Synthesis and Characterization of Sulfonated-Fluorinated, Hydrophilic-Hydrophobic Multiblock Copolymers for Proton Exchange Membranes

*Xiang Yu, Abhishek Roy, Stuart Dunn, Juan Yang, James E. McGrath**

Summary: Nanophase separated ionic-hydrophobic block copolymers may be more suitable as proton exchange membranes than random copolymers. A series of multiblock copolymers, composed of alternating segments of fully disulfonated poly(arylene ether sulfone) and highly fluorinated poly(arylene ether sulfone), were synthesized from hydrophilic and hydrophobic telechelic oligomers having a variation of molecular weights. The high reactivity of the fluorinated oligomers made unnecessary the use of high reaction temperatures, and thus the coupling reactions may be free of ether-ether interchange side reactions. The copolymers were characterized with regard to proton conductivity, water uptake and self-diffusion coefficient of water, and the results were compared to those of Nafion and a partially disulfonated BPSH-35 random copolymer.

Keywords: block copolymer; fluorinated polymer; proton exchange membrane

Introduction

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy.[1,2] Proton exchange membrane fuel cells (PEMFCs) have shown promise as alternative automotive and stationary power sources.[2,3] The proton exchange membrane (PEM), which is the electrolyte that transfers protons from the anode to the cathode, is the key component of the system. A successful PEM should have high proton conductivity, low electronic conductivity, good mechanical strength, high oxidative and hydrolytic stability, low fuel permeability, ease of fabrication into MEA, and controlled swelling-deswelling behavior under low relative humidity (RH) cycling.[3,4]

The current state-of-the-art PEMs are perfluorosulfonic acid membranes such as Nafion®.[5] Its highly acidic perfluosulfonic acid groups impart high proton conductivity, whereas the semicrystalline backbone provides excellent chemical and electrochemical stability. However, Nafion® and other perfluorosulfonated PEMs suffer from disadvantages including high cost, limited operating temperature (80 °C), and high fuel permeability (in DMFC).[4,5] Recently significant effort has been made to develop alternative proton exchange membranes. McGrath et al., for instance, developed partially disulfonated poly(arylene ether sulfone) random copolymers (BPSH) as potential PEMs.[6–8] These materials have shown performances comparible to Nafion under fully hydrated conditions.

For the optimal performance of a PEMFC, it is desirable to keep the level of hydration low. For instance, 120 °C and 50% relative humidity (RH) has been established as the target operating conditions for automotive applications. PEMs based on partially sulfonated random copolymers have been reported to show strong dependence of proton conductivity on humidity. Although the conductivity of

Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061, USA
E-mail: jmcgrath@vt.edu

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

BPSH and other random copolymer membranes at fully hydrated conditions (i.e. in liquid water) is comparable to that of Nafion®, it tends to decrease remarkably as the level of hydration decreases.[9] This may be because a substantial number of water molecules are required to establish connectivity among the randomly distributed sulfonic acid groups. Nafion®, on the other hand, is a modestly crystalline copolymer which may be above its T_g at room temperature, and has been reported to show a nanophase separated morphology in the dry state, featuring ionic clusters that are interconnected by narrow ionic channels.[5] The challenge therefore lies in developing alternative PEMs which feature associated ionic domains at even low hydration levels. Nanophase separated hydrophilic-hydrophobic block copolymer ionomers are desirable for this purpose. In contrast to the random copolymers, in block copolymer membranes the ionic groups are selectively incorporated in one or more blocks and may exist in ordered sequences. Continuous proton conducting channels may thus be formed even with low concentration of water. It is postulated that high proton conductivity can therefore be sustained under partially hydrated conditions.

We have been engaged in the synthesis of hydrophilic-hydrophobic multiblock copolymer ionomers, the structures of which are shown in Figure 1, where X represents an isopropylidene unit (Figure 1, a), a hexafluoroisopropylidene unit (Figure 1, b), or a sulfone group (Figure 1, c). The corresponding copolymers are termed BisAF-BPSH, 6FBisAF-BPSH, and BisSF-BPSH, respectively. We have previously published some work on the first two types of multiblock copolymers.[9–11] In this work we will discuss the synthesis of the BisSF- BPSH series copolymers and some characterization results relating to their potential as alternative proton exchange membranes.

