Synthesis and Characterization of Multiblock Sulfonated Poly(arylenethioethersulfone) Copolymers for Proton Exchange Membranes

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising clean power sources for automotive and portable applications. The proton exchange membrane (PEM) is one of the most critical components for PEMFCs.[1,2] In the past decade, the most widely utilized and commercial available PEM is Nafion, a tetrafluoroethylene copolymer containing pendent perfluorinated sulfonic acid groups. However, high cost, low operation temperature and high methanol crossover of Nafion and other similar perfluorinated membranes have limited their widespread commercial application in PEMFCs.[2] These drawbacks have stimulated worldwide research activities for developing new materials as PEMs based on sulfonated aromatic polymers.[3−5] These alternative materials are expected to have low cost as well as similar electrochemical properties.

Multiblock copolymers are synthesized to combine the properties of the constituent homopolymers. The combination of supramolecular phase separation in multiblock copolymers with self-ordering occurring on a molecular scale can provide interesting properties compared to random polymers. The unique morphology of multiblock copolymers used for PEMs is known to play an important role in determining the membrane mechanical strength, water uptake, thermal stability, and proton conductivity.[6] It is well-known that perfluorosulfonate ionomers have high proton conductivity due to the existence of "channel-like" network of ions, even with lower ion-exchange capacity (IEC).[7] In other words, Nafion membranes have high phase-separated hydrophilic and hydrophobic domains, which give them superior performance in fuel cell applications. For the sulfonated aromatic polymer membranes, block copolymerization is a potential route to achieve phase-separated morphology.[8] The phase of unsulfonated blocks should enable good mechanical stability and reduce the swelling of the sulfonated blocks, while the hydrophilic sulfonated blocks enable high proton conductivity.[9]

Recently, our groups have developed sulfonated poly(arylenethioethersulfone) (SPTES) as PEM for fuel cell applications.[10,11] Although they show very good potential usages in PEM, there still have several drawbacks to solve, such as, inadequate mechanical stability and low proton conductivity of random SPTES copolymer especially that with low sulfonated degrees (or low IEC). The purpose of this work is to prepare multiblock SPTES-50 copolymer to balance the distribution of hydrophobicity and hydrophilicity along the polymer backbone. The proper balance should be enable good mechanical properties and to reduce the swelling of the sulfonated blocks, and to produce greater proton transport channel in the microstructure, which will further enhance proton conductivity of the polymer membranes.

Experimental Section

Materials. 4-Fluorophenylsulfone (99%, Sigma-Aldrich Co.), potassium carbonate (99%, ACS reagent, Sigma-Aldrich Co.), tetramethylene sulfone (99%, Sigma-Aldrich Co.), and *N*,*N*-dimethylacetamide (DMAc, anhydride, 99%, Sigma-Aldrich Co.) were used as received. 4,4′-Thiobisbenzethiol (98%, GC, TCI America Chemical) was recrystallized from toluene and dried at 80 °C in a vacuum oven prior to use. Sulfonated monomer, 3,3′-disulfonate-4,4′-difluorodiphenylsulfone, was prepared following the procedures, disclosed elsewhere.[10] Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

Synthesis of Unsulfonated Block A: Poly(arylenethioethersulfone) (PTES). 4-Fluorophenylsulfone (5.0850 g, 20 mmol), 4,4′-thiobisbenzethiol (4.7578 g, 19 mmol), and potassium carbonate (6.6340 g, 48 mmol) were charged into a 250 mL round-bottom flask maintained under a back pressure of nitrogen and equipped with a magnetic stirrer and an oil bath on a hot plate. DMAc (100 mL) was added into the flask, stirred for 45 min at room temperature and at 100 °C for 1 h, and then 40 mL of toluene was added. The reaction mixture was heated to 120 °C for 2 h, 140 °C for 2 h, and 160 °C for 3 h, then cooled down to room temperature, quenched with acetic acid, and precipitated in methanol/water (2:1 v/v). The polymer was filtered, Soxhlet-extracted with methanol for 48 h, and dried in vacuum at 80 °C overnight to afford a yield of 96%. The polymerization scheme and the chemical structures were showed in Figure 1A.

