
V.G.9 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

James E. McGrath (Primary Contact) and Donald G. Baird
University Distinguished Professor, Chemistry
Macromolecules and Interfaces Institute
Virginia Polytechnic Institute and State University (VT)
Blacksburg, VA 24061
Phone: (540) 231-5976; Fax: (540) 231-8517
E-mail: jmcgrath@vt.edu

DOE Technology Development Manager:
Terry Payne
Phone: (202) 586-9585; Fax: (202) 586-9811
E-mail: Terry.Payne@hq.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Technical Advisor: John Kopasz
Phone: (630) 252-7531; Fax: (630) 972-4405
E-mail: kopasz@anl.gov

Contract Number: DE-FG36-06G016038

Start Date: May 1, 2007
End Date: March 31, 2011

Objectives

Develop a superior material for polymer electrolyte membranes (PEMs), which will meet performance requirements associated with higher temperatures and lower relative humidities 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 examine the behavior of block copolymers based upon hydrophilic-hydrophobic moieties as an approach to develop performance criteria at high temperatures and low relative humidity (RH).
- Determine the effects of solution-casting conditions such as solvent type, drying rate, and drying

temperature on the morphology and final properties of PEMs.

- Utilize a quantitative model for phase separation kinetics and mass transfer to establish conditions for obtaining a desired morphology which leads to the formation of membranes based on sulfonated block copolymers with optimum performance.
- Identify the effect of the wet/dry cycle on the properties of continuous cast PEM films.

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

- The membrane performs for more than 4,000 wet/dry cycles, which is a four-fold increase over existing hydrocarbon membranes and approaches the target of 5,000 cycles.
- Cost estimates are at \$20/kW, which is approaching the target of \$10/kW.
- The target is to develop block copolymer membranes that show enhanced performance at higher temperatures and lower humidities: proton conductivity is 0.1 S/cm at 70% RH. (0.1 S/cm at 120°C and PH₂O of 40-80 kPa.)

Accomplishments

- Methodologies for the synthesis of hydrophobic-hydrophilic block copolymers based upon stable polyarylene ether systems were developed.
- 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.
- Methodologies developed for predicting protonic conductivity from diffusion characteristics of water through PEM systems.
- Developed a mathematical model of drying which eventually will incorporate the development of structure which will lead to optimum PEM performance.
- Identified the effects of solvent casting conditions (drying rate, drying temperature, shearing, initial solution concentration) on PEM performance and their relation to the morphology of random and block copolymer systems.
- Derived the appropriate equations for predicting the morphology generated during solvent removal which will lead to PEMs with optimum performance.



Introduction

The VT research effort on Advanced Materials for Fuel Cells began in May 2006. The approach was quite broad and included the development of important membrane materials for automotive fuel cell applications. It was recognized that the membrane variables included molecular weight, ion content, chemical composition, and sequence. It was proposed to conduct extensive mechanical and electrochemical characterization of the components, and to generate membrane electrode assemblies as a function of time, temperature, and electrochemical history. The overall objective is the relation of molecular design in the membrane to transport at low or ambient relative humidities. The remainder of this report will provide highlights of the progress made during the past year.

Approach

The main direction over the last year is to maintain proton conductivity under partially hydrated conditions. Block copolymers displaying nanophase separation will permit transport and enhance conductivity by a co-continuous hydrophilic sequence. The nanophase separation follows along classical ideas that the two-phase structure should develop at some critical degree of polymerization and as a function of the interaction parameter. The χ parameter for ionomer systems is quantitatively unknown. However, we can model this empirically using the concept of hydrophobic-hydrophilic interactions. Well-developed block copolymers based on a hydrophobic partially-fluorinated arylene ether linked together with a very hydrophilic reactive water soluble oligomer was achieved. The

resulting block copolymer materials make very good, strong films. The proton conductivity in liquid water is better than Nafion[®], and is a function of the block lengths. It was demonstrated that proton conductivity under partly hydrated conditions improved with block length and this was related to the morphological developments. A simplified methodology for synthesizing the block copolymers using endcapping of either decafluorobiphenyl or hexafluorobenzene on the hydrophobic block, which allows the polymerization temperature to be much lower (approximately 100°C) was developed. This produces a very clean reaction production which has definite characteristics and long-range order as determined by both atomic force microscopy and transmission electron microscopy. All of the block copolymers show anisotropic swelling with relatively low in plane x-y swelling.