Experimental

Materials

4,4′-Dihydroxydiphenyl sulfone (Bisphenol-S) and decafluorobiphenyl were obtained from aldrich and dried under vacuum before use. 4,4′-Dichlorodiphenylsulfone (DCDPS) was obtained from Solvay Advanced Polymers and used as received. 3,3′-Disulfonated-4,4′- dichlorodiphenylsulfone (SDCDPS) was synthesized from DCDPS according to a process reported elsewhere.[12] 4,4′-Biphenol was obtained from Eastman Chemical and used as received. *N*-methyl-2-pyrrolidone (NMP), purchased from Aldrich, was vacuum-distilled from calcium hydride and stored under nitrogen.

Synthesis of the Fluorinated Hydrophobic BisSF Oligomers

Bisphenol-S (1.287 g, 5.142 mmol) was added to a three neck round bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet and a Dean-Stark trap. NMP (10 mL) was added to the flask and the mixture was dissolved. Then K_2CO_3 (1.183 g, 7.20 mmol) was added, followed by 5 mL of cyclohexane. The reaction bath was heated to 150 °C and kept at this temperature for 2 h to dehydrate the system. The reaction was cooled to 50 °C and decafluorobiphenyl (2.046 g, 6.124 mmol) was added. The bath temperature was raised to 110 °C and the reaction was allowed to proceed at this temperature for 5 h.

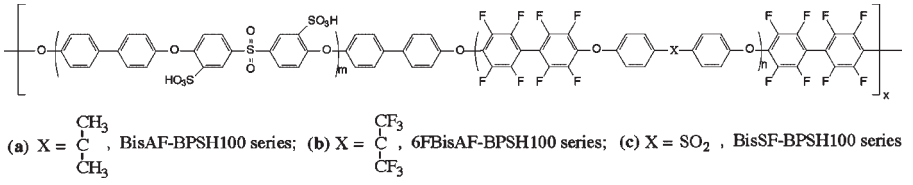

Figure 1.
Structures of sulfonated-fluorinated multiblock copolymers.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

The mixture was precipitated into 200 mL of water/methanol (50/50 v/v) and rinsed with water and methanol. The precipitated polymer was dried under vacuum at 100 °C.

Synthesis of the Diphenoxide Functional BPS100 Oligomers

A three neck round bottom flask, equipped with a mechanical stirrer, a condenser, a nitrogen inlet and a Dean-Stark trap, was charged with biphenol (0.412 g, 2.213 mmol), SDCDPS (0.912 g, 1.856 mmol), and 10 mL of NMP. The mixture was dissolved, then K_2CO_3 (0.430 g, 3.12 mmol) and 5 mL of toluene was added. The reaction bath was heated to 150 °C to dehydrate the system. Then the bath temperature was then slowly raised to 190 °C by the controlled removal of toluene. The polymerization was allowed to proceed at this temperature for 30 h, and the resulting oligomer was used in the block copolymer synthesis without isolation.

Synthesis of the BisSF-BPSH Multiblock Copolymer

The reaction bath for the hydrophilic oligomer synthesis was cooled to 80 °C, and the perfluoro hydrophobic oligomer (1.050 g, 0.350 mmol) was dissolved in 10 mL of NMP and added to the same reaction flask. The bath temperature was raised to 110 °C and kept at this temperature for 4 days. The reaction mixture was precipitated into 300 mL of isopropanol to obtain a fibrous polymer. The product was stirred in deionized water at 60 °C for 12 h and in acetone for 12 h, and dried under vacuum at 120 °C for 24 h.

Membrane Preparation

The salt form copolymers were redissolved in NMP to afford transparent solutions with 5% solids, then the solutions were cast onto clean glass substrates. The films were dried for 2 days with infrared heat at gradually increasing temperatures, and then dried under vacuum at 110 °C for 2 days. The membranes were converted to their acid form by boiling in 0.5 M H_2SO_4 for 2 h, and were then boiled in deionized water for 2 h.

Measurement of Proton Conductivity

Proton conductivity at 30 °C at full hydration (in liquid water) was determined in a window cell geometry[13] 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.[14] In determining proton conductivity in liquid water, membranes were equilibrated at 30 °C in DI water for 24 h prior to the testing. 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 24 h before each measurements.