Synthesis of Sulfonated Block B: Sulfonated Poly(arylenethioethersulfone) (SPTES). 4,4′-Thiobisbenzethiol (2.5041 g, 10 mmol), 3,3′-disulfonate-4,4′-difluorodiphenylsulfone (4.4316 g, 9 mmol), and potassium carbonate (3.3168 g, 24 mmol) were charged into a 250 mL round-bottom flask maintained under a back pressure of nitrogen and equipped with a magnetic stirrer and an oil bath on a hot plate. Sulfolane (60 mL) was added into the flask and stirred at 100 °C overnight, and the reaction mixture was then heated to 180 °C for 6 h, then cooled down to 140 °C, and kept for the next step. Chemical reaction scheme was shown in Figure 1B.

Synthesis of Multiblock SPTES-50 Copolymers. The block B solution was stirred at 140 °C; the block A polymers with the same equivalent amount (50% mol) were dissolved in 60 mL DMAc, then added it to the block B solution at 140 °C. The mixture solution was stirred for 1 h, then heated up to 180 °C for 4−6 h. The copolymers were precipitated in methanol/water (2:1 v/v) with acetic acid. The copolymer was filtered, Soxhlet-extracted with methanol for 48 h, and dried in vacuum at 80 °C overnight to afford a yield of 89%. Chemical structures were shown in Figure 1C.

Preparation of Multiblock SPTES-50 Copolymer Membranes. The salt form of multiblock SPTES-50 copolymers was dissolved in the DMAc at 100 °C to a clear solution. The membranes were directly cast in a flat dish at 80 °C in vacuum for 24 h. The clear membranes were converted to the corresponding sulfonic acids in the presence of diluted sulfuric acid (4 M) at room temperature for 48 h. The membranes were dried at room temperature for 4 h, and at 100 °C in vacuum for 24 h, which produced the tough, clear, flexible membranes of multiblock SPTES-50 copolymers.

Characterization of Multiblock SPTES-50 Copolymers. Gel permeation chromatography (GPC) was used to determine molecular

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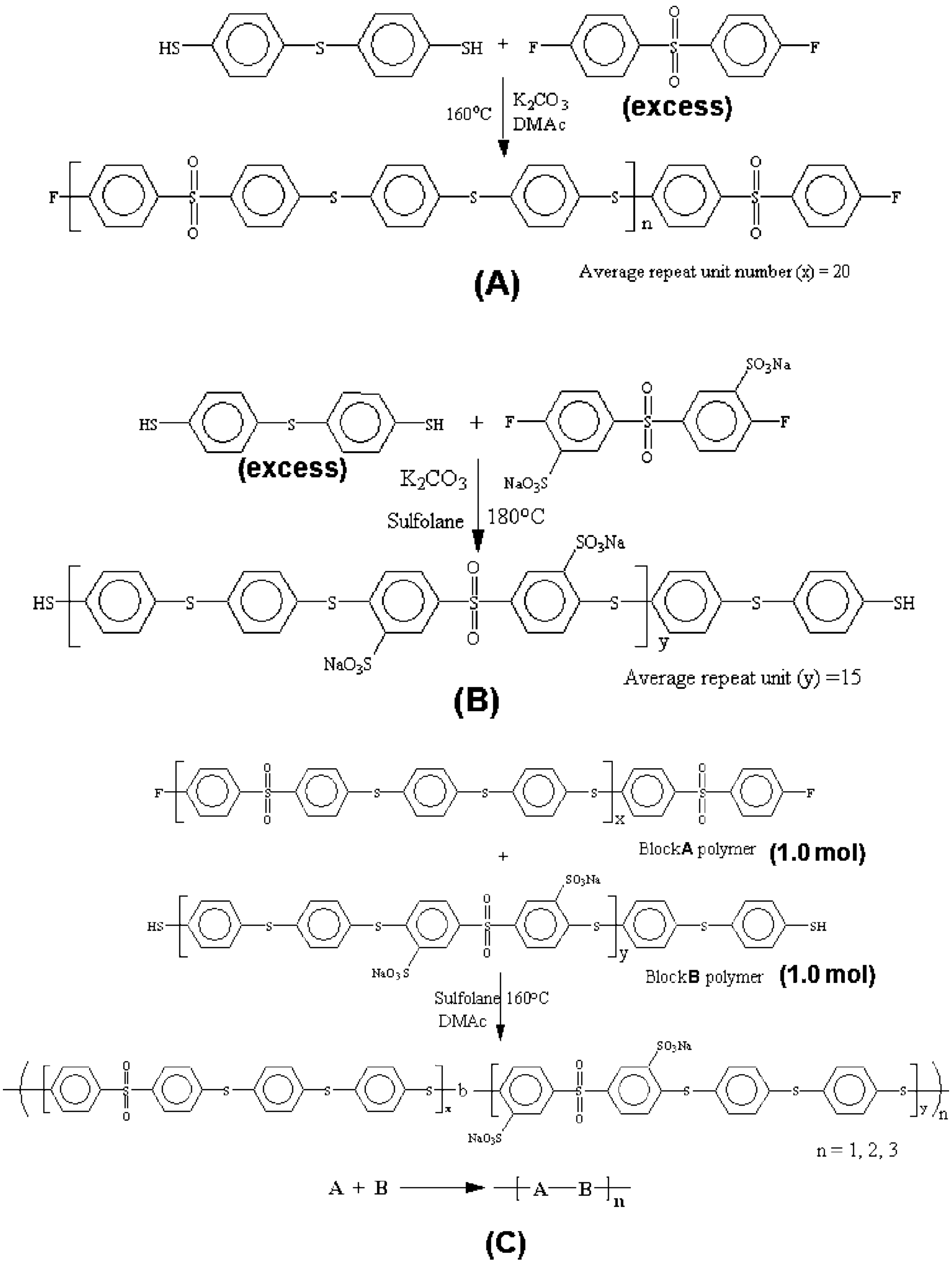

