
V.D.5 High Temperature, Low Relative Humidity, Polymer-type Membranes Based on Disulfonated Poly(arylene ether) Block and Random Copolymers Optionally Incorporating Protonic Conducting Layered Water Insoluble Zirconium Fillers

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Objectives

Develop a superior material for polymer electrolyte membranes (PEMs), which will meet performance requirements associated with higher temperatures and lower relative humidities (RHs) by the year 2010.

- The new materials will outperform the present standard material, Nafion®.
- The work builds upon earlier results from VT wherein thermally, oxidatively, hydrolytically stable tough high T_g ion-containing copolymers based on polyarylene ethers were successfully used as PEM systems under relatively high humidity conditions.
- Current objectives are to synthesize and characterize hydrophilic-hydrophobic sequenced block copolymers based upon high performance polymer materials as an approach to develop performance criteria at high temperatures and low RH.

- Determine the hydrophilic-hydrophobic block length effect on the formation of nanophase separated morphologies.
- Provide a clearer understanding about the structure/property relationship of the hydrocarbon-based PEMs.
- Establish the effects of solution-casting conditions (solvent type, film drying temperature, and solvent removal rate) on the final morphology and properties of block polysulfone ether polymers-bi phenyl sulfone (BPSH-BPS) multiblock copolymer PEMs for the optimization of the casting process.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

- Area specific resistance of 0.02 ohm-cm² at 120°C and P_{H₂O} of 40-80 kPa, corresponds to a conductivity of 0.1 S/cm for a 20 micron thick membrane.

Accomplishments

- Novel methodologies for the synthesis of hydrophilic-hydrophobic block copolymers without sequence randomization were developed by utilizing highly reactive perfluorinated small molecules as linkage units.
- Reactive hydrophilic oligomers were successfully coupled with reactive hydrophobic oligomers to make tough film forming compositions with good mechanical strength and conductivities either in liquid water or as a function of RH which are as good as or better than the Nafion® benchmark controls.
- Fundamental membrane properties including ion exchange capacity (IEC), water uptake, and hydration number (λ) were characterized with the hydrophilic-hydrophobic multiblock copolymers.

- Morphologies of the hydrophilic-hydrophobic multiblock copolymers were investigated and well-defined nanophase separated morphology was obtained with longer block lengths copolymers.
- Through chemical structure and processing methodology reached the DOE goal of 70 mS/cm at 80% RH and 30°C.



Introduction

The goal of this research is to develop a material suitable for use as a PEM which by the year 2010 will meet all the performance requirements associated with fuel cell operation at high temperatures and low RH, and will out-perform the present standard Nafion[®]. In particular, it is our objective to extend our previous research based on the use of thermally, oxidatively, and hydrolytically, ductile, high Tg ion containing polymers based on poly(arylene ethers) to the production of polymer electrolyte membranes which will meet all the performance requirements in addition to having an areal resistance of <0.02 ohm-cm² at a temperature of up to 120°C, RH of 25 to 50%, and up to 2.5 atm total pressure. In many instances, our materials already out perform Nafion[®], and it is expected that with some modification by either combining with conductive inorganic fillers and/or synthesizing as a block copolymer it will meet the performance criteria at high temperatures and low RH. A key component in improving the performance of the membranes (and in particular proton conductivity) and meeting the cost requirements of \$40/m² is our development of a film casting process, which shows promise for generation of void free thin films of uniform thickness with controlled polymer alignment and configuration.

Results

Hydrophilic and hydrophobic telechelic oligomers with controlled molecular weight were synthesized via step-growth polymerization. The hydrophilic oligomers were fully disulfonated poly(arylene ether sulfone)s (BPS100) and the hydrophobic oligomers were partially fluorinated poly(arylene ether ketone)s (6FK). The fluorination of the hydrophobic segment is expected to promote nanophase separation with the hydrophilic segment, resulting in improved proton transport properties. The phenoxide terminated 6FK hydrophobic oligomers were then end-capped with hexafluorobenzene (HFB) to facilitate a coupling reaction with the phenoxide terminated BPS100 hydrophilic blocks. Multiblock copolymers with various block lengths were synthesized by coupling the phenoxide terminated BPS100 and the HFB end-capped

6FK oligomers (Figure1). The coupling reaction was conducted at 105°C, which was low enough to prevent possible trans-etherification.