Determination of Water Uptake

The water uptake of all membranes was determined gravimetrically. First, the membranes were soaked in water at 30 °C for 2 days after acidification. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. The membranes were then dried at 120 °C under vacuum for at least 24 h and weighed again. The water uptake of the membranes was calculated according to Equation 1 where mass_{dry} and mass_{wet} refer to the mass of the dry membrane and the wet membrane, respectively.

$$\text{water uptake}\% = \frac{\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}}}{\text{mass}_{\text{dry}}} \times 100 \quad (1)$$

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 Equation 2, where MW_{H2O} is the molecular weight of water (18.01 g/mol) and IEC is the ion exchange capacity of the dry copolymer in equivalents per gram.

$$\lambda = \frac{(\text{mass}_{\text{wet}} - \text{mass}_{\text{dry}})/\text{MW}_{\text{H}_2\text{O}}}{\text{IEC} \times \text{mass}_{\text{dry}}} \quad (2)$$

Pulsed-Field Gradient Spin Echo Nuclear Magnetic Resonance

Water self diffusion coefcients were measured using a Varian Inova 400 MHz (for

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

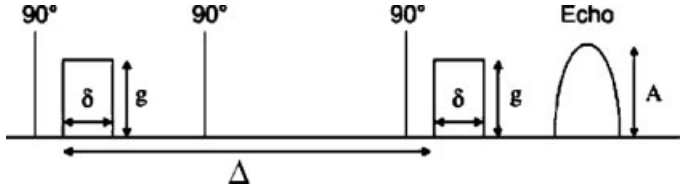

Figure 2.
Pulse sequence schematic for PGSE NMR experiments.

protons) nuclear magnetic resonance spectrometer with a 60 G/cm gradient diffusion probe. A total of 16 points were collected across the range of gradient strength and the signal to noise ratio enhanced by co-adding 4 scans. The standard stimulated-echo NMR pulse sequence is shown in Figure 2.

The measurement was conducted by observing the echo signal intensity (A) as a function of the gradient strength. The diffusion coefficient (D) was determined by fitting the data to Equation 3, where A is the NMR signal intensity (A) as a function of gradient strength, γ is the gyromagnetic ratio (26,752 rad G^{-1} s^{-1} for protons), δ is length of the gradient pulse, Δ is the time between gradient pulse.[15,16]

$$A(\mathrm{g}) = A(o)\exp[-\gamma^2 D\mathrm{g}^2\delta^2(\Delta - \delta/3)] \quad (3)$$

Membrane samples of approximately 5 mm × 15 mm × 150 μm were equilibrated in liquid water for at least 24 h. The samples were removed from the liquid water, blotted to remove droplets, quickly inserted into the NMR tube, and immediately measured over a span of about 5 min. Measurements were repeated by reimmersing the sample in DI water, waiting at least 30 min, and then repeating the transfer and measurement process. Separate measurements were collected with different times between the gradient pulses.

NMR Spectroscopy and Intrinsic Viscosity

^{1}H and ^{19}F NMR analysis were conducted on a Varian Unity 400 spectrometer. All spectra were obtained from a 10% solution (w/v) in a DMSO.d6 solution at room temperature. Intrinsic viscosities were determined in 0.05 M LiBr NMP at 25 °C using a Cannon Ubbelholde viscometer.

Results and Discussion

Synthesis of Telechelic Oligomers and Multiblock Copolymers

Multiblock or segmented copolymers can be synthesized by the step or condensation

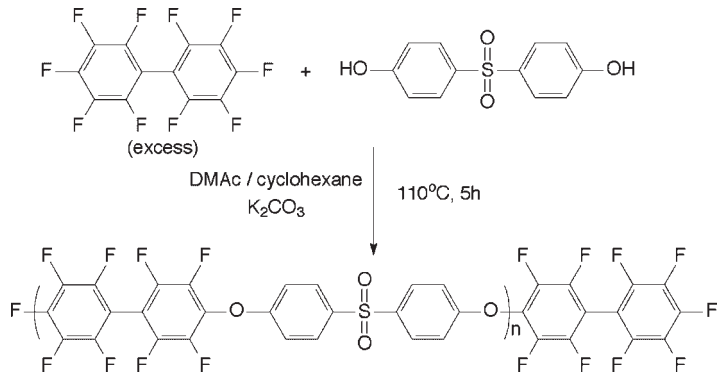

Figure 3.
Synthetic scheme for BisSF hydrophobic oligomers.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