Figure 1. Chemical structure and reaction scheme of multiblock SPTES-50 copolymers: (A) Reaction scheme of PTES (block A polymer), (B) reaction scheme of SPTES (block B polymer), and (C) block polymerization scheme and chemical structure of multiblock SPTES-50 copolymers.

weights and molecular weight distributions (M_w/M_n). Molecular weight measurement was performed on TriSEC Version 3.00 in NMP, 0.5% LiBr at 70 °C. Intrinsic viscosity (IV) was measured at 30 °C in NMP, 0.5% LiBr using an Ubbelohde Viscometer. Thermogravimetry (TGA) was conducted using an Auto TGA 2950HR V5.4A instrument in air and nitrogen at a heating rate of 10 °C/min. Tapping mode AFM was used to obtain height and phase imaging data simultaneously on a Dimension 3100 Nanoscope III Controller from Veeco, CA. Etched silicon probes (Nanoprobes, Veeco) were used at their fundamental resonance frequencies which typically varied from 270 to 350 Hz. The measurement of proton conductivity of polymer membranes was using AC Impedance Spectroscopy and utilized a standard 4-electrode measurement setup to eliminate electrode and interfacial effects. The water uptake was measured according to following procedure: Polymer membranes were vacuum-dried at 100 °C for 24 h, weighed, and immersed in deionized water at room temperature for 24 h.

Results and Discussion

Structures and Properties of Multiblock SPTES-50 Copolymers. The multiblock SPTES-50 copolymers with high molecular weight were successfully synthesized in sulfolane/DMAc at temperatures up to 180 °C. The water uptake of the multiblock SPTES-50 copolymer comparing with those of the random SPTES-50 copolymer and Nafion117 was shown in Table 1. The multiblock SPTES-50 copolymer shows higher water uptake than Nafion 117 and random SPTES-50 copolymer at the room temperature. Table 1 also shows the IEC of the multiblock SPTES-50 copolymer and random SPTES-50 copolymer, comparing to the results indicate that they have almost same IEC values, which are correlated to the proton conductivity. However, the multiblock SPTES-50 copolymer has a significantly high value of proton conductivity (256 mS/cm)

Table 1. Characteristic of the Multiblock SPTES-50, Random SPTES Copolymers, and Nafion-117 Membranes[a]

polymers	water uptake (25 °C, wt %)	cal. IEC (meq./g; EW, mg/meq.)	exp. IEC (meq./g; EW, mg/meq.)	M_w/M_n (GPC, $k = 10^3$)	proton conductivity (mS/cm)
multiblock SPTES-50 copolymer	45	1.82 (550)	1.74 (575)	51 k/23 k	256
random SPTES-50 copolymer	25	1.82 (550)	1.64 (610)	85 k/38 k	100
Nafion-117	19	0.91 (1100)	N/A	N/A	80

[a] Note: proton conductivity of the membranes was measured at 65 °C, 85 % relative humidity.

