Preparation and Characterization of Proton-Conducting Crosslinked Diblock Copolymer Membranes

Do Kyoung Lee, Yong Woo Kim, Jin Kyu Choi, Byoung Ryul Min, Jong Hak Kim

Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea

ABSTRACT: The synthesis and properties of crosslinked diblock copolymers for use as proton-conducting membranes are presented. A polystyrene-*b*-poly(hydroxyl ethyl methacrylate) diblock copolymer at 56 : 44 wt % was sequentially synthesized via atom transfer radical polymerization. The poly(hydroxyl ethyl methacrylate) (PHEMA) block was thermally crosslinked by sulfosuccinic acid (SA) via the esterification reaction between —OH of PHEMA and —COOH of SA. Proton nuclear magnetic resonance and Fourier transfer infrared spectra revealed the successful synthesis of the diblock copolymer and the crosslinking reaction under the thermal condition of 120°C for 1 h. The ion-exchange capacity continuously increased from 0.25 to 0.98 mequiv/g with increasing SA concentration because of the increasing number of charged groups in the membrane. However, the water uptake increased up to an SA concentration of 7.6 wt %, above which it decreased monotonically (maximum water uptake ~ 27.6%). The membrane also exhibited a maximum proton conductivity of 0.045 S/cm at an SA concentration of 15.2 wt %. The maximum behavior of the water uptake and proton conductivity with respect to the SA concentration was considered to be due to a competitive effect between the increase of ionic sites and the crosslinking reaction according to the SA concentration. All the membranes were thermally quite stable at least up to 250°C, presumably because of the block-copolymer-based, crosslinked structure of the membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 819–824, 2008

Key words: atom transfer radical polymerization (ATRP); block copolymers; membranes

INTRODUCTION

In recent years, solid polymer electrolyte membranes have been identified as promising materials for applications to fuel cells,[1–3] dye-sensitized solar cells,[4–6] and facilitated olefin-transport membranes.[7–9] Among them, proton-conducting polymer electrolytes, which have negatively charged groups attached to the polymer backbone, are extensively used in fuel-cell applications. The most common proton-conducting polymer electrolyte membranes are based on perfluorinated membranes, such as the Nafion series from DuPont and the Aciplex series from Asahi Chemical. All of these membranes possess good thermal, chemical, and mechanical properties because of their perfluorinated polymer backbones. However, high cost, low proton conductivity, and low water uptake at high temperatures are the main obstacles for the commercialization of polymer electrolyte membranes for fuel cells. Therefore, significant research efforts have been devoted to the development of alternative sulfonated polymeric materials.[10–12]

Concerning the improvement of the efficiency of fuel cells, high proton conductivity for sulfonated polymer membranes has been considered essential. The proton-transport properties are strongly associated with the water uptake of membranes. Thus, sulfonated polymers with a high degree of sulfonation exhibit high proton conductivity but consequently high water solubility, which leads to their inadequate use for fuel cells or other applications. Thus, crosslinking has been used as a good solution to maintaining a proper sulfonation level and to enhancing the mechanical properties.[13–20]

Microphase separation of copolymers can be used to create well-defined periodic microdomains of controlled morphology on the nanoscale. Especially in sulfonated polymer membranes, the use of self-organized, nanophase-separated structures can allow better control of both the sulfonation degree and the distribution of sulfonic acid groups. Thus, the proton conductivities of polymer electrolyte membranes with a phase-separated structure and self-organized ionic aggregates are higher than those of homogeneous materials.[21] Among microphase-separated materials, block copolymers consisting of more than two

domains with different chemical properties are considered to offer an effective approach to incorporating higher ionic properties into a material while retaining desirable mechanical properties of the polymer.[22–24] The advantages of the use of microphase-separated block copolymers include (1) control of the swelling of the ion-conducting domains by the surrounding nonconducting domains, (2) lowering of the methanol permeability due to decreased swelling, and (3) high mechanical stability due to the inert matrix of nonsulfonated segments.[22]