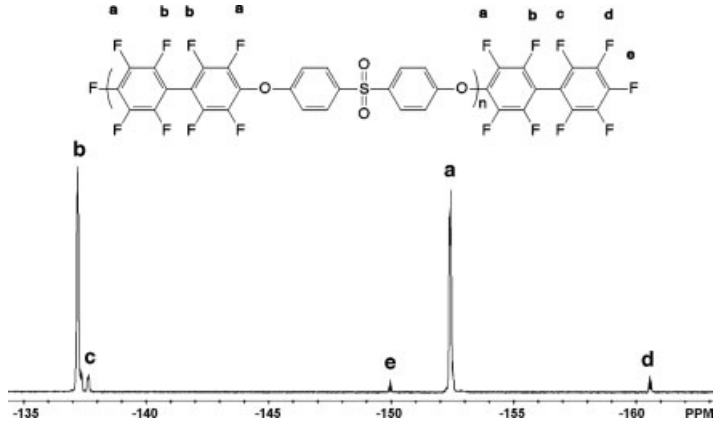

Figure 4.
^{19}F NMR spectra of a BisSF oligomer.

polymerizations of telechelic oligomers bearing appropriate end-groups and molecular weights. As shown in Figure 3, Fluoro-terminal BisSF oligomers were obtained by polymerizing bisphenol-S and excess decafluorobiphenyl. The reaction proceeded readily at 110 °C thanks to the highly reactive perfluorinated monomer. The ^{19}F NMR spectrum of a BisSF oligomer is shown in Figure 4. The experimental M_n of the oligomers can be calculated based on the integrals of the peaks due to main chains and end-groups, and were found to be in decent agreement with the target values.

Biphenol and SDCDPS were polymerized to synthesize the phenoxide-functional, fully disulfonated BPS-100 oligomers (Figure 5). A 1 ~ 2 mol% excess of SDCDPS relative to the calculated amount was usually used to compensate for its impurity, caused by the inevitable presence of salt and/or water. Figure 6 shows the ^{1}H NMR spectrum of a BPS-100 oligomer.

The synthetic scheme of BisSF-BPSH multiblock copolymers is demonstrated in Figure 7. The synthesis of a multiblock copolymer requires that the telechelic oligomers be readily reactive toward each other and able to form stable linkages. The use of the highly reactive fluorinated oligomers enables the block copolymerizations to be conducted at a much lower temperature than the non-fluorinated

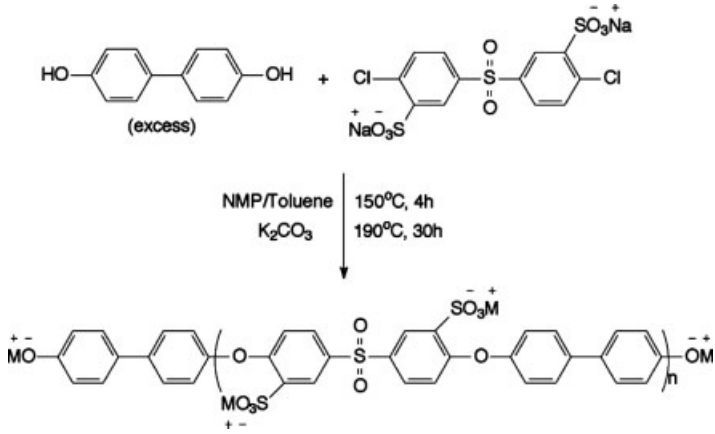

Figure 5.
Synthetic scheme for BPS100 hydrophilic oligomers.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

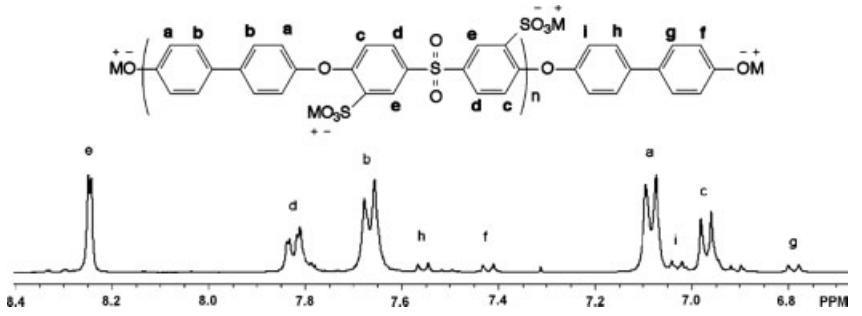

Figure 6.
^{1}H NMR spectrum of a BPS100 oligomer.