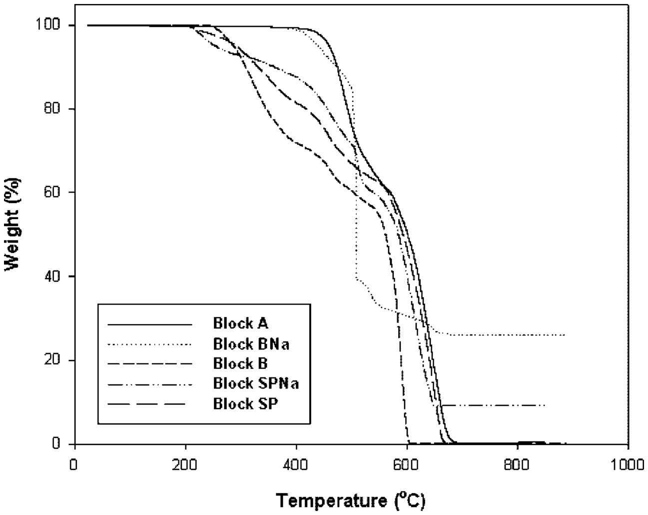

Figure 2. TGA results of multiblock SPTES-50 copolymers. Block A: unsulfonated polymer (PTES); block BNa: sulfonated polymer (salt form); block B: sulfonated polymer (acid form); block SPNa: multiblock SPTES-50 copolymer salt; block SP: multiblock SPTES-50 copolymer.

compared to the random SPTES-50 copolymer (100 mS/cm) as well as Nafion-117 (80 mS/cm), which was determined at 65 °C and 85% relative humidity conditions (see Table 1). This may be attributed to the existence of nanostructure morphology forming sulfonated hydrophilic domains surrounded by hydrophobic blocks as supported by AFM data. In another word, the proton conductivity of multiblock SPTES-50 copolymer also depend on the morphology of membranes, unlike the random SPTES-50 copolymer increased as the sulfonated content (IEC) increased.[11]

Thermal Properties of Multiblock SPTES-50 Copolymers. Figure 2 show the TGA curves of multiblock SPTES-50 copolymer and its salt form, as well as block A polymer (PTES) and block B polymer (SPTES) in air, respectively. The block A polymer show single step degradation around 450 °C; the block B polymer in salt form is the same trend like block A polymer, however, it has a residual due to contain Na in the polymer side chain. The block B polymer in acid form and multiblock SPTES-50 copolymer exhibited a two step degradation pattern. The first weight loss was observed around 250 °C in Figure 2. It is attributed to the splitting-off of sulfonate acid group. The second degradation step around 440 °C corresponds to the main chain decomposition. It is surprising that salt form of multiblock SPTES-50 copolymer shows a first step thermal degradation lower than their corresponding acid form copolymer. This may be caused by the thermal degradation of sulfonate groups at relative low temperature compared to the backbones of polymers. From Figure 2, it is clear that the hydrophobic segments length should have less influence on the thermal stability of multiblock SPTES-50 copolymer both in salt and acid form.

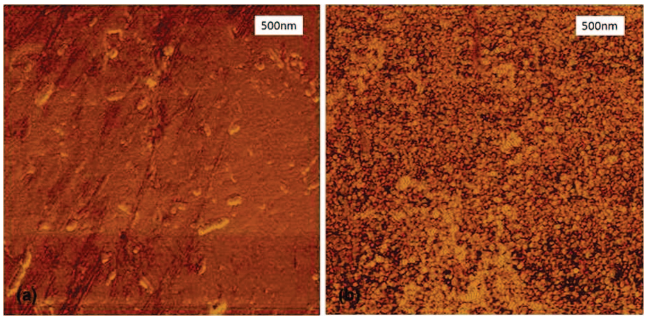

Figure 3. AFM micrographs of (a) random SPTES-50 copolymer and (b) multiblock SPTES-50 copolymer.

