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Proton Conducting Crosslinked Membranes by Polymer Blending of Triblock Copolymer and Poly(vinyl alcohol)

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Abstract: Proton conducting crosslinked membranes were prepared using polymer blends of polystyrene-*b*-poly(hydroxyethyl acrylate)-*b*-poly(styrene sulfonic acid) (PS-*b*-PHEA-*b*-PSSA) and poly(vinyl alcohol) (PVA). PS-*b*-PHEA-*b*-PSSA triblock copolymer at 28:21:51 wt% was synthesized sequentially using atom transfer radical polymerization (ATRP). FT-IR spectroscopy showed that after thermal (120 °C, 2 h) and chemical (sulfosuccinic acid, SA) treatments of the membranes, the middle PHEA block of the triblock copolymer was crosslinked with PVA through an esterification reaction between the -OH group of the membrane and the -COOH group of SA. The ion exchange capacity (IEC) decreased from 1.56 to 0.61 meq/g with increasing amount of PVA. Therefore, the proton conductivity at room temperature decreased from 0.044 to 0.018 S/cm. However, the introduction of PVA resulted in a decrease in water uptake from 87.0 to 44.3%, providing good mechanical properties applicable to the membrane electrode assembly (MEA) of fuel cells. Transmission electron microscopy (TEM) showed that the membrane was microphase-separated with a nanometer range with good connectivity of the SO_3H ionic aggregates. The power density of a single H_2/O_2 fuel cell system using the membrane with 50 wt% PVA was 230 mW/cm^2 at 70 °C with a relative humidity of 100%. Thermogravimetric analysis (TGA) also showed a decrease in the thermal stability of the membranes with increasing PVA concentration.

Keywords: polymer electrolyte membrane fuel cell (PEMFC), crosslinked, triblock copolymer, proton conductivity, polymer blend.

Introduction

Polymer electrolyte membranes, referred to as proton exchange membranes, are the most promising electrolyte medium for low temperature fuel cells. The ideal membranes are chemically, mechanically, thermally and electrochemically stable, maintaining a high proton conductivity and low cost. Generally, polymer electrolyte membranes are ion containing polymers bearing pendant cation-exchange sites such as sulfonic acids.[1-3] Upon hydration of a membrane, the ionic clusters of sulfonic acid groups are expanded, leading to an interconnected network of ionic channels that account for efficient proton transport. The most common polymer electrolyte membranes used in fuel cells are perfluorinated polymer membranes, e.g. the Nafion membrane. These membranes exhibit excellent thermal, mechanical and electrochemical properties, but their commercialization to fuel cells is limited to some degree by disadvantages such as high cost, high methanol permeability, and loss of membrane performance at evaluated temperature/low humidity conditions. Over the past years, thus, significant research efforts have been devoted to the development of alternative sulfonated polymeric materials to perfluorinated membranes.[1-5]

Concerning the improvement of the efficiency of fuel cells, a high proton conductivity of sulfonated polymer membranes has been considered essential. The properties of proton transport are strongly associated with the water uptake of membranes. Thus, sulfonated polymers with the high degree of sulfonation exhibit high proton conductivity but consequently high water uptake (swelling), leading to their inadequate use for fuel cells or other applications. Thus, crosslinking has been used as a good solution to maintain a proper sulfonation level and to enhance the mechanical properties.[6-10]

Recently, significant interest has turned to block copolymers containing ionic groups. Block copolymers possess well-known and well-defined structures that confer ordered morphologies.[11,12] Various morphologies such as hexagonal cylinders, close-packed spheres, bicontinuous phases, and other structures can be achieved by changing the relative length or the degree of segregation of the blocks. Incorpora-

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tion of ionic groups into block copolymers provides a system where conductivity and structure can be tuned and their correlation can be studied systematically. Especially, the use of microphase-separated block copolymers may allow to control the swelling of the ion conducting domains by the surrounding non-conducting domains, and to reduce the methanol permeability due to decreased swelling.[13-17]