Here we report on crosslinked sulfonated polymer membranes consisting of a diblock copolymer, that is, polystyrene-*b*-poly(hydroxyl ethyl methacrylate) (PS-*b*-PHEMA) at 56 : 44 wt %, synthesized via atom transfer radical polymerization (ATRP).[25–27] The poly(hydroxyl ethyl methacrylate) (PHEMA) block was thermally crosslinked by sulfosuccinic acid (SA) via the esterification reaction between —OH of PHEMA and —COOH of SA. The detailed properties of the proton conductivity, ion-exchange capacity (IEC), and water uptake as well as the thermal properties of the membranes are also reported.

EXPERIMENTAL

Materials

Styrene (99%), 2-hydroxyl ethyl methacrylate (HEMA; 99%), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA; 99%), copper(I) chloride (CuCl; 99%), methyl 2-bromopropionate (MBP), and SA (70 wt % in water) were purchased from Aldrich and used as received without further purification.

Synthesis of the bromine-terminated PS macroinitiator

In a 250-mL, pear-shaped flask, 20 g of styrene, 0.296 g of CuCl, and 1.24 mL of HMTETA were added, and then the green mixture was stirred until a homogeneous solution was obtained. Nitrogen was purged to the solution 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 resultant polymer was diluted with tetrahydrofuran (THF). After the passage of the solution through a column with activated Al₂O₃ to remove the catalyst, it precipitated into methanol. The PS–Br macroinitiator was obtained and dried in a vacuum oven overnight at room temperature.

Synthesis of the PS-*b*-PHEMA diblock copolymer

In a 250-mL, pear-shaped flask, 6 g of PS–Br was dissolved in 10 mL of toluene with stirring. HEMA (7 g), 0.0888 g of CuCl, and 0.372 mL of HMTETA

were added to the solution. The green mixture was stirred until a homogeneous solution was obtained and was purged with nitrogen for 30 min. The mixture was placed in a 50°C oil bath for 7 h. After polymerization, the resultant block copolymer was diluted with THF. After the passage of the solution through a column with activated Al₂O₃ to remove the catalyst, it precipitated into methanol. The PS-*b*-PHEMA diblock copolymer was obtained and dried in a vacuum oven overnight at room temperature.

Preparation of the crosslinked diblock copolymer membranes

One gram of the PS-*b*-PHEMA diblock copolymer was dissolved in 15 mL of NMP with stirring. Different amounts of SA were added to the solution and stirred for more than 30 min. The mixtures were cast onto a glass dish and dried in an oven at 80°C for 2 days. The obtained membranes were peeled off from the dishes and then annealed at 120°C for 1 h for a thermal crosslinking reaction. The membranes were washed with water several times to remove unreacted SA.

IEC

IEC of the membranes was measured by the classical titration method. The membranes were soaked in a 1.0M NaCl solution for 24 h before IEC was measured. The protons released by the exchange reaction with Na ions were titrated against a 0.01M standardized NaOH solution with phenolphthalein as an indicator. The experimental IEC of the membranes was calculated with the following equation:

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

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

The theoretical IEC value was also calculated with the following equation:

$$\text{Theoretical IEC (mequiv/g)}$$
$$= \frac{\text{SA fraction in membrane}}{M_w \text{ of SA}} \times 10^3 \quad (2)$$

where M_w is the weight-average molecular weight.

