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Synthesis and characterization of partially fluorinated hydrophobic–hydrophilic multiblock copolymers containing sulfonate groups for proton exchange membrane

Yanxiang Li[a], Abhishek Roy[a], Anand S. Badami[a], Melinda Hill[b], Juan Yang[a], Stuart Dunn[a], James E. McGrath[a,*]

[a] *Macromolecular Science and Engineering & Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*

[b] *MPA-11, Sensors and Electrochemical Devices, Los Alamos National Laboratory, Los Alamos, NM 87544, USA*

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Abstract

A new hydrophobic–hydrophilic multiblock copolymer has been successfully synthesized based on the careful coupling of a fluorine terminated poly(arylene ether ketone) (6FK) hydrophobic oligomer and a phenoxide terminated disulfonated poly(arylene ether sulfone) (BPSH) hydrophilic oligomer. ^{19}F and ^{1}H NMR spectra were used to characterize the oligomers' molecular weights and multiblock copolymer's structure. The comparison of the multiblock copolymer ^{13}C NMR spectrum with that of the random copolymer showed that the transetherification side reaction was minimized in this synthesis. The morphologies of membranes were investigated by tapping mode atomic force microscopy (AFM), which showed that the multiblock membrane acidified by the high temperature method has sharp phase separation. Membrane properties like protonic conductivity, water uptake, and self-diffusion coefficient of water as a function of temperature and relative humidity (RH) were characterized for the multiblock copolymer and compared with ketone type random copolymers at similar ion exchange capacity value and Nafion® controls. The multiblock copolymers are promising candidates for proton exchange membranes especially for applications at high temperatures and low relative humidity.

Keywords: Proton exchange membrane fuel cell; Poly(arylene ether ketone); Poly(arylene ether sulfone); Multiblock copolymer; Morphology

1. Introduction

Proton exchange membrane (PEM) materials have attracted much attention due to the environmentally friendly nature of PEM fuel cells and their potential applications in automobiles, stationary power, and small electronics [1,2]. Currently nearly all commercially available membranes are based on copolymers containing perfluorosulfonic acid groups such as DuPont's Nafion®. Nafion®-type materials have exceptional oxidative and chemical stability as well as high protonic conductivity, which are critical to PEM fuel cells. But they have limitations like low performance at high temperature due to a low hydrated T_g value, high methanol permeability in direct methanol fuel cells, and high cost [2,3]. Therefore, many polymeric materials with ionic groups have been explored as alternative PEM candidates, such as poly(arylene ether)s [4–8], polyimides [9,10], poly(arylene sulfide sulfone)s [11], substituted polyphenylenes [12], etc. The wholly aromatic partially disulfonated poly(arylene ether sulfone) (BPSH) random copolymer developed in the McGrath group [6] is a potential PEM candidate due to its good acid and thermal oxidative stabilities, high glass transition temperature and excellent mechanical strength [13]. For example, with 35 mol% degree of sulfonation, the BPSH copolymer has excellent oxidative stability as shown in open circuit test. The test was conducted at 100 °C under H_2/O_2 environment at 25% RH. BPSH outperformed the benchmarked material Nafion® and

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* Corresponding author. Tel.: +1 540 2315976; fax: +1 540 2318517.
E-mail address: jmcgrath@vt.edu (J.E. McGrath).

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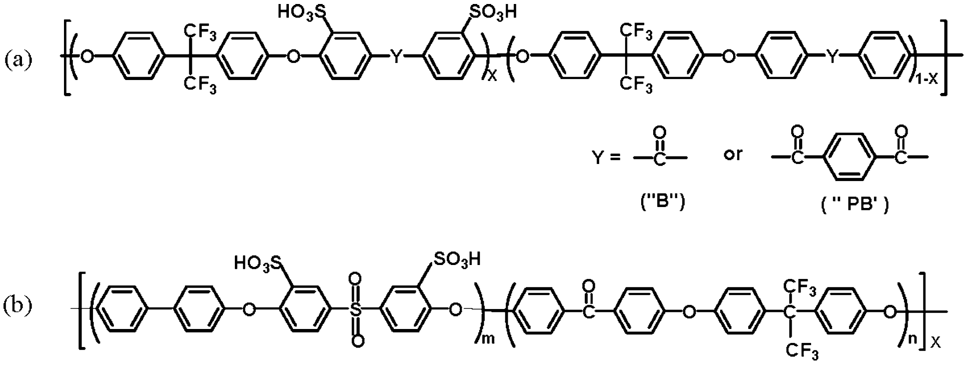

Fig. 1. Copolymer chemical structures studied in this work: (a) B-ketone-xx and PB-diketone-xx copolymers and (b) 6FK-BPSH multiblock copolymer.

was stable up to 300 h. This inherent stability was attributed to the extremely low oxygen permeability (10 times lower than Nafion®) [14].

Most of the copolymers developed are random or "statistical" copolymers because monomer units are connected irregularly and the sulfonic acid groups are also randomly distributed along the copolymer chain. These randomly located ionic groups will lead to isolated morphological domains especially at low hydration level, which limit the transport properties. While under fully hydrated conditions, water assisted percolated morphology ensures connectivity between the hydrophilic domains. As a result, the random copolymers show satisfactory performance under fully hydrated conditions, but they will lose the performance dramatically at low relative humidity. The big challenge here is how to modify the chemistry of the polymers to obtain significant proton conductivity at low hydration levels which will make the PEM fuel cell more applicable under ambient environments. Recent research results showed that the hydrophobic–hydrophilic block copolymers with tailored chemical structure of the polymer backbone may achieve this goal [15].

