}	24.21
PSSU1500-2-3	1.11	8.13×10^{-7}	26.71
PSSU1500-3	1.04	6.78×10^{-7}	29.99
PSSU1500-4	1.02	7.88×10^{-7}	40.89

effects such as low mechanical strength, poor hydrolytic stability, low dimensional stability, and high methanol permeability, especially in DMFC applications. So a proton conducting membrane should have proper level of water uptake to reduce methanol permeation with maintaining acceptable level of proton conduction.[25–27]

At the same weight ratio of UAN/styrene/NaSS in the preparation composition, PSSU 200 membranes showing the lowest water uptake and proton conductivity exhibited the lowest methanol permeability. This can be interpreted as due to the smallest hydrophilic domain formed at PSSU 200 membranes. When proton conduction occurs through hydrated hydrophilic domains, large molecules such as methanol can permeate through these hydrophilic channels. High methanol permeation is a serious obstacle in the PEM for DMFC. Methanol permeability strongly depends on hydrophilic channel size, water uptake, membrane compaction, and other operating conditions.[25,26] As mentioned earlier, PSSU 200 membranes were fabricated using UAN 200 having the smallest chain length of polyethylene oxide, so that the smallest size of hydrophilic domains were formed at hydrophobic matrix. Consequently, methanol permeation through hydrophilic domains of PSSU 200 is largely retarded. The highest methanol permeability of PSSU 1000 membranes could also be explained as being due to their bigger hydrophilic domains.

Even though methanol permeability of PSSU 1500 membranes is higher than PSSU 200 and 600 membranes and increased with the weight percent of NaSS in the preparation composition, their methanol permeability was much lower compared to that of Nafion® 117 ($P_{\text{Nafion}117}$ = 2.8 $\times$ 10^{-6} cm^2/s, measured). That is, PSSU 200 and 600 exhibited much reduced methanol permeability compared to Nafion® 117. This reduced methanol permeability of PSSU membranes may be because of their microphase-separated structure. As presented in Figures 3 and 5, PSSU membranes have dispersed nanosize hydrophilic domains formed by hydrophilic/hydrophobic microphase separation. So, it can be thought that their nanosized hydrophilic domains largely hinder methanol permeation through PSSU membranes.

CONCLUSIONS

New proton conductive membranes could be fabricated through a simple copolymerization process like curing process of epoxy or unsaturated polyester resins. Fabricated PSSU membranes showed proton conductivity higher than 10^{-2} S/cm and methanol permeability lower than Nafion membranes, which is due to the microphase-separated structure of PSSU membranes.

UAN having amphiphilicity and reactivity with vinyl groups prevented macrophase separation between two immiscible polymers polystyrene and poly(NaSS), but caused microphase separation between hydrophilic moieties and hydrophobic moieties in the membranes, resulting in formation of microphase-separated structure. This microphase-separated structure is locked-in by crosslinking copolymerization reaction. TEM image of the PSSU membranes showed that nanosized hydrophilic domains formed by hydrophilic/hydrophobic microphase separation were dispersed at hydrophobic matrix phase. These nanosized hydrophilic domains enhanced proton conduction and hindered methanol permeation.

Size of hydrophilic domains formed at the membranes could be controlled by varying the chain length of polyethylene oxide segments of UAN used in the fabrication of the membranes. Consequently, proton conductivity, water uptake, and methanol permeability could be varied by changing size of hydrophilic domains formed at the membranes. PSSU membranes having bigger size of hydrophilic domains exhibited higher proton conductivity, water uptake, and methanol permeability, due to the bigger size of hydrophilic domains.

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