Water uptake

The water uptake was determined by the weighing of a vacuum-dried membrane and a fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with
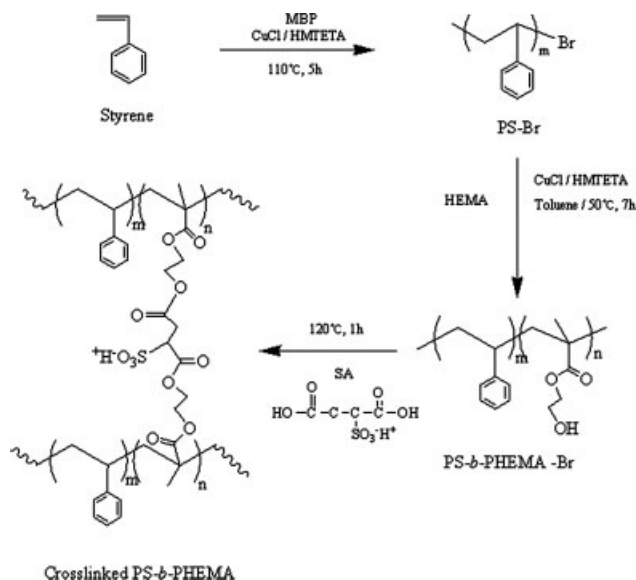
Scheme 1 Synthesis procedures for crosslinked PS-*b*-PHEMA membranes.

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 as follows:

$$\text{Water uptake (wt \%)} = \frac{W_w - W_d}{W_d} \times 100 \qquad (3)$$

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

Proton conductivity

A four-point probe method was used to measure the proton conductivity of the membranes. Before the measurement of the proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range of 1 Hz to 8 MHz at 25°C with a Zahner IM-6 impedance analyzer (Kronach, Germany). The impedance spectra of the membranes were used to generate Nyquist plots, and the proton conductivity was calculated from the plots.[2,14]

Characterization

Gel permeation chromatography (GPC) was performed at room temperature (25°C) with a Waters 600E system equipped with Waters Styragel columns and a Waters 410 differential refractometer (Toronto, Canada) as a detector. The polymer solutions were 0.2 wt % solutions, and THF was the eluent at a flow rate of 1.0 mL/min. The GPC curves were calibrated with narrow molecular weight distribution polystyrene (PS) standards. Proton nuclear magnetic resonance (^{1}H-NMR) measurements were performed with a 600-MHz, high-resolution NMR spectrometer (Avance 600-MHz FT-NMR spectrometer, Bruker, Ettlingen, Germany). Fourier transfer infrared (FTIR) spectra of the samples were collected with an Excalibur series FTIR instrument (DIGLAB Co., Hannover, Germany) in the frequency range of 4000–400 cm^{-1} with an attenuated total reflection facility. The thermal properties of the copolymer membranes were determined by thermogravimetric analysis (TGA; TGA/SDTA 851e, Mettler Toledo Columbus, OH). TGA measurements were performed from room temperature to 500°C at a rate of 20°C/min under an N$_2$ atmosphere. The amounts of the membranes were determined as weight-loss percentages during heating.

RESULTS AND DISCUSSION

The synthetic route of the crosslinked PS-*b*-PHEMA membrane is outlined in Scheme 1. The first step that produced bromine-terminated PS involved the homopolymerization of styrene in bulk at 110°C for 5 h in the presence of MBP/CuCl/HMTETA. The obtained PS exhibited a narrow molecular distribution (polydispersity index = 1.3) and a molecular weight of 14,000 g/mol, which was determined by GPC (Fig. 1). The polymerization yield was as high as 90%. The PS-*b*-PHEMA diblock copolymer was then synthesized with PS–Br and CuCl/HMTETA as a macroinitiator and catalyst/ligand, respectively. The resultant diblock copolymer showed a narrow molecular distribution (polydispersity index = 1.4) and a molecular weight of 24,000 g/mol.