Multiblock thermally stable copolymers are interesting because the morphology of the copolymer membrane can be better controlled by varying the two sequences length in the multiblock structures [16]. In hydrophobic–hydrophilic multiblock copolymers, the ionic groups located within the hydrophilic blocks provide protonic conductivity, and the hydrophobic blocks offer good mechanical strength. It is especially interesting when the molecular weight ratio of the two blocks is about 1:1, since a hydrophilic cocontinuous phase may form under this condition, which may form associated hydrophilic domains even under low hydration levels. This may greatly facilitate transport and the proton conductance. Furthermore, the microphase separation in multiblock copolymers may be helpful in controlling the water swelling and generating copolymers which have good conductivity even at low relative humidity. The McGrath group [17–22] has recently focused on this topic and developed several series of thermally stable multiblock copolymers to investigate both composition and chemical structure effects on PEM properties. It was found that the cocontinuous phase can form at certain oligomer block lengths according to atomic force microscopy (AFM) images, and under partially hydrated conditions the block copolymers showed much improved proton conductivity over the random copolymers [23,24]. The block copolymers also showed higher self-diffusion coefficients of water over the Nafion® control and random copolymers, suggesting a lower morphological barrier to transport [15,23,24].

In this paper, a novel multiblock copolymer (Fig. 1(b)) has been successfully synthesized based on a fluorine terminated hydrophobic poly(arylene ether ketone) (6FK) oligomer and a phenoxide terminated hydrophilic poly(arylene ether sulfone) (BPSH) oligomer. Keeping the chemical backbone similar to BPSH, one may hope to get the same or even better oxidative stability. The comparison of ^{13}C NMR spectra between the multiblock copolymer and the random copolymer shows that the ether–ether interchange side reaction, which may result in a randomized copolymer chain, has been minimized in this copolymerization. The multiblock copolymer can form a tough film. Membrane properties of this multiblock copolymer like morphology, proton conductivity, and water uptake were characterized and compared with Nafion® control and ketone random copolymers (Fig. 1(a)). This paper aims to understand that how the differences between multiblock and random copolymer morphologies affect water and proton transport. This will be instructional in designing better membranes for improved fuel cell performance.

2. Experimental

2.1. Materials

4,4′-Hexafluoroisopropylidenediphenol (6F-BPA), received from Ciba, was purified by sublimation. 4,4′-Difluorobenzophenone (DFBP) was purchased from Aldrich, and biphenol (BP) was kindly provided by Eastman Chemical. They were used as received. The ionic comonomer 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone (SDCDPS) was synthesized as reported earlier [8]. All these monomers were well-dried in a vacuum oven before polymerization. The solvents *N*-methyl-2-pyrrolidinone (NMP) and dimethylacetamide (DMAc) were vacuum-distilled from calcium hydride onto molecular sieves. Potassium carbonate was dried *in vacuo* before use. Toluene, ethanol, and isopropanol were obtained from Aldrich and used as received. B ketone-xx and PB diketone-xx series random copolymers were synthesized in house [8,15], where xx refers to the degree of sulfonation. Nafion® 112 and Nafion® 1135 were obtained from ElectroChem.

2.2. Synthesis of fluorine terminated hydrophobic oligomers

Fluorine terminated poly(arylene ether ketone) oligomers (6FK) with target molecular weights were synthesized via step growth polymerization. For example, the 4 kg mol^{-1} 6FK oligomer was prepared in a three-neck 100 ml flask with DFBP (2.580 g, 11.82 mmol) and 6F BPA (3.500 g, 10.41 mmol) dissolved in 20 ml DMAc, 1.65 g potassium carbonate was added, and toluene (10 ml) was used as an azeotropic agent. The reaction temperature was first set to 150 °C to dehydrate the system for about 4 h, and the toluene was removed completely. The oil bath temperature was then raised to 175 °C for 16 h. The oligomer solution was cooled to room temperature and filtered to remove most of the salt, then precipitated in IPA. The oligomers were collected by filtration and washed with DI water and ethanol thoroughly to remove residual salt and monomer residues. The resulting oligomers were dried *in vacuo* at 100 °C for at least 24 h.

2.3. Synthesis of multiblock copolymers

The step growth copolymerization employed a two-step procedure for the multiblock copolymer synthesis. A copolymerization of a 4k–4k multiblock copolymer is described as follows: first, phenoxide terminated disulfonated poly(arylene ether sulfone) (BPSH) with target molecular weight 4 kg mol^{-1} was synthesized by charging biphenol (1.776 g, 9.54 mmol) and 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone (4.044 g, 8.23 mmol) to a three-neck 100 ml flask equipped with mechanical stirrer, nitrogen inlet and a Dean Stark trap. Potassium carbonate (1.15 equivalents) and dry NMP were introduced to afford 20% solid concentration. Toluene (NMP/toluene = 2/1 v/v) was used as an azeotropic agent. The reaction mixture was heated under reflux at 150 °C for 4 h to remove water. Then, the bath temperature was raised slowly to 190 °C for 16 h. The oligomer solution was cooled to 160 °C for the next step reaction without isolation. In the second step, 6FK/NMP solution was added dropwise to the BPSH system. Then the temperature was raised again to 190 °C for 2 days. The copolymer was isolated by precipitation in IPA and deionized water (1:1), filtered, and dried in a vacuum oven for 24 h at 120 °C.

2.4. Characterization of oligomers and multiblock copolymers

The ^{19}F, ^{1}H and ^{13}C NMR spectra were conducted with a Varian Unity 400 NMR spectrometer. Solvent $CDCl_3$ was used for the hydrophobic oligomers, and DMSO-d_6 was used for the hydrophilic oligomers and multiblock copolymers. Intrinsic viscosities (IV) were determined in NMP at 25 °C using an Ubbelohde viscometer for ionic copolymers with 0.05 M LiBr in the NMP solvent to suppress the polyelectrolyte effect [25].