Poly(vinyl alcohol) (PVA) is an attractive material for preparing proton exchange membranes because PVA can function as a good methanol barrier.[18] In addition, PVA has good mechanical properties and chemical stability, which are adequate for preparing polymer electrolyte membranes.[19] Although PVA itself does not possess fixed ionic charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be successfully incorporated into membranes to impart hydrophilicity or charged properties.[20]

In this work, proton conducting crosslinked membranes were prepared using polymer blends of polystyrene-*b*-poly(hydroxyethyl acrylate)-*b*-poly(styrene sulfonic acid) (PS-*b*-PHEA-*b*-PSSA) and poly(vinyl alcohol) (PVA). The middle PHEA block of triblock copolymer was crosslinked with PVA via the esterification reaction using sulfosuccinic acid (SA) as a crosslinking agent. Several characteristics of crosslinked polymer electrolyte membranes, e.g. ionic exchange capacity (IEC), proton conductivity, water uptake, thermal properties and single cell performance are reported in this paper.

Experimental

Materials. Styrene (99%), 2-hydroxyethyl acrylate (HEA, 99%), 4-styrenesulfonic acid sodium salt hydrate (SSA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), methyl 2-bromopropionate (MBP) and sulfosuccinic acid (70 wt% in water), poly(vinyl alcohol) (PVA, 99% hydrolyzed, M_n 85,000) were purchased from Aldrich and used as received without further purification.

Synthesis of PS-Br Macroinitiator. In a 250 mL pearshaped flask, 20 g of styrene, 0.296 g of CuCl, and 1.24 mL of HMTETA were added. This green mixture was stirred until it formed a homogeneous solution. The solution was purged with nitrogen for 30 min, and then 0.22 mL of MBP was added. The mixture was placed in a 110 °C oil bath for 5 h. After polymerization, the polymer product was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-Br homopolymer was then dried in a vacuum oven overnight at room temperature.

Synthesis of PS-*b*-PHEA Diblock Copolymer. In a 250 mL pearshaped flask, 6 g of PS-Br was dissolved in 10 mL of toluene. Then, 6.5 mL of HEA, 0.089 g of CuCl, and 0.372 mL of HMTETA were added to the solution. This green mixture was stirred until a homogeneous solution formed. The solution was purged with nitrogen for 30 min, and then placed in a 50 °C oil bath for 7 h. After polymerization, the block copolymer was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-*b*-PHEA diblock copolymer was then dried in a vacuum oven overnight at room temperature.

Synthesis of PS-*b*-PHEA-*b*-PSSA Triblock Copolymer. In a 250 mL pearshaped flask, 5 g of PS-*b*-PHEA and 60 mL of NMP were added. The contents were stirred until the PS-*b*-PHEA completely dissolved. Ten grams of SSA dissolved in 50 mL of DMSO was added to the flask. Then, 0.074 g of CuCl and 0.31 mL of HMTETA were added to the solution. This green mixture was stirred until homogeneous, and then was purged with nitrogen for 30 min. The mixture was placed in a 110 °C oil bath for 24 h. After passing the solution through an activated Al_2O_3 column to remove the catalyst, the polymer was precipitated out with methanol. The PS-*b*-PHEA-*b*-PSSA triblock copolymer was dried in a vacuum oven overnight at room temperature.

Preparation of Crosslinked Triblock Copolymer/PVA Membrane. 1 g of PS-*b*-PHEA-*b*-PSSA triblock copolymer was dissolved in 20 mL of DMSO with stirring. Different amounts of PVA and SA were added into the solution and stirred for more than 2 h. The concentration of SA was always fixed at 10 wt% relative to total amounts of membrane. The mixtures were cast on a Teflon-coated glass dish, and dried in an oven at 80 °C for two days. The obtained membranes were peeled off from the dishes and then annealed at 120 °C for 2 h for crosslinking reaction. The membranes were washed with water several times to remove unreacted SA.