The diblock copolymer was thermally crosslinked with SA at 120°C for 1 h via the esterification reaction between —OH of PHEMA and —COOH of SA. Because SA contains sulfonic acid groups, the cross-
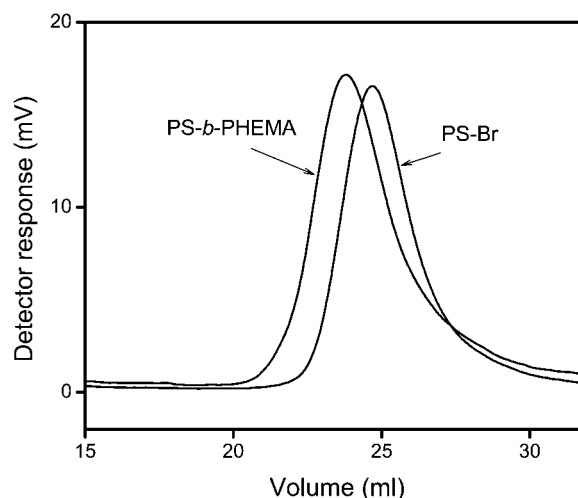

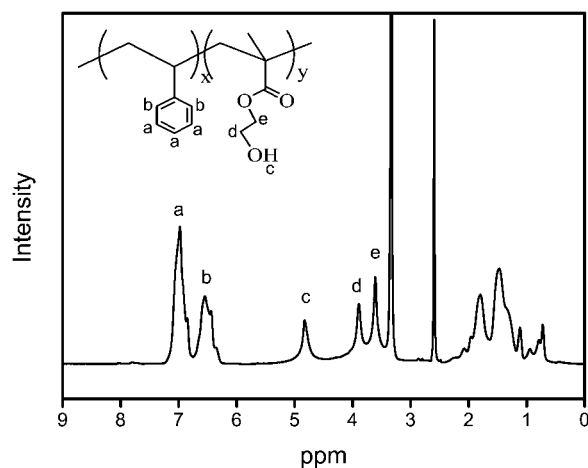**Figure 1** GPC traces of PS–Br and diblock copolymer PS-*b*-PHEMA.

Figure 2 ¹H-NMR spectrum of diblock copolymer PS-*b*-PHEMA.

linked PHEMA block is considered to be conducting domains. Thus, the crosslinked diblock copolymer unites the rigid, hydrophobic, nonconducting PS block with the crosslinked, conducting PHEMA block. This combination affords direct control over the polymer nanostructure within the membrane, resulting in reasonable proton-conducting properties and mechanical strength of the membranes.[28] It should be noted that a PS-*b*-PHEMA membrane is a little bit brittle, but the crosslinking reaction of the membrane by SA results in an enhancement of the mechanical properties. This is presumably related to both the crosslinked structure of the membrane and the microphase-separated morphology of hydrophobic and hydrophilic domains.

The chemical structure and composition of the diblock copolymer were investigated with ¹H-NMR spectroscopy. Figure 2 shows the ¹H-NMR spectrum of the PS-*b*-PHEMA diblock copolymer. Signals a and b at 7.0 and 6.6 ppm, respectively, are attributed to benzene groups of PS. Signals c, d, and e at 4.8, 3.9, and 3.5 ppm result from the PHEMA block. The ¹H-NMR spectrum shows that the diblock copolymer has a composition of 56 : 44 wt % in PS-*b*-PHEMA, and the synthesis via ATRP is successful.

Figure 3(a) presents the FTIR spectra of the PS homopolymer and PS-*b*-PHEMA diblock copolymer synthesized by ATRP. The aromatic C=C stretching modes of neat PS produced four peaks at 1601, 1583, 1494, and 1451 cm⁻¹.[29] Upon diblock copolymerization, new stretching bands appeared at 3432, 1720, and 1156 cm⁻¹, which were assigned to —OH, —C=O, and C—O of PHEMA, respectively. These FTIR spectroscopy results are clear evidence of the sequential synthesis of the triblock copolymer by ATRP.