2.5. Membrane preparation and acidification

The salt form copolymers were redissolved in DMAc to afford transparent 5 wt.% solutions, which were then cast onto clean glass substrates. The films were slowly dried for 48 h with infrared heat at gradually increasing temperatures, and then dried under vacuum at 110 °C for 2 days. Two methods can be employed to convert the sodium salt form membranes to their acid form [26]. In Method 1, the membranes were immersed in 1.5 M sulfuric acid solution at 30 °C for 24 h followed by immersion in deionized water at 30 °C for 24 h. Method 2 involved boiling the membranes in 0.5 M H_2SO_4 for 2 h, and then boiling in deionized water for another 2 h to remove any residual acid. Membranes were stored in deionized water after the acidification until they were used for measurements.

2.6. Characterization of membranes

2.6.1. Morphology characterization by atomic force microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using a Digital Instruments MultiMode scanning probe microscope with a NanoScope IVa controller (Veeco Instruments, Santa Barbara, CA) in tapping mode. A silicon probe (Veeco) with an end radius of <10 nm and a force constant of 5 N m^{-1} was used to image samples. Samples were equilibrated at 30% RH for at least 12 h before being imaged immediately at room temperature and approximately 15–33% RH.

2.6.2. Ion exchange capacity (IEC) and conductivity

Sulfonic acid concentration in the copolymers (IEC, mequiv. g^{-1}) was quantitatively determined by titration. The acid form membrane was immersed in 50–60 ml DI water with 1 M sodium sulfate. The solution was stirred overnight to allow the protons to exchange with sodium completely. The solution was then titrated with 0.01 M sodium hydroxide solution in which phenolphthalein was used as an indicator.

Proton conductivity was determined in a window cell geometry [27] using a Solartron 1252 + 1287 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz to 1 MHz following the procedure reported in the literature [28]. In determining proton conductivity in liquid water, membranes were equilibrated at 30 °C in DI water for 24 h prior to the testing. The temperature range chosen for calculation of activation energy for proton transport was from 30 to 80 °C. For determining proton conductivity under partially hydrated conditions, membranes were equilibrated in a humidity-temperature oven (ESPEC, SH-240) at the specified RH and 80 °C for 6 h before each measurements.

2.6.3. Water uptake and water self-diffusion coefficients

The water uptake of the membranes was determined by measuring the difference in the weight between dry and fully hydrated membranes. The sample films were equilibrated in deionized water at room temperature for at least 48 h. The membranes were dried in the vacuum oven at 110 °C for

24 h. Weights of wet and dry membranes were measured. The water uptake was calculated as follows: water uptake $\% = [(\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}})/\text{mass}_{\text{dry}}] \times 100\%$, where mass_{dry} and mass_{wet} refer to the mass of the wet membrane and the mass of the dry membrane, respectively.

The hydration number (λ), number of water molecules absorbed per sulfonic acid, can be calculated from the mass water uptake and the ion content of the dry copolymer as shown in the equation: $\lambda = [(\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}})/\text{MW}_{\text{H}_2\text{O}}]/\text{IEC} \times \text{mass}_{\text{dry}}$, where $\text{MW}_{\text{H}_2\text{O}}$ is the molecular weight of water (18.01 g mol^{-1}) and IEC is the ion exchange capacity of the dry copolymer in equivalents per gram.

Water self-diffusion coefficients were measured in a Varian Inova 400 MHz (for protons) nuclear magnetic resonance spectrometer with a 30 G cm^{-1} gradient diffusion probe as described in the literature [15,29].

2.6.4. MEA fabrication and fuel cell testing

Membrane electrode assemblies (MEAs) were prepared from protonated membranes and standard unsupported Pt catalyst inks by procedures developed at Los Alamos National Laboratory [30]. The catalyst loading was approximately 6 mg cm^{-2} on both the anode and the cathode. The polymer binder in the catalyst layers was Nafion, and the active cell area was 5 cm^2. Gas diffusion layers (GDLs) were comprised of carbon cloth from E-TEK. The cell temperature was maintained at 80 °C and humidified hydrogen (200 sccm) and air (500 Sccm) were supplied to the anode and cathode, respectively.

3. Results and discussions

3.1. Synthesis and characterization of oligomer and multiblock copolymer

Fig. 2 shows the synthesis of fluorine terminated 6FK hydrophobic oligomers. The molecular weights and the fluorine endgroups were controlled by using excess DFBP monomer. The theoretical molecular weights were calculated according to the Carothers equation. ^{19}F NMR spectrum (Fig. 3) was used to determine the resulting oligomer molecular weight. For the ^{19}F NMR integrals of the two peaks, one is attributed to the fluorine in the chain (−63.7 ppm, integration value: 225.91), another one is the end group aromatic fluorine peak (−107.6 ppm, integration value: 10), and the two kinds of fluorine have the number ratio of 6*n* to 2, therefore the M_n can be calculated by the equation: $6n/2 = 225.91/10$, where *n* is the number of repeat unit and was calculated to be 7.53. Accordingly the actual number average molecular weight (M_n) of oligomer was calculated to be 4089 g mol^{-1}, which is very close to the target value (4 kg mol^{-1}).

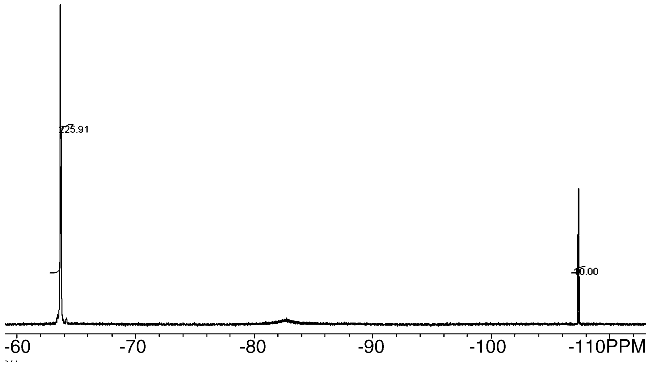

Fig. 3. Molecular weight of 6FK hydrophobic oligomer can be calculated from the ^{19}F NMR spectrum (6FK oligomer with target MW 4 kg mol^{-1} in $CDCl_3$).