Four BPSH-6FK multiblock copolymers with different block lengths were systematically synthesized and their fundamental membrane properties were evaluated, which are summarized in Table 1, along with values for the control PEM materials, Nafion[®] 112 and biphenyl based disulfonated polysulfone (35% saturation; BPSH35). The intrinsic viscosity of the copolymers ranged from 0.62 to 0.88 dL/g, which was sufficiently high to obtain tough ductile membranes. As expected, the water uptake results for the multiblock copolymers were shown to be strongly dependent on their IEC values, which is associated with increased ionic moieties in the system. In addition to the impact of IEC, the water uptake behavior of the multiblock copolymers was also strongly influenced by hydrophilic and hydrophobic block lengths. Specifically, the water uptake values for the multiblock copolymers with similar IECs increased with increasing block length. For example, the BPSH3-6FK3, BPSH5-6FK5, and BPSH10-6FK10 copolymers displayed very similar IEC values of around 1.5 meq/g. If water uptake is exclusively dependent on IEC, then the water uptake values for these copolymers should have been very similar. However, our results showed that water uptake was strongly influenced by the hydrophilic and hydrophobic block lengths, which increased from 31% for the BPSH3-6FK3, to 81% for the BPSH10-6FK10. It should be noted that while the BPSH15-6FK15 displayed somewhat lower IEC (1.34 meq/g) than other equal length block copolymers, its water uptake was even higher than that of the BPSH10-6FK10.

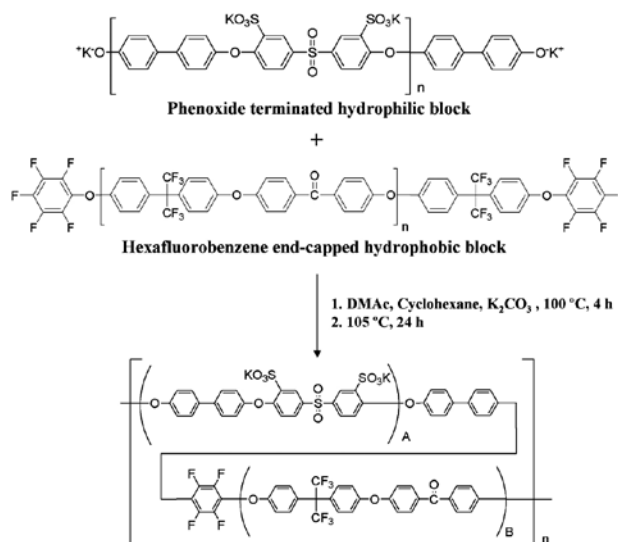


FIGURE 1. Synthesis of Segmented Sulfonated Multiblock Copolymers (BPSH-6FK) with HFB Linkage Group

TABLE 1. Fundamental Membrane Properties

Copolymers	Experimental IEC (meq g ⁻¹) ^a	Intrinsic Viscosity (dL g ⁻¹) ^b	Water Uptake (%)	Conductivity (S cm ⁻¹) ^c	Hydration Number (λ)
Nafion [®] 112	0.90	-	25	0.090	15.0
BPSH 35	1.50	0.70	36	0.070	13.3
BPSH 3 – 6FK 3	1.51	0.78	31	0.08	12
BPSH 5 – 6FK 5	1.53	0.62	69	0.10	25
BPSH 10 – 6FK 10	1.48	0.88	81	0.11	30
BPSH 15 – 6FK 15	1.34	0.70	100	0.12	41

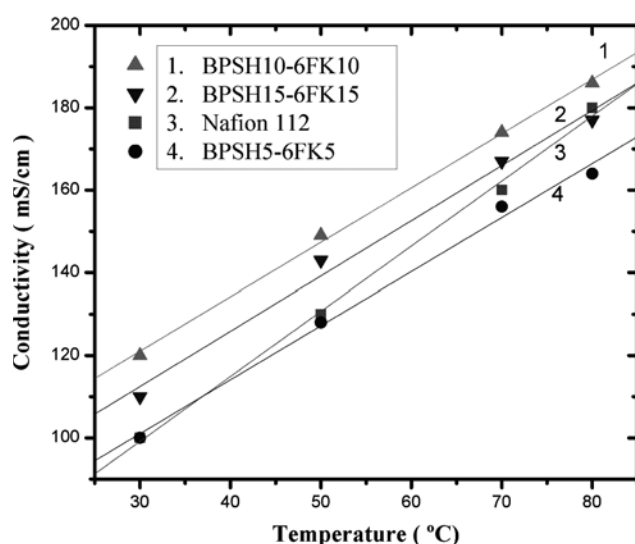
^a Determined by titration with NaOH.