Morphology and Properties of Multiblock SPTES-50 Copolymers. The electrochemical behaviors of sulfonated polymer membranes are closely associated with their morphology. For the random sulfonated polymer membranes, sulfonated groups may aggregate into hydrophilic clusters. These ion clusters lead to a random distribution of ion channels in the polymer matrix, which can transport ions or protons through the interfacial region in the presence of a small amount of water.[12] Block copolymers comprising of hydrophobic and hydrophilic blocks are known to exhibit microphase separation of the incompatible domains. Spherical, cylindrical, or lamellar shape of minor phase embedded in major phase matrix depends on the relative block volume fractions.[13,14]

Figure 3 shows phase image tapping mode-AFM micrographs of random SPTES-50 copolymer (Figure 3a) and multiblock SPTES-50 copolymer (Figure 3b). Figure 3a shows the representative surface morphology of random SPTES-50 copolymer, which contained 50% sulfonated and 50% unsulfonated monomer. TM-AFM micrographs shown here were taken under partial hydration. Images from random SPTES-50 copolymer suggest that the hydrophilic groups aggregate as isolated domains with some local connection of hydrophilic domains as evidenced by the proton exchange membranes' good conductivity. Figure 3b shows a very well defined phase separation and a distinct morphological architecture of multiblock SPTES-50 copolymers compared to the random SPTES-50 copolymers. Existence of well-connected hydrophilic domains (~50 nm) is most likely the reason for high proton conductivity of the multiblock SPTES-50 copolymer compared with their random SPTES-50 copolymer counterpart.

TEM results of the multiblock SPTES-50 copolymer also exhibit phase separation shown in Figure 4. From Figure 4 (left image of TEM), large structures/channels running *perpendicular* to film surface can be seen, with average spacing of 65 nm, which showed in Figure 4 (right image of Fourier transform). This apparent phase separation along with high proton conductivity of the multiblock SPTES-50 copolymer suggest that the hydrophilic groups aggregate as isolated domains with local connection of hydrophilic domains in nano scale. Such nano phase separation can result in formation of continuous ion channels, and hence proton can be transported efficiently through the membrane, which increases the conductivity of the copolymers.

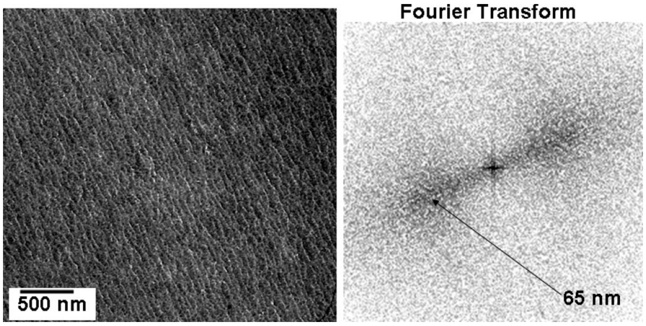

Figure 4. TEM micrograph of multiblock SPTES-50 copolymer.

Conclusions

Multiblock SPTES-50 copolymers containing hydrophilic sulfonated blocks and hydrophobic unsulfonated blocks with controlling the molecular weight of the block were successfully synthesized by a two-step polycondensation reaction. The membranes of multiblock SPTES-50 copolymers cast from a DMAc solution showed higher water uptake (45%) and higher proton conductivity (256 mS/cm) compared to the random SPTES-50 copolymer at the same condition. The observation of AFM and TEM indicated that multiblock SPTES-50 copolymers form a distinct morphological structure, which leads to higher proton conductivity, compared with the random SPTES-50 copolymers.

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Supporting Information Available: AFM images for analysis of hydrodynamic diameters and size distribution, NMR analysis spectra, and GPC for molecular weight distribution. This material is available free of charge via the Internet at http://pubs.acs.org.

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