The multiblock copolymer was synthesized via a two-step technique (Fig. 4). First, the phenoxide terminated disulfonated poly(arylene ether sulfone) (BPSH) hydrophilic oligomer with target molecular weight 4 kg mol^{-1} was synthesized using biphenol and SDCDPS in NMP, following the similar polycondensation method as the hydrophobic oligomer. After 16 h reaction, the temperature was lowered to 160 °C without isolation. Then the 6FK (4 kg mol^{-1}) oligomer dissolved in NMP was added dropwise to the BPSH system in about 1 h. Finally the temperature was raised to 190 °C for 2 days. The completion of the reaction can be monitored by ^{19}F and ^{1}H NMR during the reaction. It was found the endgroup fluorine peak was gone after 2 days reaction (not shown) and in the ^{1}H NMR the small proton peaks close to the hydroxyl group in BPSH oligomer (Fig. 5 (top), peaks h, g, i and f) also disappeared. The ^{1}H NMR spectrum (Fig. 5(bottom)) showed all proton peaks from both hydrophilic and hydrophobic seg-

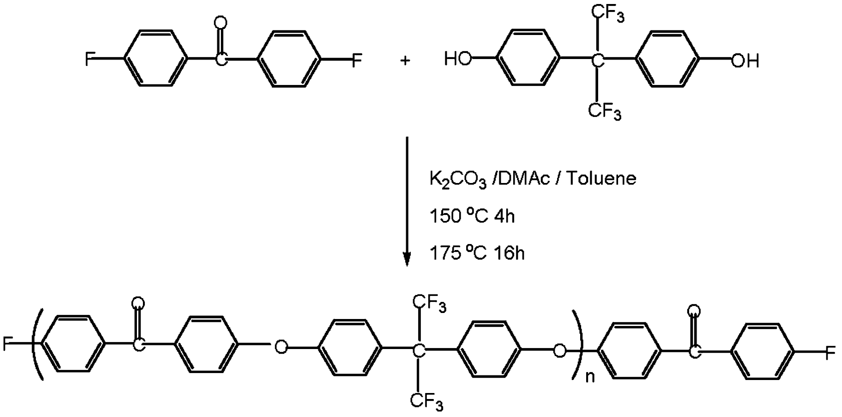

Fig. 2. Synthesis of fluorine terminated poly(arylene ether ketone) (6FK) hydrophobic oligomer.

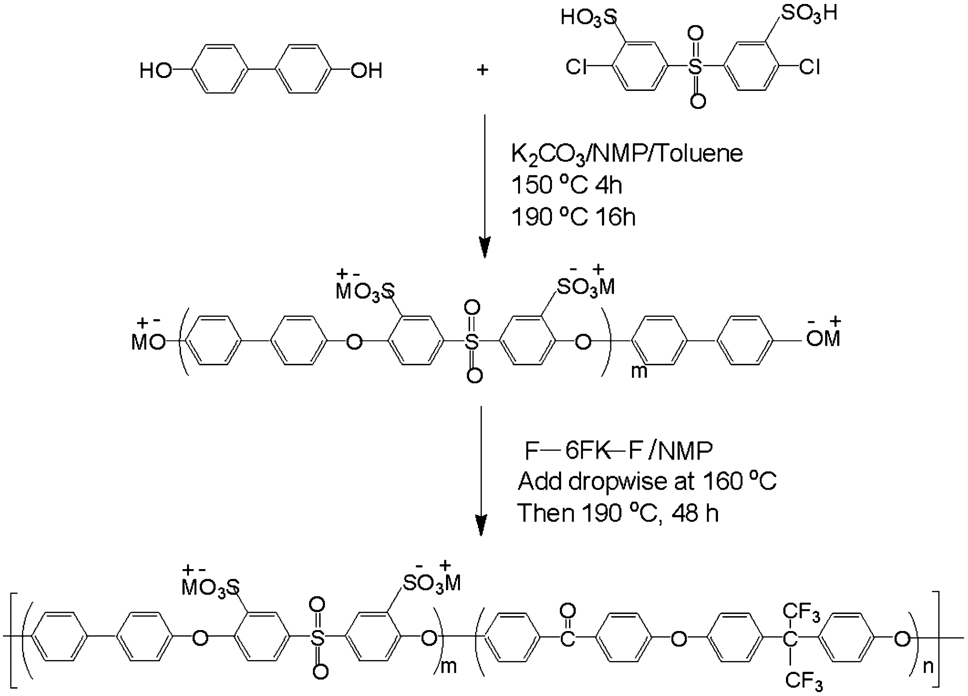

Fig. 4. Synthesis of 6FK-BPSH multiblock copolymers via two-step technique.

ments as assigned, which confirmed the success of the coupling reaction.