Figure 3(b) shows the FTIR spectra of the crosslinked PS-*b*-PHEMA membranes at 120°C for 1 h

with different amounts of SA. With increasing amounts of SA, three stretching bands at 1722, 1240, and 1155 cm⁻¹ grew noticeably. The bands at 1722 and 1155 cm⁻¹ can be attributed to —C=O and C—O in the ester bond, respectively.[30] These FTIR spectroscopy results are clearly suggestive of a crosslinking reaction by the esterification between —OH of PHEMA and —COOH of SA.[31] The shoulder peak at 1240 cm⁻¹ is assigned to the stretching vibrations of the sulfonic acid groups of SA. The crosslinked PS-*b*-PHEMA membranes also exhibited absorption bands at 3417 and 1642 cm⁻¹, which can probably be attributed to the water bound to ionic groups of the diblock copolymer.[31]

The IEC value represents the quotient of the molar content of sulfonic acid groups to the membrane weight. The IEC data of the PS-*b*-PHEMA diblock copolymer membranes crosslinked with different amounts of SA are presented in Figure 4. As expected, the IEC values continuously increased from 0.25 to 0.98 mequiv/g with increasing amounts
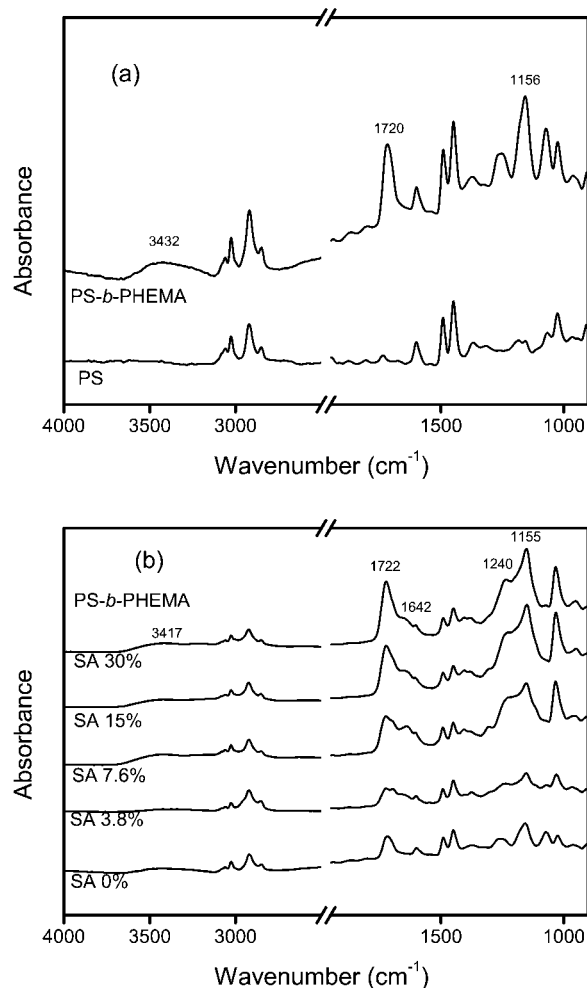

Figure 3 FTIR spectra of (a) PS and PS-*b*-PHEMA and (b) crosslinked PS-*b*-PHEMA membranes with different amounts of SA at 120°C for 1 h.
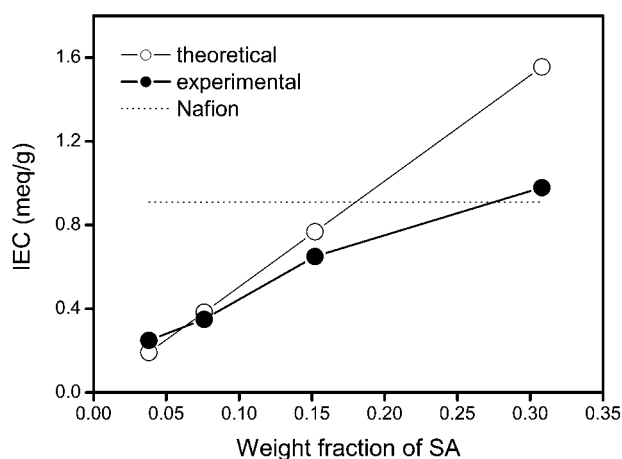
Figure 4 IEC of crosslinked PS-*b*-PHEMA membranes with different amounts of SA.