Results

Structure Property Relationship of PEMs

Over the last few years our group has been actively synthesizing thermally stable multi-block copolymers with varying chemical structures and compositions, for potential applications as proton exchange membranes. The multi-block copolymer showed superior performance under both fully hydrated conditions and more importantly under partially hydrated conditions when compared to the existing state-of-the-art Nafion[®] and earlier the random copolymers. Besides the improvement in transport properties, it was possible to alter the trade-off between the water uptake and proton conductivity by synthesizing multi-block copolymers with unequal block lengths (keeping the hydrophobic segments longer than the hydrophilic segments). When compared with equal block length materials, for example, the performance characteristics of the BisSF-BPSH (17:12) with an ion exchange capacity (IEC) of 1.5 meq/g were comparable to those of the equal block length BisSF-BPSH (15:15) materials—but with a significantly lower water uptake (45%) compared to BisSF-BPSH (15:15) (70%) (Figure 1). By creating the correct balance between ionic content and block length, one can tailor the morphology of PEMs for improved performance at low RH with reduced water uptake.

In addition to these, the unequal block length approach allowed us to significantly reduce the in-plane swelling of these materials. These results along with our earlier publications highlight the potential and promise for the multi-block copolymers as the next generation PEMs. At this point, it is important to revisit the synthetic aspects for multiblock copolymer as it may be another tool for altering or having a precise control on both morphology and the process chemistry.

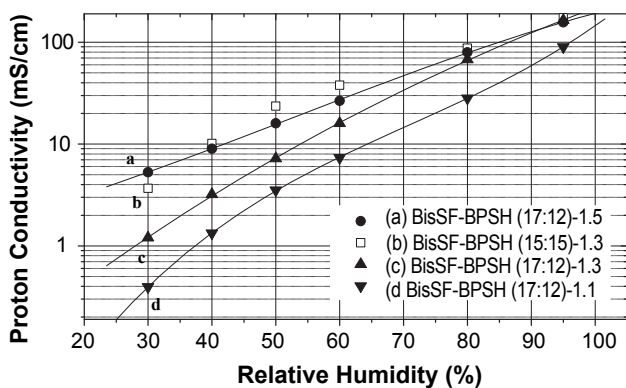


FIGURE 1. Proton conductivity as a function of relative humidity for the BisSF-BPSH (17:12) with varying IEC, the number after the parenthesis represents IECs in meq/g.

Very recently, we have been able to synthesize segmented block copolymer with simultaneous formation of hydrophobic segments. Compared to the multiblock copolymer synthesis, this approach allows us to scale-down the three step process to two, simplifying the overall synthesis process. The research has involved the initial syntheses of the hydrophilic oligomer with a controlled molecular weight. In the second step, simultaneous addition of the hydrophobic monomers with the growth of the hydrophobic oligomer from the two functional ends of the hydrophilic oligomer leading to the formation of the segmented ion containing block copolymers. In a summary, these are the following advantages one might expect from this process.

- Stoichiometric control of hydrophobic-hydrophilic blocks to control IEC
- Eliminates at least one reaction set-up
- The altered sequencing of blocks may positively influence PEM properties by providing superior ordering

As a proof-of-concept and to demonstrate the principle, we have chosen the BisSF-BPSH system as the starting series. However, it is possible to extend this approach to many other multiblock copolymers synthesized in our group.

Synthesis of Segmented Block Copolymers

Phenoxide terminated hydrophilic blocks (BPSH100) were synthesized using a previously published procedure. The procedure is outlined in Figure 2.

Multi-block Copolymer Synthesis

A BisSF-BPSH(xK-yK) series was synthesized using the procedure reported earlier. The copolymer block lengths and IECs were systematically varied. Efforts were made to have the block lengths and IECs similar to those synthesized using the segmented synthesis approach. This was done to allow the comparison of the different transport properties between the copolymer synthesized by these two methods at similar IECs and block lengths.