In this coupling reaction, a concern is that the ether–ether chain interchange side reaction will occur, which may result in the randomized copolymer chain. For comparison, a random copolymer possessing the same chemical composition as the multiblock copolymer was synthesized by the one-step copolymerization of SDCDPS, BP, 6F-BPA, and DFBP. Because the crystalline segments comprised of BP and DFBP would precipitate out of the reaction solution and upset the stoichiometry, the high molecular weight random copolymer was difficult to obtain. However, the comparison of ^{13}C NMR spectra between low molecular weight random and the multiblock copolymers still provided enough information of the sequence connection. As shown in Fig. 6, the carbons in random copolymer all have multiple peaks, suggesting the irregular connection of the repeating

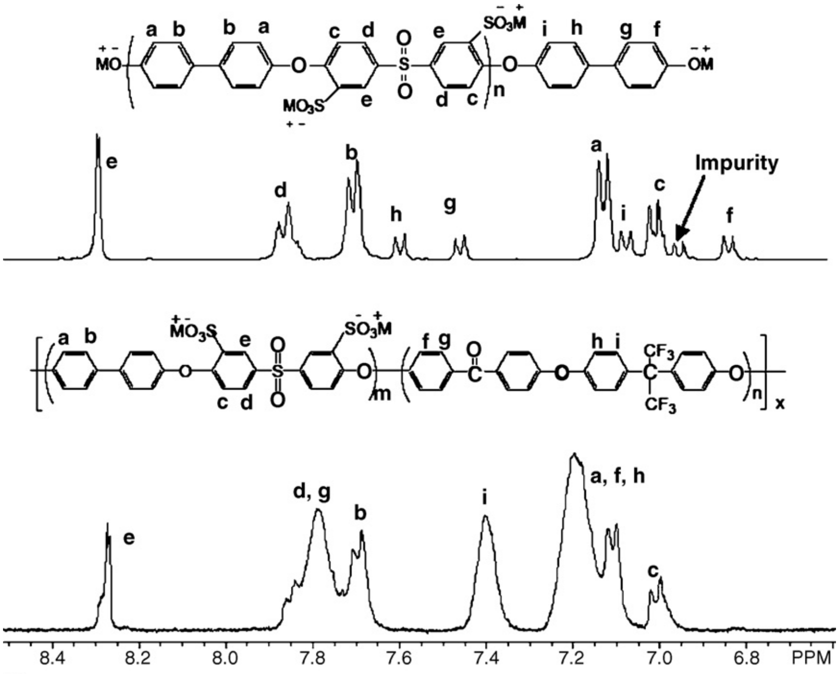

Fig. 5. ^{1}H NMR spectra of BPS hydrophilic oligomer (top), and multiblock 6FK-BPS copolymer (bottom).

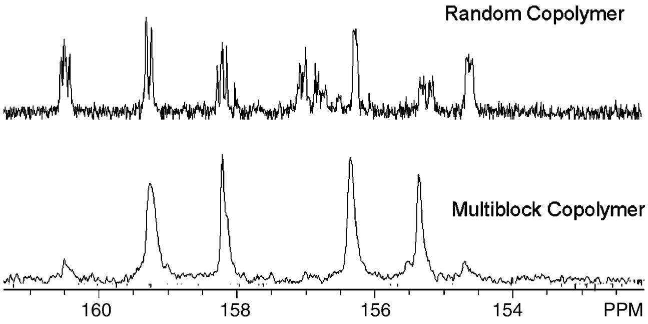

Fig. 6. ^{13}C NMR spectra of random (top) and 6FK-BPS multiblock (bottom) copolymers.

sequence. In contrast, the carbons in the multiblock copolymer showed strong single peaks, which confirmed the multiblock structure [31].

All of the above results indicated that a multiblock 6FK-BPS (4:4)k copolymer with approximately 4 kg mol^{-1} for each segmental lengths has been successfully synthesized with high intrinsic viscosity. The block copolymer can be dissolved in dipolar aprotic solvents like NMP and DMAc. Tough films were prepared by solution casting from 5% DMAc solution.

3.2. Morphology of membranes

The multiblock 6FK-BPS (4:4)k copolymer membrane was acidified to assess the effect of acidification upon its phase separation. Film samples of the multiblock copolymer were acidified in sulfuric acid either by “Method 1” at 30 °C or by “Method 2” at 100 °C [26]. Films were imaged by tapping mode atomic force microscopy (AFM) after acidification (Fig. 7(a)–(d)) When the phase images for acidification by Method 1 (Fig. 7(a)) and Method 2 (Fig. 7(c)) are compared, two observations can be made. First, the connectivity between the hydrophilic ionic domains (which appear darker) is greater following acidification by Method 2. Second, acidification by Method 2 results in a sharper contrast between the ionic domains and the hydrophobic non-ionic domains (which appear brighter).