of SA, mostly because of the increasing number of charged groups in the membrane. It should be noted that SA contains a negatively charged fixed ion, that is, a sulfonic acid group. The membrane with 30.8 wt % SA exhibited a 0.98 mequiv/g IEC value, which was slightly higher than that of Nafion. Higher IEC values of the crosslinked diblock copolymer demonstrate that higher amounts of sulfonic acid groups are contained in the membranes. Theoretical IEC values are also compared with measured IEC values in Figure 4. Experimental IEC values were almost identical to theoretical values, except for an SA concentration of 30.8 wt %. The discrepancy between the calculated and measured IEC values at a high SA concentration may have resulted from the occurrence of the reaction between OH and SO$_3$H during the thermal treatment.[32] Thus, it might be important to find the optimum conditions for the crosslinking reaction in terms of the SA concentra-
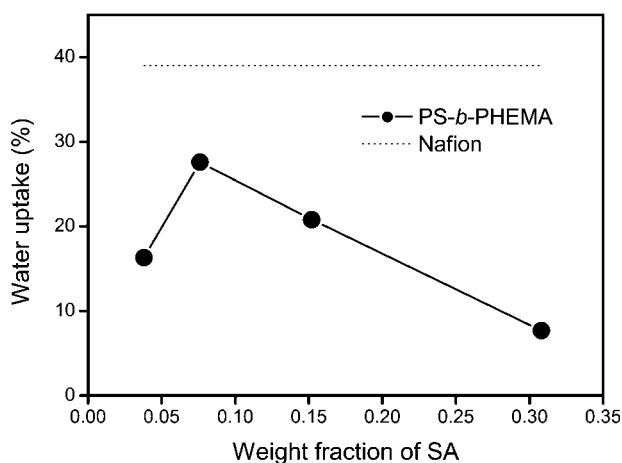
tion and thermal treatment conditions, which in turn should help to prevent a significant loss of fixed charge groups by an undesirable chemical reaction.

Figure 5 shows the water uptake of PS-*b*-PHEMA diblock copolymer membranes crosslinked with different amounts of SA. Upon the introduction of SA, the water uptake increased up to an SA concentration of 7.6 wt %, after which it decreased monotonically (maximum water uptake ∼ 27.6%). The water uptake may be related to the concentration of ionic sites, that is, sulfonic acid groups. In this work, however, the water uptake did not follow the behavior of IEC values of the membranes. This may be due to the fact that the introduction of SA produced crosslinking of the diblock copolymer, leading to a more rigid and compact structure of the membranes.

The proton conductivities of crosslinked PS-*b*-PHEMA diblock copolymer membranes with different amounts of SA are shown in Figure 6. As shown in this figure, the proton conductivities were largely dependent on the contents of acidic SO$_3^-$ groups. Overall, the proton conductivities of the crosslinked diblock copolymer membranes were of the order of 10^{-3} to 10^{-2} S/cm at room temperature. Higher proton conductivities of the crosslinked diblock copolymer membranes probably resulted from higher IEC values in the membranes. It should be also noted that all the membranes were mechanically strong, although the uncrosslinked PS-*b*-PHEMA membrane was a little bit brittle. A maximum proton conductivity of 0.045 S/cm was achieved at 15.2 wt % SA, and this was presumably related to the well-developed connectivity of proton-conducting domains in the crosslinked diblock copolymer membranes.