Ion Exchange Capacity (IEC). IEC of the membranes was measured by the classical titration method. The membranes were soaked in 1.0 M NaCl solution for 24 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated against 0.01 M standardized NaOH solution, using phenolphthalein indicator. The experimental IEC of the membranes was calculated using the following equation.

$$\text{IEC(mEq/g)} = \frac{X \times N_{NaOH}}{\text{Weight(polymer)}} \quad (1)$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

Proton Conductivity. A four-point probe method was used to measure the proton conductivity of the membranes using home made conductivity cell. The salt-form membranes were converted into the acid form by submersing in 0.5 M H_2SO_4 solution for 16 h, followed by washing with deionized water. Before the measurement of proton conductivity, the prepared membranes were equilibrated with

deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz-8 MHz at 25 °C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots.

Water Uptake. Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of the membrane was determined from

$$\text{Water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

where W_w and W_d are the weights of wet and dried membranes, respectively.

Characterization. FT IR spectra were recorded Excalibur Series FT IR (DIGLAB Co.) instrument between the frequency range of 4000 to 400 cm^{-1} using ATR facility. TEM picture was obtained from a Philips CM30 microscope operating at 300 kV after ion-exchanging with 1 M $AgNO_3$ aqueous solution. Tensile evaluation was performed on universal testing machine (UTM, a LR10KPlus Series) at a speed of 5 mm/min. TGA data were obtained from thermogravimetry analyzer (Mettler Toledo TGA/SDTA 851e) at a heating rate of 10 °C/min under N_2 atmosphere.

Electrochemical Single Cell Performances. The membrane-electrode assemblies (MEA) were fabricated using catalyst coated membrane method with a well-dispersed catalyst slurry. The catalyst slurry was sprayed on the membranes at ambient temperature. The resulting MEAs were dried at 60 °C in a vacuum oven. 20 wt% Pt/C (E-TEK, NJ, USA) was used to make a catalyst slurry and the Pt loading content on each electrode was 0.3 mg/cm^2. Meanwhile, Pt black and Pt-Ru black (Johnson Matthey Fuel Cells, PA, USA) were used for electrode fabrication with a constant loading content of 3 mg/cm^2.

Results and Discussion

PS-*b*-PHEA-*b*-PSSA triblock copolymer was synthesized using atomic transfer radical polymerization (ATRP). First, the homopolymerization of styrene in bulk initiated by MBP/CuCl/HMTETA was carried out at 110 °C for 5 h. PS-*b*-PHEA diblock copolymer was then synthesized using PS-Br and CuCl/HMTETA as a macroinitiator and catalyst/ligand complex, respectively. PS-*b*-PHEA-*b*-PSSA triblock copolymer was sequentially synthesized using solution polymerization with cosolvent, i.e. NMP and DMSO. The chemical structure and composition of the triblock copolymer was confirmed by ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectrum of the PS-*b*-PHEA-*b*-PSSA triblock copolymer. Signals (a) at 7.5 and (b) at 7.0 ppm are attributed to

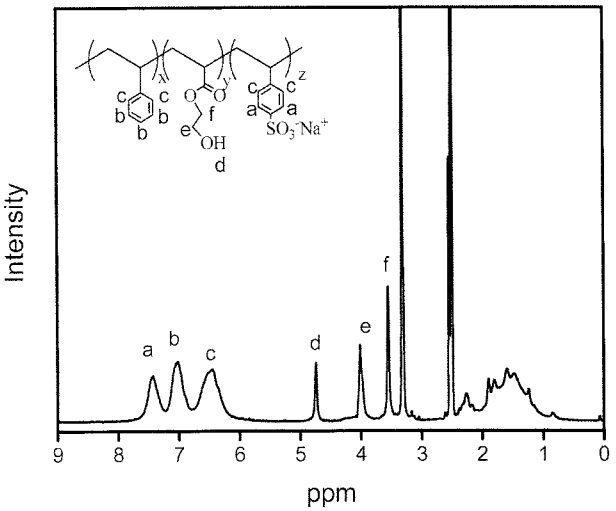
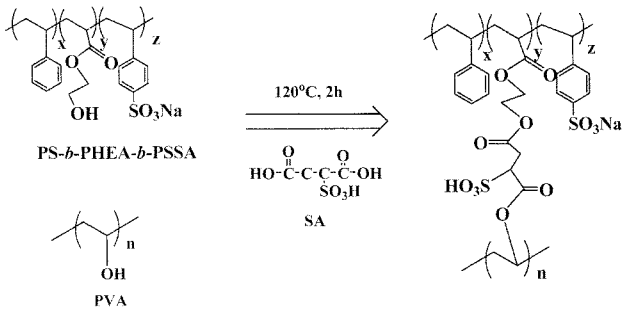