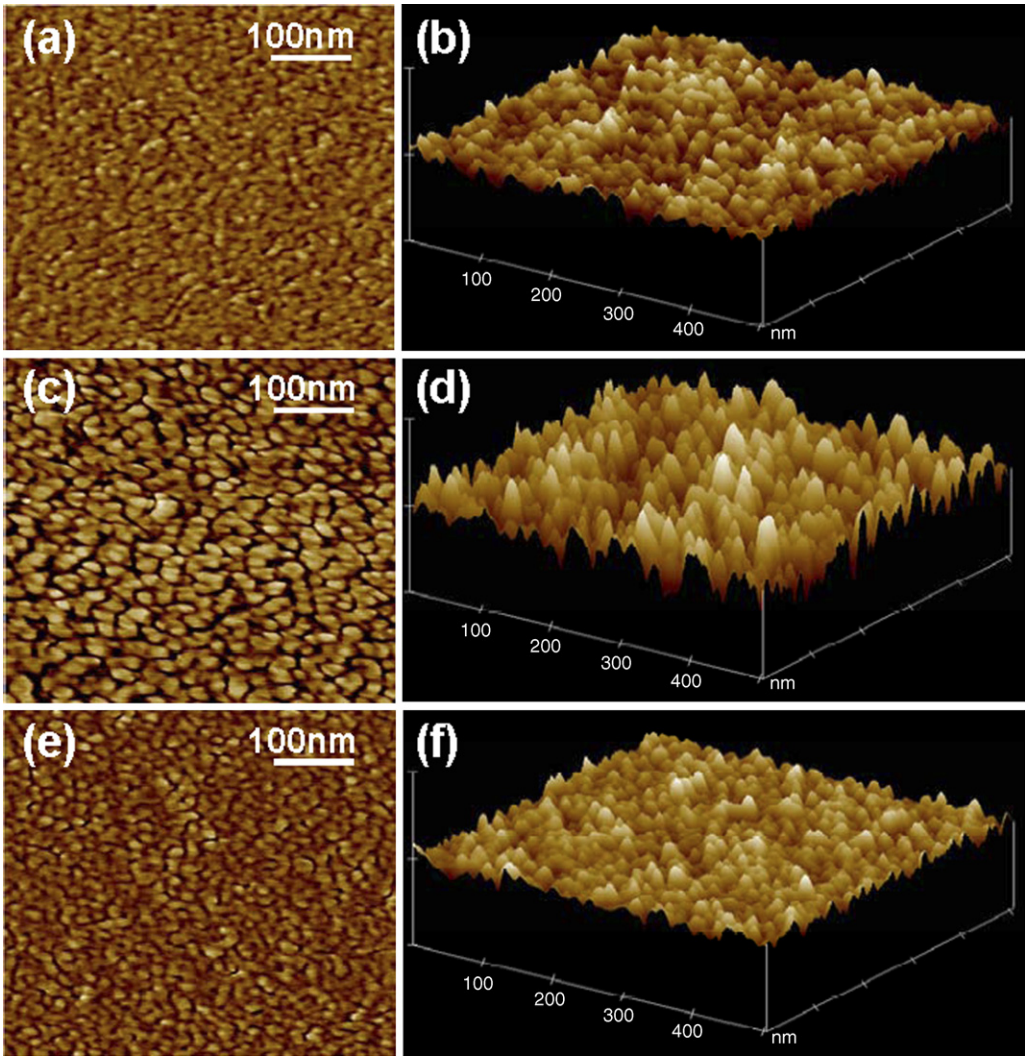

Fig. 7. Tapping mode atomic force microscopy images: (a) phase image and (b) height image of a 4k-4k 6FK-BPSH multiblock copolymer film acidified by Method 1 at 30 °C, (c) phase image and (d) height image of the same film acidified by Method 2 at 100 °C, (e) phase image and (f) height image of a sulfonated poly(arylene ether ketone) random copolymer film (B-30) acidified by Method 2. Image size: 500 nm; z ranges: (a) 4°, (c) 12°, (e) 8°, all height ranges: 10 nm.

These observations suggest that there is a greater degree of phase separation in the multiblock copolymer following acidification by Method 2. These results are consistent with previous results for phase separation of sulfonated poly(arylene ether sulfone) random copolymers acidified by both methods [26,32] and those subjected to different hydrothermal treatments [5]. Height image micrographs (Fig. 7(b) and (d)) obtained concurrently with the phase images for the same area suggest that acidification temperature may increase the difference between the highest and lowest topographical features of the film. It is speculated that the hydrothermal treatment of "Method 2" acidification imparts greater segmental mobility to the polymer chains within the film compared to "Method 1" because the water depresses the glass transition temperature of the polymer while it is concurrently heated at elevated temperature. While temperature-induced topographic differences were not reported for poly(arylene ether sulfone) random copolymer membranes [5], it is possible that this observation may be a result of two factors. The first is the increased flexibility of ketone linkages compared to that of sulfone linkages. The second and possibly more important factor is that the multiblock structure of this copolymer may allow more phase separation to occur during acidification than a random copolymer structure could.

To confirm this latter hypothesis, a sulfonated poly(arylene ether ketone) random copolymer film was acidified by Method 2 to evaluate the differences in phase separation between random and multiblock copolymers with sulfonated poly(arylene ether ketone) components. AFM phase images (Fig. 1(c) and (e)) and height images (Fig. 1(d) and (f)) of the two copolymers indicate that phase separation is sharper for the multiblock copolymer than for the random copolymer, supporting the hypothesis that multiblock structure may contribute to increased differences in topography. These results are understandable given that the length of the ion-containing blocks in these multiblock copolymers is longer than the length of an ion-containing comonomer in the random copolymers. Consequently, the ionic groups should be located closer to each other in the multiblock copolymer when ionic group aggregation occurs during acidification, facilitating phase separation and resulting in larger domains and greater differences in topography.

3.3. Characterization of PEM properties

As discussed in Section 3.2, ion containing polymers tend to phase separate into hydrophobic and hydrophilic domain like morphology. The extent of phase separation is critical for both proton and water transport. It is known that in block copolymers, the sequence lengths play an important role in phase separation. In order to understand the importance of block copolymer morphology on transport properties, B and PB random copolymers with similar chemical structures and IECs were used as controls.

Table 1 lists the various properties for the random, block and Nafion® copolymers. At similar IECs, a significant increase in proton conductivity was observed for the 6FK-BPSH (4:4)k multiblock copolymer over the random B-30 and PB-40 copolymers. A similar trend in water uptake is also observed. The sharpness of phase separation seems to increase both proton and water transport. To investigate in details, water uptake was studied over a wide range of water activities and so as proton conductivity.

Table 1
Characterization of multiblock, random copolymers and Nafion® control

Copolymers	IEC[a] (mequiv. g^{-1})	Water uptake (%)	Proton conductivity[b] (S cm^{-1})	I.V.[c] (dl g^{-1})
Nafion® 112	0.9	22	0.08	–
PB-50	1.4	66	0.08	1.4
PB-40	1.2	26	0.04	1.2
B-30	1.1	25	0.02	0.5
6FK-BPSH(4:4)k	1.2	53	0.08	0.7

[a] IEC values for the copolymers (except Nafion®) were measured by titration.
[b] Proton conductivities were measured in liquid water at 30 °C.
[c] Intrinsic viscosities (IV) were measured in NMP with 0.05 M LiBr.