^b In N-methylpyrrolidone with 0.05 M LiBr at 25°C.

^c Measured in deionized water at 30°C.

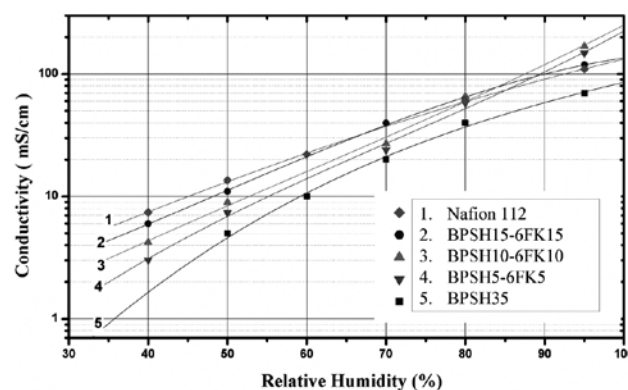
Figure 2 shows the relationship between temperature and the proton conductivity of the fully hydrated multiblock copolymers. As clearly demonstrated, proton conductivity increased with increasing temperature, reaching 185 mS/Cm at 80°C for the BPSH10-6FK10. Moreover, the conductivity-temperature slope for each of the copolymers is similar, implying that the copolymers have a similar conduction mechanism. Compared with Nafion[®] 112, the multiblock copolymers displayed a slightly lower temperature dependence on proton conductivity.

Proton conductivity as a function of RH at 80°C was also studied. As shown in Figure 3, the proton conductivity of the BPSH35 random copolymer dropped rapidly at lower RH values. Although BPSH35 demonstrated acceptable proton conductivity under fully hydrated conditions on account of sufficient water content, its proton conductivity under partially hydrated conditions decreased significantly due to the scattered

**FIGURE 2.** Proton Conductivities of BPSH-6FK and Nafion[®] 112 in terms of Temperature

hydrophilic domains in the random copolymer. In short, the absence of the hydrophilic domain connectivity and insufficient water content in the membrane was unable to maintain high proton conduction under partially hydrated conditions. Conversely, the performance of the multiblock copolymers under partially hydrated conditions was shown to be superior to the random copolymer, and also improved with increasing block lengths. For example, the conductivity of the BPSH15-6FK15 under partially hydrated conditions was comparable to that of Nafion[®] 112.

Figure 4 shows transmission electron microscopy (TEM) images of the BPSH-6FK multiblock copolymers with different block lengths. The bright and dark regions in the images correspond to the hydrophobic and hydrophilic segments, respectively. Although no distinct phase-separation was observed for the BPSH5-6FK5 system (Figure 4 (a)), enhancements in connectivity of hydrophilic domain were found in longer block lengths multiblock systems (Figure 4 (b)). Further increase in the block length resulted in higher degree of phase separation showing a clear lamellar morphology (Figure 4 (c)). Thus, by utilizing the well-connected hydrophilic regime for proton conduction, improved

**FIGURE 3.** Proton Conductivities of BPSH-6FK and Nafion[®] 112 under Partially Hydrated Conditions at 80°C

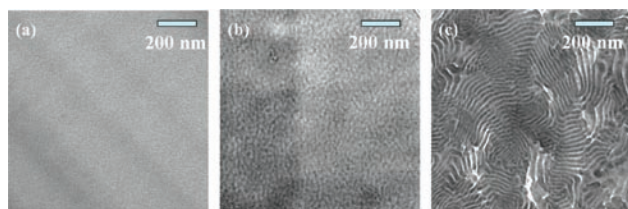


FIGURE 4. TEM Phase Images of BPSH-6FK Multiblock Copolymers (a) BPSH5-6FK5, (b) BPSH10-6FK10, and (c) BPSH15-6FK15

proton conductivity under partially hydrated conditions was achieved.