Figure 1. ^{1}H NMR spectrum of the PS-*b*-PHEA-*b*-PSSA triblock copolymer.



Scheme I. Synthetic procedures for the crosslinked membranes consisting of PS-*b*-PHEA-*b*-PSSA triblock copolymer and PVA via SA.

the benzene groups of the PSSA and PS, respectively.[21] The signals (d, e, f) at 4.8, 4.0, and 3.6 ppm are a result of the middle block, PHEA.[22] The composition of the triblock copolymer was determined from the integral ratio of the signals originating from the PS block at 7.0 ppm (signal b), the PHEA block at 4.0 ppm (signal e), and the PSSA block at 7.5 ppm (signal a). It is thus found that the triblock copolymer has a composition of 28:21:51 wt% PS-*b*-PHEA-*b*-PSSA, and the synthesis of block copolymer via ATRP was successful.

The synthetic procedures for crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes are presented in Scheme I. The resultant triblock copolymer and PVA was crosslinked with SA via the esterification between -OH of PHEA (or PVA) and -COOH of SA. Since SA contains sulfonic acid groups, crosslinked PHEA/PVA blocks became proton conducting domains. Thus the crosslinked membranes consist of the hydrophobic nonconducting PS block, the crosslinked conducting PHEA/PVA block and the hydrophilic conducting PSSA block.

Figure 2 shows the FT IR spectra of PS-*b*-PHEA-*b*-PSSA

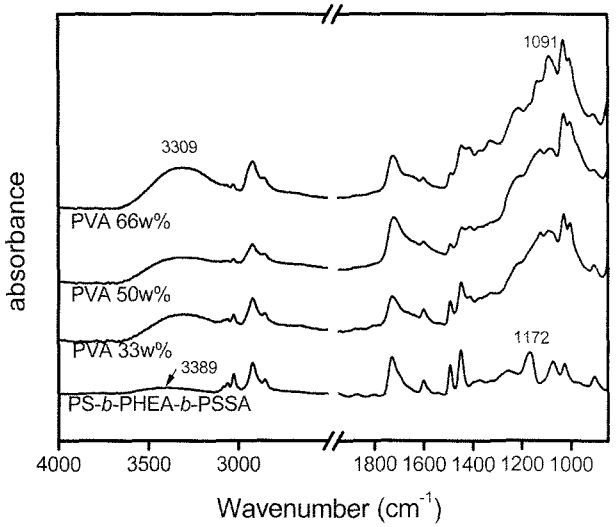


Figure 2. FT IR spectra for the PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations.

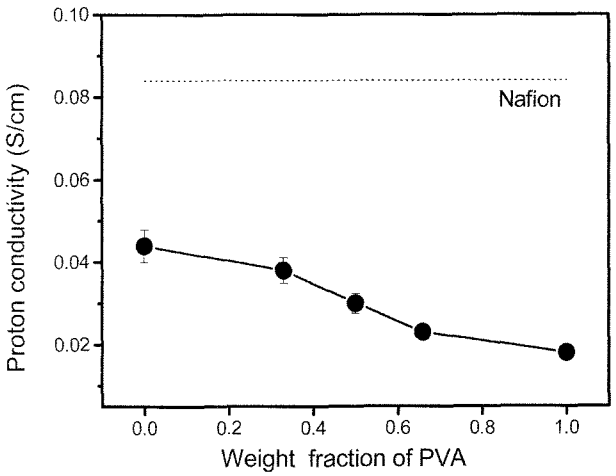


Figure 4. Proton conductivity for the PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations.