The thermal stabilities of pristine and crosslinked PS-*b*-PHEMA diblock copolymer membranes were investigated by TGA, as shown in Figure 7. It has been reported that (1) the weight change around
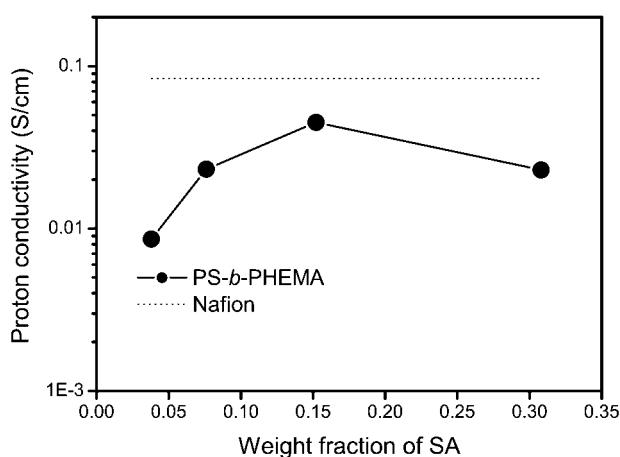

Figure 5 Water uptake of crosslinked PS-*b*-PHEMA membranes with different amounts of SA.

Figure 6 Proton conductivity of crosslinked PS-*b*-PHEMA membranes with different amounts of SA.
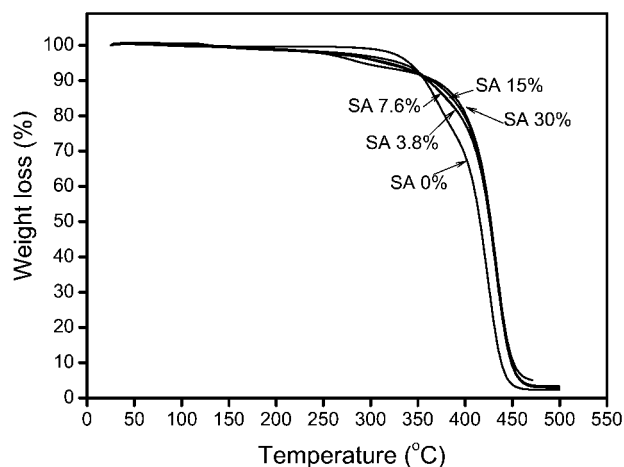
Figure 7 TGA data of crosslinked PS-*b*-PHEMA membranes with different amounts of SA.

$100–150^\circ$C corresponds to a weight loss of absorbed water in the membranes and (2) the weight loss of membranes around $250–400^\circ$C is due to a weight loss of the sulfonic acid groups and breakage of the ester bonds ($-$COO$-$).[31] The pristine diblock copolymer membrane exhibited excellent thermal stability almost up to 350°C. Analogously, the crosslinked diblock copolymer membranes showed good thermal stability, although the degradation around 300°C became noticeable with an increase in the SA content. This degradation might be related to the relatively weak bond strength of ester groups connecting the PHEMA and SA groups as well as partially monoreacted SA in the membranes. However, all the membranes were thermally quite stable at least up to 250°C, presumably because of the block-copolymer-based, crosslinked structure of the membranes.

CONCLUSIONS

Polymer electrolyte membranes with controlled microstructures were prepared, and their properties, that is, the proton conductivity, IEC, and water uptake, were investigated. A PS-*b*-PHEMA diblock copolymer at 56 : 44 wt % was synthesized through ATRP followed by the crosslinking of the PHEMA block with SA. The IEC value continuously increased from 0.25 to 0.98 mequiv/g, whereas the water uptake increased to 27.6% with an SA concentration up to 7.6 wt %, above which it decreased. The maximum proton conductivity of 0.045 S/cm was achieved at an SA concentration of 15.2 wt %. These maximum behaviors have been explained on the basis of a competitive effect between the increase of ionic sites and the crosslinking reaction as more SA is introduced into the membranes. The block-copolymer-based, crosslinked structure of the membranes provided good thermal stability at least up to 250°C.

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