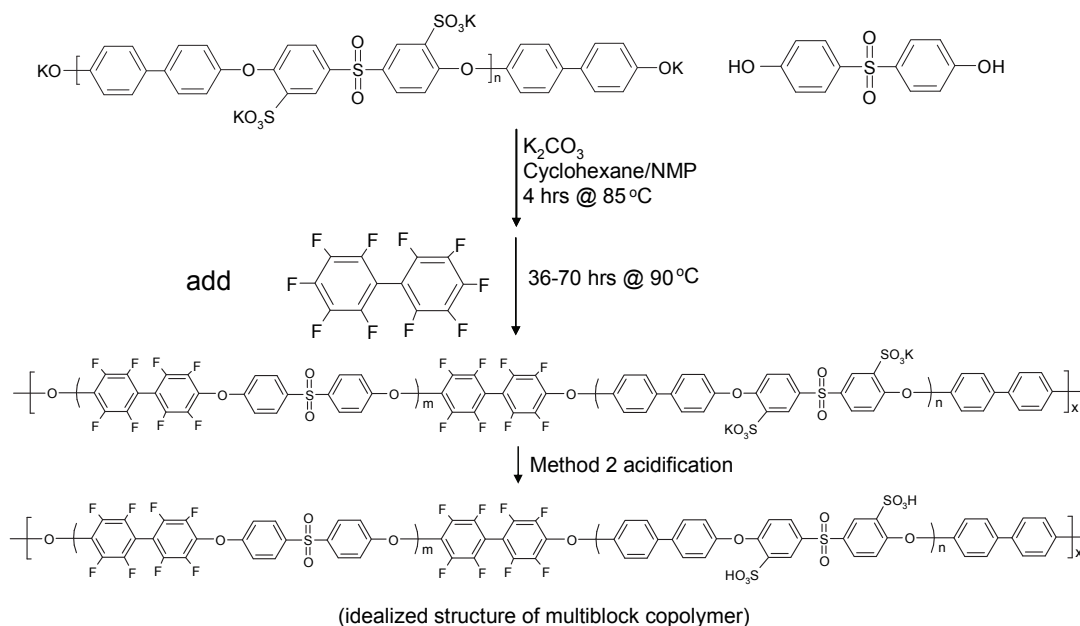


FIGURE 2. Synthesis of Segmented Block Copolymer (BisSF-BPSH100) via Simultaneous Formation of Hydrophobic Block (BisSF)

Water up-take and proton conductivity were determined for the segmented and the multi-block copolymers as reported in Figure 3. At a similar IEC and block length, both multiblock and segmented copolymers showed similar water uptake and proton conductivity values. An influence of block length on water sorption was observed for both of the two copolymer series. At least under fully hydrated conditions no significant differences in properties were observed between the segmented and the multiblock copolymers.

Our earlier study indicated a profound role of morphology on proton transport particularly under the partially hydrated conditions. Morphology is a strong function of the copolymer microstructure, including composition and sequence length. Figure 3 demonstrates the plots of proton conductivity vs. RH for the multi-block and segment copolymers at 5-5 and 9-9 block lengths at 80°C. At least under similar experimental conditions, no significant difference was observed between the two systems on proton transport behavior, under partially hydrated conditions. This indirectly supports that the segmented block copolymer approach have resulted in similar morphology to that of the multi-block copolymer morphology.

In summary, we were successful in designing and synthesizing segmented ion containing multiblock copolymers using a much simpler and, arguably a more precise synthetic method in comparison to the conventional multiblock copolymer synthesis method. It was possible to synthesize high molecular weight segmented multiblock copolymers, as evidenced by current-voltage, spectroscopy and conductivity measurements. Spectroscopic analysis confirmed no significant changes in chemical composition or distribution between these two processes.