triblock copolymer and the crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes with SA at 120 °C for 2 h. The pristine uncrosslinked PS-*b*-PHEA-*b*-PSSA exhibited the stretching bands at 3389 and 1172 cm^{-1}, attributed to -OH of the water mostly bounded to PSSA and the sulfonic group with a sodium form, respectively. With increasing amounts of PVA in membranes, the stretching band of -OH became more intensive and shifted to a lower wavenumber at 3309 cm^{-1}. It is because the stretching band appears at a lower wavenumber as hydrogen bonding interaction is stronger. Because of the different form of sulfonic acid group in SA from PSSA, the crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membrane exhibited the stretching band at a higher wavenumber of 1091 cm^{-1} for sulfonic group.[23]

The IEC value represents the quotient of the molar content of sulfonic acid groups to membrane weight. The IEC

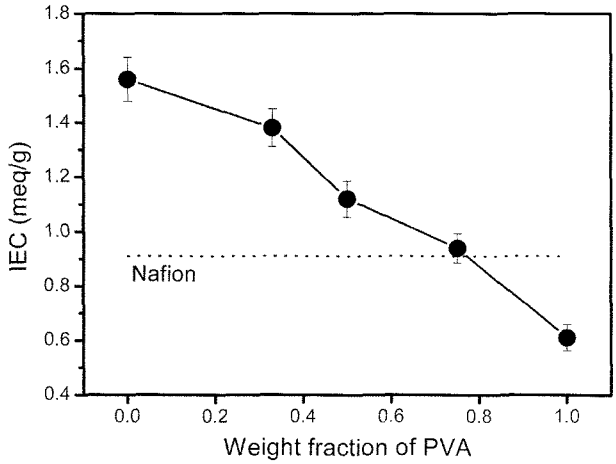


Figure 3. IEC for the PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations.

data of PS-*b*-PHEA-*b*-PSSA/PVA membranes are presented in Figure 3. The IEC values continuously decreased from 1.56 to 0.61 meq/g with increasing amounts of PVA, mostly due to the reduced portion of charged groups in the membrane. The membrane with 50 wt% of PVA exhibited 1.1 meq/g of IEC value, which is slightly higher than that of Nafion. Higher IEC values of the membrane demonstrate that the higher amounts of sulfonic aicd groups are contained in the membranes.

The proton conductivities of PS-*b*-PHEA-*b*-PSSA/PVA membranes are shown in Figure 4. As shown in this figure, proton conductivities were largely dependent upon the contents of PVA mostly due to different concentrations of acidic SO_3^- groups. Overall the proton conductivities of PS-*b*-PHEA-*b*-PSSA/PVA membranes were in the order of ~10^{-2} S/cm at room temperature, even though they are lower than Nafion membrane. Higher proton conductivities of the PS-*b*-PHEA-*b*-PSSA/PVA membranes probably result from higher IEC values in the membranes. The proton conductivity of crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes decreased with increasing PVA amounts mostly due to the reduced concentrations of sulfonic acid. However, the crosslinked membranes with higher PVA contents exhibited better mechanical properties than those with lower PVA. For example, the water uptake of membranes continuously decreased from 87.0 to 44.3% with increasing amounts of PVA, as seen in Figure 5. It is mostly because the concentration of sulfonic acid group in crosslinked membrane decreased with PVA contents. This result represents that triblock copolymer is more hydrophilic than PVA. The change of mechanical properties of crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes was also directly characterized using UTM measurement. As shown in Table I, both Young's modulus and tensile strength at yield continuously increased from 15.0 to 38.5 MPa and from 5.6 to 25.6 MPa, respec-

Table I. Mechanical Properties of PS-*b*-PHEA-*b*-PSSA/PVA Membranes with Various Concentrations