Fig. 8 represents the plots of hydration number as a function of water activity for 6FK-BPSH (4:4)k multiblock, Nafion® and B ketone-30 copolymers. The multiblock showed much higher water uptake at all hydration levels. In contrast to the random copolymer, both the multiblock and Nafion® showed a sudden increase after 0.85 water activity. Kreuer et al. [33] reported similar observation for Nafion®. The dielectric constant of the water in the membrane at higher water activities was found close to bulk or free water. Earlier studies have demonstrated the importance of the presence of free water on the transport properties. At low water activities, the phase separated morphology of the block copolymers tends to hold up more water than the random and Nafion®. This may be important when addressing the proton conductivity under partially hydrated conditions.

The temperature dependency on proton transport was determined over the temperature range of 30–80 °C for the copolymers studied (Fig. 9). Both the block and Nafion® copolymers showed higher proton conductivities over the temperature range. The slope of the graphs can be related to the activation

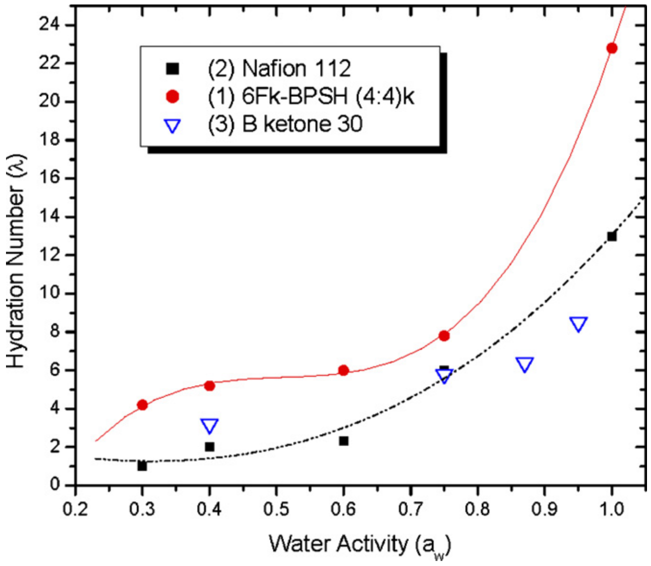

Fig. 8. Retention of water as a function of water activity is enhanced for the block copolymer.

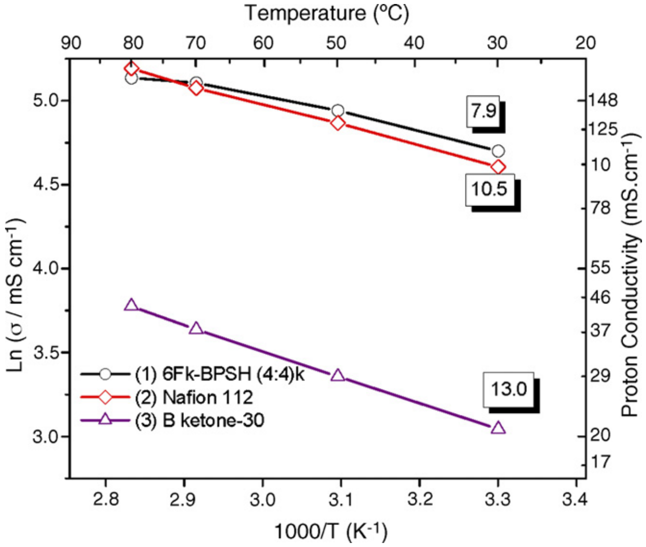

Fig. 9. Proton conductivity as a function of temperature for multiblock 6FK-BPSH (4:4)k, B-ketone-30, and Nafion® 112 (the numbers in the box are activation energy, kJ mol^{-1}).

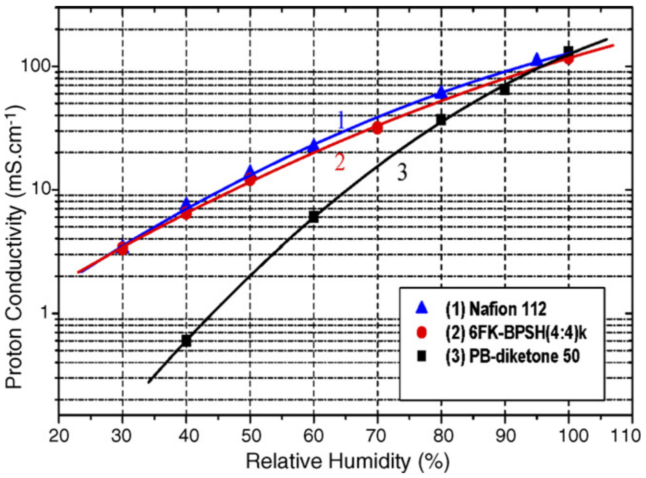

Fig. 11. Comparison of conductivity vs. RH for 6FK-BPSH (4:4)k multiblock, PB-diketone-50 random copolymers, and Nafion® 112.

energy for proton transport. It follows that the multiblock has the lowest activation energy. The well phase separated block copolymer morphology may increase the extent of connectivity between the hydrophilic domains and lowers the activation energy for transport.

Self-diffusion coefficient of water gives a better understanding on the importance of connectivity on water or proton transport. Higher value indicates well phase separated morphology. Also under partially hydrated conditions, self-diffusion coefficient scales with proton diffusion coefficient for Nafion® [27,33]. Hence a clear understanding about the influence of block lengths on self-diffusion coefficient of water is needed. Fig. 10 shows the self-diffusion coefficients of water measured at 25 °C for the copolymers studied. Although the ion exchange capacity and chemical composition of the multiblock copolymer is similar to that of random, a change in sequence length distribution increases the self-diffusion coefficient value significantly. This reflects the importance of morphology and is consistent with the activation energy results.