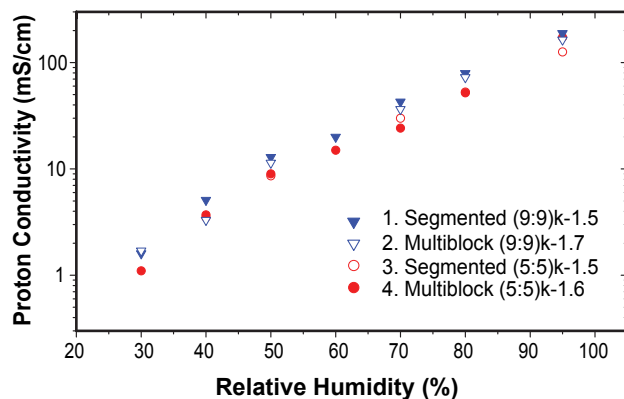


FIGURE 3. Comparison between the Segmented and Multiblock Copolymers on Proton Conductivity under Partially Hydrated Conditions at 80°C

Results on Effects of Solution-Casting Conditions

The effects of solution-casting conditions on the properties of PEMs were investigated for the scale-up of the film casting process using a previously constructed batch convection drying apparatus designed and developed in our laboratory to generate industrial-level drying conditions. Film drying was carried out at two temperatures, 22°C (room temperature) and 80°C. Room temperature was the lowest temperature which was available without any additional equipment, and 80°C was a critical temperature, above which bubbling defects occurred because of high vapor pressure. A non-selective solvent, NMP, and a selective solvent, DMAC, were used as casting solvents. The result of proton conductivity measurements is presented in Figure 4.

As previously reported, it was observed that the proton conductivity increased with the segment length despite the similar values of ion exchange capacity. The

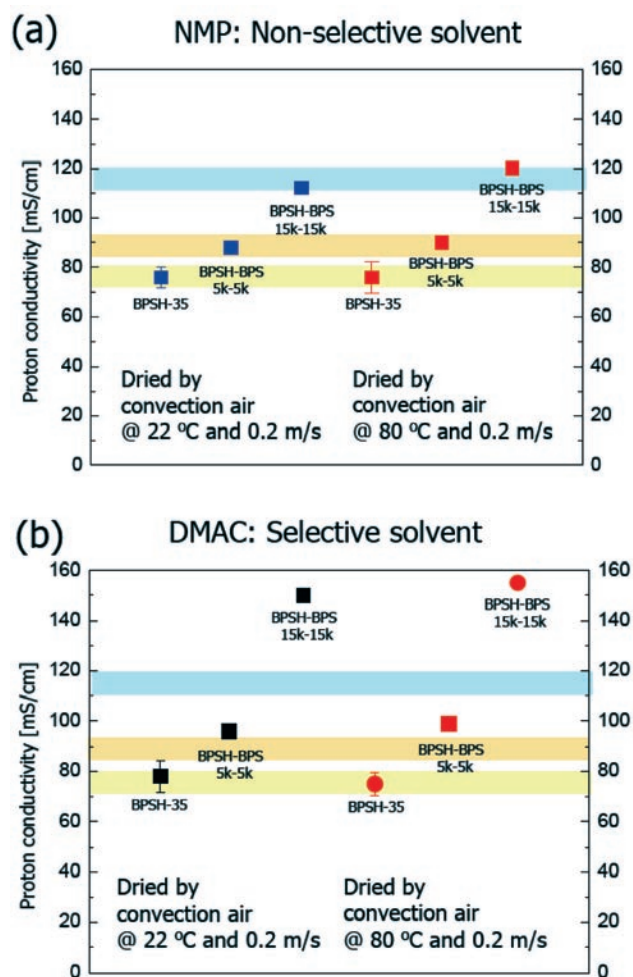


FIGURE 4. Effects of molecular structure, drying temperature and solvent type on proton conductivity measured at 30°C and fully hydrated condition.

proton conductivity of BPSH100-BPS0 (5k-5k) film cast with NMP was slightly higher than that of BPSH-35 film cast in NMP, but the proton conductivity of BPSH100-BPS0 (15k-15k) cast with NMP was considerably higher than those of BPSH-35 and BPSH100-BPS0 (5k-5k). On the other hand, no substantial effect of drying temperature was observed. It was believed that, when the films were dried using convection air at 80°C, the total drying time (less than 30 min) was too short for any microstructural change to occur. Further investigation will be performed to clarify if drying temperature may cause any significant changes in the final properties. In Figure 4 (b), the proton conductivity of the copolymer films cast with DMAC is presented. As observed from the proton conductivity of the copolymer films cast with NMP, the higher proton conductivity was achieved from the copolymer with longer segment length and no noticeable effect of drying temperature was observed. It is worthy to note that the proton conductivities of the BPSH100-BPS0 films cast with DMAC were higher than those of the equivalent films cast with NMP, whereas the proton conductivity of BPSH-35 films did not vary regardless of solvent type and drying temperature. It was also obvious that the magnitude of proton conductivity increase of BPSH100-BPS0 (15k-15k) was larger than that of BPSH100-BPS0 (5k-5k).