PVA Content (wt%)	0	33	55	67
Young's Modulus (MPa)	15.0	20.8	31.6	38.5
Tensile Strength (MPa)	5.6	10.2	20.3	25.6

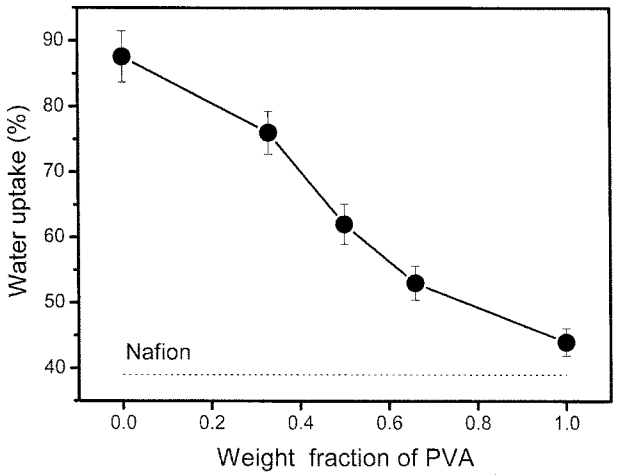


Figure 5. Water uptake for the PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations.

tively, with increasing PVA concentration.

The microphase-separated morphology of ionic aggregates in PS-*b*-PHEA-*b*-PSSA/PVA membranes was investigated using TEM analysis. Figure 6 shows the TEM picture of PS-*b*-PHEA-*b*-PSSA/PVA membrane with 33 wt% of PVA after silver ion staining. Thus the dark regions were attributed to both the PSSA and PHEA/PVA domains containing ionic SO_3Ag aggregates. On the contrary, the bright regions are attributable to unstained non-conducting PS domains, which was isolated due to low concentration in the membrane. TEM picture clearly shows that the PS-*b*-PHEA-*b*-PSSA/PVA membrane is microphase-separated with a nanometer range and well developed to provide the connectivity of ionic SO_3Ag aggregates. This morphology would be beneficial in achieving higher proton conductivity in polymer electrolyte membranes.[24,25]

Thus PS-*b*-PHEA-*b*-PSSA/PVA membranes with 50 and 33 wt% of PVA were used to prepare membrane electrode assembly (MEA) for fuel cells. Figure 7 shows the current vs potential curve of H_2/O_2 fuel cell using the crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes. The crosslinked membrane containing PVA 50 wt% exhibited higher power density than that containing PVA 30 wt% at 70 °C. The maximum cell performance of 230 mW/cm^2 was achieved for crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes with 50 wt% of PVA at 70 °C and relative humidity of 100%.

The thermal stability of crosslinked PS-*b*-PHEA-*b*-PSSA/PVA membranes was investigated by TGA, as shown in

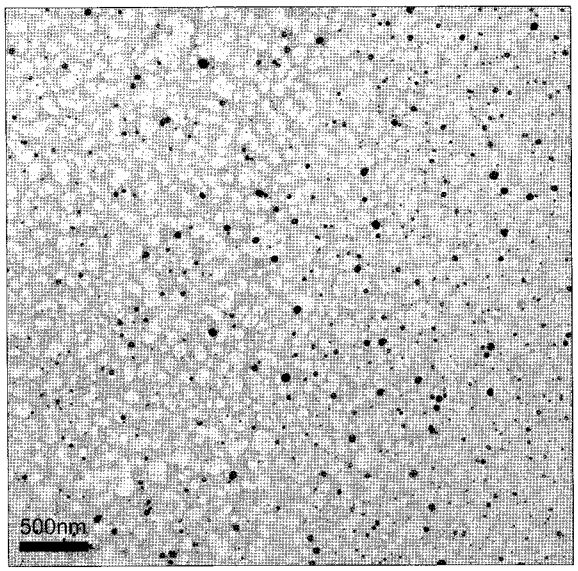


Figure 6. TEM picture of PS-*b*-PHEA-*b*-PSSA/PVA membrane with 33 wt% of PVA.