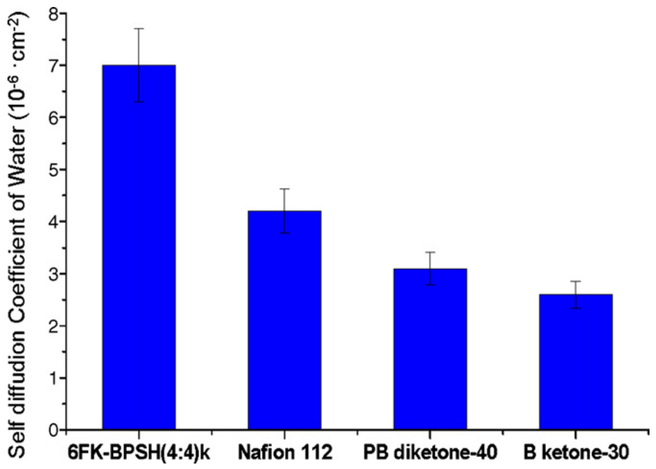

Fig. 10. The block copolymer has a much higher self-diffusion coefficient of water (multiblock copolymer has similar IEC value to the PB-40 and B-30 random copolymers).

Studying proton conductivity as a function of relative humidity illustrated the effect of morphology on proton conductivity under partially hydrated conditions (Fig. 11). For the random copolymer, PB-diketone 50, proton conductivity drops significantly at lower RH values. Random copolymers show decent performance under fully hydrated conditions since there are sufficient water molecules to provide proton transport through water molecules in a scattered morphology; however, they lack the connectivity among sulfonic acid groups for proton transport under partially hydrated conditions. Conversely, with the multiblock copolymers, the performance under partially hydrated conditions was very much comparable to Nafion®. Presence of long, co-continuous channels improved the proton transport along the sulfonic acid groups and water molecules.

3.4. Fuel cell performance

Evaluation of this multiblock copolymer also included fuel cell performance testing. All tests were conducted at Los Alamos National Laboratory at an elevation of approximately 7000 ft. A 6FK-BPS (4:4)k multiblock membrane was evaluated and compared with a commercial Nafion® 1135 membrane under full humidification of the inlet gases (Fig. 12). The novel multiblock copolymer showed very promising fuel cell performance, which was similar to Nafion® under these conditions. The high frequency resistance (HFR) of the Nafion® membrane was 0.072 Ω cm^2, while that of the 6FK-BPS (4:4)k was 0.087 Ω cm^2. Since the conductivity of the membranes is very similar, the difference in HFR is thought to be due at least partially to the resistance at the interface between the membrane and the electrodes [34]. This incompatibility might be due to the difference in water uptake between the novel multiblock copolymer and the Nafion®-based electrode layers. Performance might be further improved by replacement of the Nafion® binder in the anode and cathode with one more similar to the membrane.

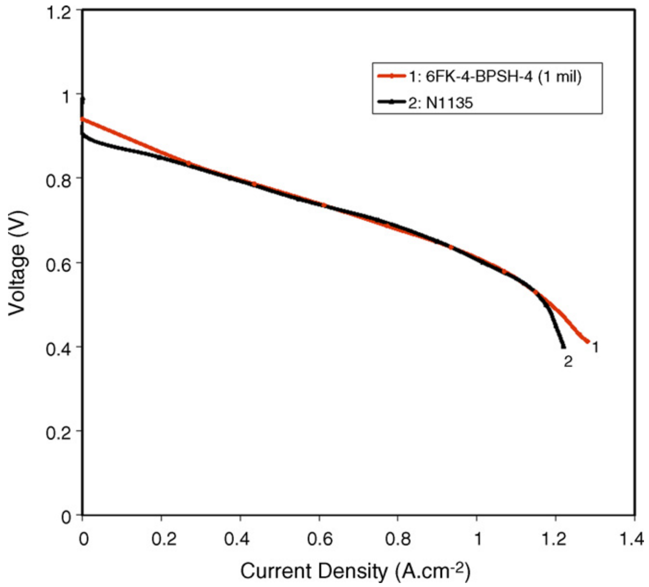

Fig. 12. Hydrogen-air fuel cell performance of 6FK-BPSH (4:4)k and Nafion at 80 °C under fully humidified conditions.

4. Conclusions

A new hydrophobic–hydrophilic multiblock 6FK-BPSH (4:4)k copolymer was successfully synthesized via a two-step polycondensation method. ^{19}F and ^{1}H NMR spectra were used to characterize the oligomers' molecular weight and multiblock copolymer's structure. ^{13}C NMR was a powerful tool to confirm the sequence connection in the block copolymer. Good film-forming material with high conductivity was obtained. Morphologies of the membranes characterized with tapping mode atomic force microscopy showed that the high temperature acidification method can improve the phase separation. The results were consistent with previous studies on the BPSH random copolymer. The AFM images also indicated that the phase separation is sharper for the multiblock than for the random copolymer.

This well phase separated block copolymer morphology increases the extent of connectivity between the hydrophilic domains and improves the PEM properties. It was found that, compared with the random ketone type copolymer with the similar IEC value, the multiblock copolymer has higher protonic conductivity, lower activation energy, and much improved self-diffusion coefficient of water. It can keep more free water than the random copolymer, which results in much improved protonic conductivity under partially hydrated conditions. The multiblock copolymer also showed very promising fuel cell performance, which was comparable to Nafion®. Larger block lengths are currently being investigated.

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