Conclusions

- Utilization of a selective solvent induced higher proton conductivity of BPSH100-BPS0 measured at 30°C and fully hydrated conditions.
- Wet/dry cycle caused the change in the dimensions of continuous cast PEM films by releasing the stress built-up in the films during film manufacturing, which may be potentially useful for enhancing the durability of the films.
- A method for quantifying the rate of phase transformation during solvent removal was developed which will be incorporated into a drying model for optimizing the process for solvent removal.

Future Directions

- Further investigation on the effect of wet/dry cycle on the properties of continuous cast membranes in consideration of other properties such as proton conductivity, mechanical property and morphology.
- Reveal the cause and mechanism of the effects of solution-casting conditions using scattering, spectroscopy and rheological measurement techniques.
- On-going work for the development of rheological measurement technique for the study of transformation and kinetics of block copolymers in solution-cast films in drying process.

Special Recognitions & Awards/Patents Issued

1. James E. McGrath, Recipient of the American Chemical Society Award in Polymer Chemistry, 2008.
2. U.S. Patent 7,361,729 “Ion-Conducting Sulfonated Polymeric Materials” issued to Mike Hickner, Yu-Seung Kim, James E. McGrath, Feng Wang. April 22, 2008.

FY 2008 Publications/Presentations

1. Huang, J., Fan, G., Zhang, Z., Badami, A., Takamuku, S., McGrath, J. E., and Baird, D. G., Continuous Film Casting and Evaluation of Polymer Membranes for Fuel Cells, 2008 Society of Plastics Engineers Annual Conference, Milwaukee, WI (May 2008).
2. Lee, Myoungbae, Ozma Lane, McGrath, James E., and Baird, Donald G., Solvent-casting of Disulfonated Poly(arylene ether sulfone) Copolymer for Proton Exchange Membranes in Fuel Cells, 2008 Society of Plastics Engineers Annual Conference, Milwaukee, WI (May 2008).
3. Huang, J., Lee, M. and Baird, D. G., Continuous Solution-Casting of Polymer Electrolyte Membranes and Effects of Casting Conditions on the Properties of the Membranes, 2008 Polymer Processing Society Annual Conference, Salerno, Italy, 2008.

References

1. Roy, A.; Yu, X.; Dunn, S.; McGrath, J. E., Influence of Microstructure and Chemical Composition on Proton Exchange Membrane Properties for Disulfonated BisSF-BPSH Multiblock Copolymers. *Submitted 2008*.
2. Li, Y.; Roy, A.; Badami, A. S.; Hill, M.; Yang, J.; Dunn, S.; McGrath, J. E., Synthesis and characterization of partially fluorinated hydrophobic-hydrophilic multiblock copolymers containing sulfonate groups for proton exchange membrane. *Journal of Power Sources* **2007**, *172*, (1), 30-38.
3. Lee, H.-S.; Badami, A. S.; Roy, A.; McGrath, J. E., Segmented sulfonated poly(arylene ether sulfone)-b-polyimide copolymers for proton exchange membrane fuel cells. I. Copolymer synthesis and fundamental properties. *Journal of Polymer Science, Part A: Polymer Chemistry* **2007**, *45*, (21), 4879-4890.
4. Lee, H.-S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E., Hydrophilic-hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low-temperature coupling reactions for proton exchange membrane fuel cells. *Polymer* **2008**, *49*, (3), 715-723.
5. Hopp, R, Lane O, Yu, X, McGrath, J.E., Segmented Hydrophilic-Hydrophobic Membranes for PEM, ACS Meeting Philadelphia, PA, August 19, 2008.