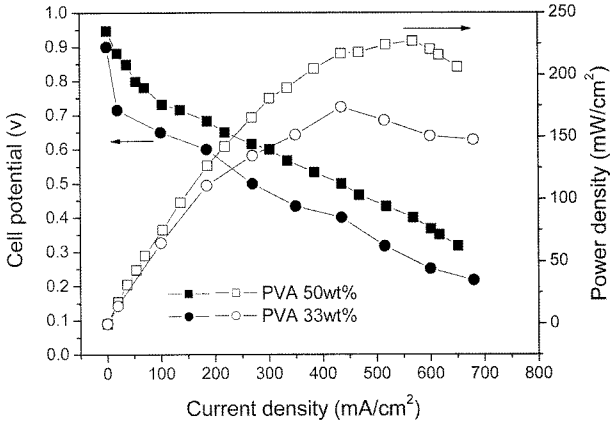


Figure 7. A single H_2/O_2 cell performance for PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations at 70 °C and RH 100 °C.

Figure 8. The degradation of the crosslinked triblock copolymer membranes exhibited multi steps in the region of around 100, 180, 280 and 450 °C, which became more prominent with the increase of PVA amounts. The first slight weight loss for all membranes was observed at around 100 °C, attributed to the loss of adsorbed water by the hygroscopic property of the membrane. The second step weight loss at 180 °C is presumably related to the degradation of PVA chains because this weight loss becomes more significant with increasing PVA contents. The weight loss at 280 °C is considered to be due to the degradation of sulfonic acid groups in the membranes. The last step weight loss is attributable to degradation of backbones of crosslinked membranes. The TGA data represent that the thermal stabil-

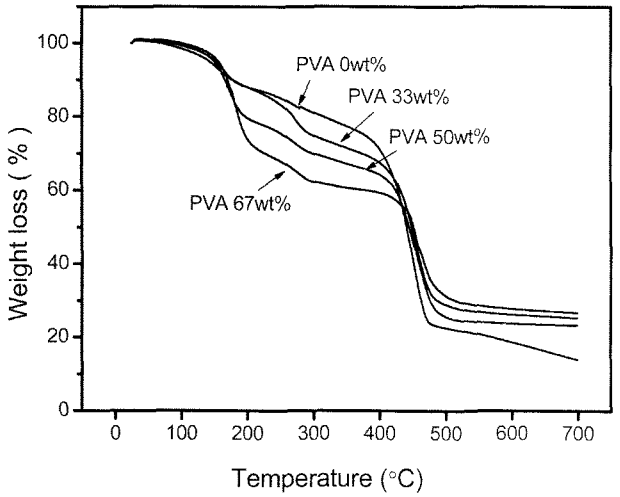


Figure 8. TGA for the PS-*b*-PHEA-*b*-PSSA/PVA crosslinked membranes with various concentrations.

ity of membranes decreased with increasing PVA concentrations.

Conclusions

The proton conducting membranes were developed by synthesizing PS-*b*-PHEA-*b*-PSSA triblock copolymer at 28:21:51 wt% through ATRP, followed by the crosslinking between -OH of middle PHEA block, -OH of PVA and -COOH of SA. The IEC values continuously decreased with increasing PVA concentrations. Accordingly, the proton conductivity of crosslinked membrane at room temperature decreased from 0.044 to 0.018. However, the mechanical properties increased with PVA concentrations, as seen in the decrease of water uptake from 87.0 to 44.3% and the increase of Young's modulus from 15.0 to 38.5 MPa. The crosslinked membrane exhibited microphase-separated morphology consisting of non-conducting PS domains and continuous PSSA, PHEA/PVA domains, as characterized by TEM picture. The crosslinked membrane containing PVA 50 wt% delivered the power density of 230 mW/cm^2 at a condition of 70 °C and relative humidity of 100%. The thermal stability of membranes decreased with increasing PVA concentrations, as revealed by TGA analysis.

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