systems (~110 °C vs. ~180 °C). This helps minimize the possibility of the ether-ether interchange process which could lead to randomized architectures. The ^{19}F and ^{1}H NMR spectra of a multiblock copolymer are shown in Figures 8 and 9, respectively. Here the peaks due to end-groups in the cases of BisSF and BPS100 oligomers are not observed; they either disappeared (Figure 8) or shifted (Figure 9). Thus high conversion of the coupling reaction should have been achieved.

In Figure 9, the small peak at about 7.3 ppm is tentatively assigned to the linkages between fluorinated and sulfonated blocks. The ^{1}H NMR spectra of a series of BisSF-BPSH copolymers, with increasing block lengths, are overlaid in Figure 10. With the other peaks normalized, it can be observed that, as the block lengths increase, the intensity of the 7.3 ppm peak gradually becomes smaller. This is consistent with the fact that, in multiblock copolymers, the longer the segments are, the smaller number of linkages would exist in each copolymer chain. Therefore it is indicated that the hydrophilic and hydrophobic sequences were preserved and not randomized.

The block lengths, molar feed ratios, intrinsic viscosity and ion exchange capacities (IEC) of the BisSF-BPSH copolymers are summarized in Table 1. As reflected in the molar ratios, an excess of the BisSF hydrophobic oligomer were used in the syntheses of all the multiblock copolymers. It seems that these coupling reactions of oligomers are more tolerant to the stoichiometric imbalance than condensation polymerizations of small monomers, because all the resulting copolymers showed reasonable intrinsic viscosities and were capable of forming tough and ductile membranes. Thus, the feed ratios, as well as the block

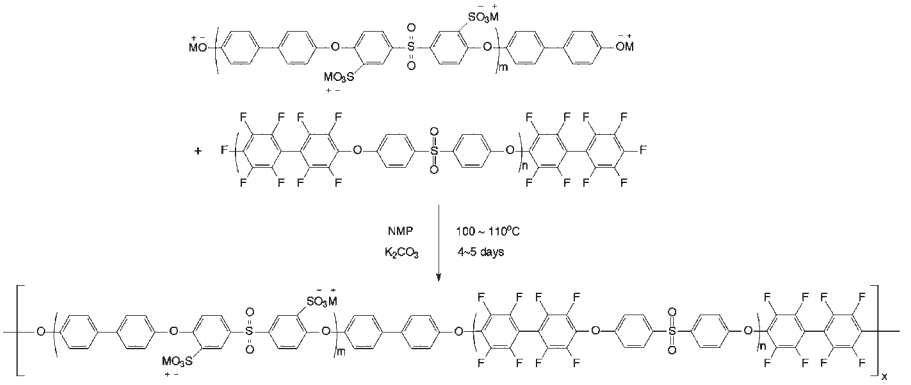

Figure 7.
Synthesis of BisSF-BPSH multiblock copolymers.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

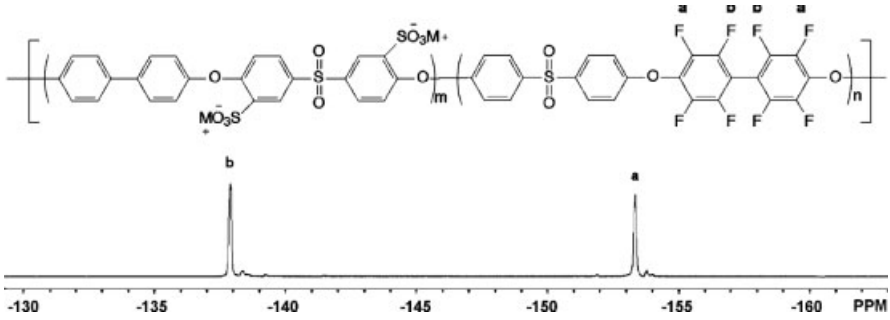

Figure 8.
^{19}F NMR spectra of a BisSF-BPSH multiblock copolymer.

lengths, are variables that can be tailored to certain extents in order to control the IEC and hence the swelling behavior of the multiblock copolymers.