Conclusions

- Novel multiblock copolymers were synthesized by coupling fully disulfonated poly(arylene ether sulfone) and partially fluorinated poly(arylene ether ketone) as hydrophilic and hydrophobic oligomers, respectively.
- To minimize a possible sequence randomization during the coupling reaction, the highly reactive perfluorinated small molecule, HFB, was utilized as a linkage group.
- The copolymers produced tough ductile membranes via dimethylacetamide solution casting. Resulting proton conductivity and water uptake measurements revealed that changes in hydrophilic and hydrophobic block length influenced membrane properties at similar IEC values by forming nanophase separated morphologies.
- The multiblock copolymer membranes showed highly anisotropic swelling behaviors in comparison to the random copolymers, which were isotropic.
- Utilization of a selective solvent, dimethyl acetamide, yielded the microstructures with more ordered and longer-range lamellar ionic domains, resulting in considerable increase in both water uptake and proton conductivity of the BPSH-BPS multiblock copolymer PEM.
- Drying temperature and/or solvent removal rate also turned out to be a critical factor for the performance of a PEM.

Future Directions

- Synthesis of multiblock copolymers with enhanced hydrophilic-hydrophobic contrast by utilizing more hydrophilic oligomers for sharper phase separations.
- Development of crosslinked PEM system with higher IEC to manage swelling and water uptake behavior.
- Further investigation on the effects of solution-casting conditions using dimethylformamide and dimethylsulfoxide, which show different degrees of

selectivity, and multiblock copolymers consisting of different block lengths, e.g., BPSH-BPS (10k-5k, 15k-10k, 5k-10k, and 10k-15k).

FY 2009 Publications/Presentations

1. Hae-Seung Lee, Abhishek Roy, Ozma Lane, Stuart Dunn, and James E. McGrath, "Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low temperature coupling reactions for proton exchange membrane fuel cells", *Polymer*, 49 (2008), 715-723.
2. Hae-Seung Lee, Abhishek Roy, Ozma Lane, and James E. McGrath, "Sulfonated Fluorinated Multiblock Copolymers with Hydrophilic-Hydrophobic Sequences for Proton Exchange Membranes", 213th ECS Meeting, May 18-22, 2008, Phoenix, Arizona.
3. Hae-Seung Lee, Ozma Lane, and James E. McGrath, "Synthesis and characterization of multiblock copolymers with hydrophilic-hydrophobic sequences for proton exchange membranes. 236th ACS National Meeting, Philadelphia, PA, August 17-21, 2008 (2008).
4. Lee M, Park J, Lee H-S, Lane O, Moore RB, McGrath JE, Baird DG, Effects of solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) multiblock copolymer films for proton exchange membranes, *Polymer*, submitted.
5. Lee M, Lane O, Lee H-S, McGrath JE, Baird DG, Effects of molecular structure and solution-casting conditions on the final morphology and properties of disulfonated poly(arylene ether sulfone) copolymer films for proton exchange membranes, 2008 American Institute of Chemical Engineers Annual Meeting, November 16-21, Philadelphia, Pennsylvania.

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1. Anand Badami, Ozma Lane, Hae-Seung Lee, Abhishek Roy, and James E. McGrath, "Fundamental investigations of the effect of the linkage group on the behavior of hydrophilic-hydrophobic poly(arylene ether sulfone) multiblock copolymers for proton exchange membrane fuel cells" *Journal of Membrane Science* (2009).
2. Abhishek Roy, Xiang Yu, Stuart Dunn, and James E. McGrath, "Influence of microstructure and chemical composition on proton exchange membrane properties of sulfonated-fluorinated, hydrophilic-hydrophobic multiblock copolymers" *Journal of Membrane Science* (2009), 327(1+2), 118-124.
3. Abhishek Roy, Hae-Seung Lee, and James E. McGrath, "Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone)s as novel proton exchange membranes - Part B" *Polymer* (2008), 49(23), 5037-5044.
4. Abhishek Roy, Hae-Seung Lee, Xiang Yu, Mou Paul, Judy Riffle, and James E. McGrath, "Structure-property relationships of proton exchange membranes" *Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry* (2008), 53(2), 752-754.