Electrochemical Characterization of Multiblock Copolymer Membranes

The multiblock copolymers synthesized were characterized on the basis of water uptake, proton conductivity and self-diffusion coefficients of water. Table 2 summarizes these properties as a function of the block lengths. Nafion 112 and BPSH 35 are represented as controls. One of the foremost important properties of proton exchange membrane is the water uptake. Water is known to reside among the hydrophilic domains of the copolymers and serves a critical function in the proton transport. Proton conductivity is known to depend on water content and increases with increasing water content for the random copolymers.[17] However, too much water uptake results in loss of dimensional and morphological stability, resulting in reduced fuel cell performance. Water uptake can be reduced by going to a lower IEC material, sacrificing the proton conductivity. Thus there has always been a search for materials with higher selectivities. In this work, the materials studied are of similar IECs. For copolymers with similar hydrophobic and hydrophilic block lengths (5 K–5 K, 10 K–8 K and 15–15 K), water uptake or the hydration number is found to increase with increasing block lengths. However, it can be implied from Table 2 that, by altering the ratio of hydrophobic to hydrophilic block lengths, one may be able to decrease the water uptake without changing the ion exchange capacity. The 17 K–12 K and 15 K–10 K samples, for instance, show a significant decrease in water uptake compared to the 15 K–15 K sample: the increased fraction of the hydrophobic block length seems to restrict the water absorption.

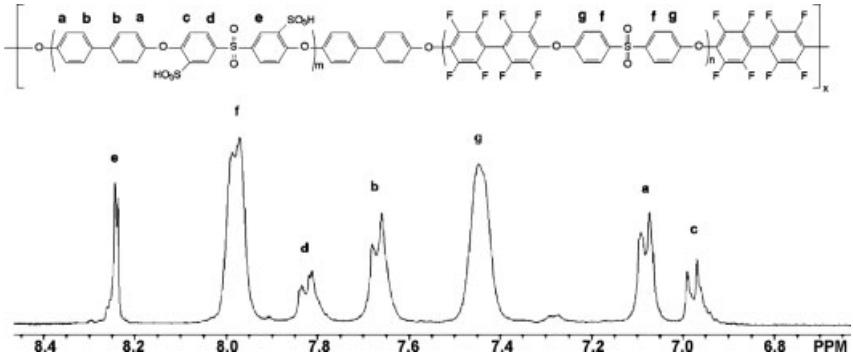

Figure 9.
^{1}H NMR spectra of a BisSF-BPSH multiblock copolymer.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

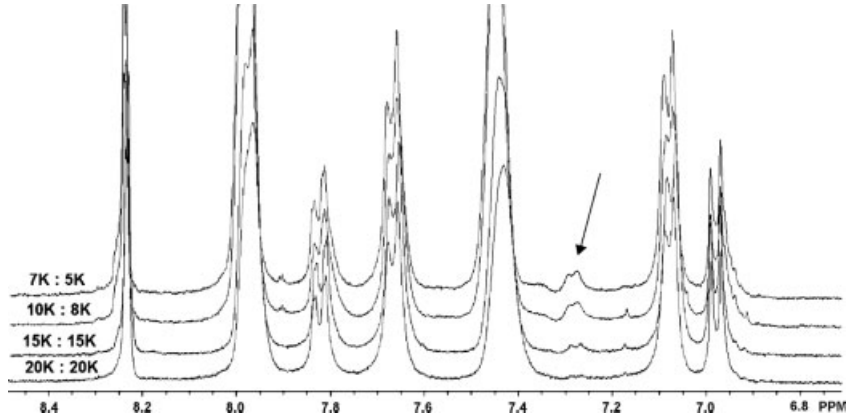

Figure 10.
^{1}H NMR spectra of BisSF-BPSH copolymers with increasing block lengths.

It is interesting to investigate the effect of block length on the transport properties. Ion-containing copolymers are known to phase separate into hydrophilic and hydrophobic domains. The extent of phase separation should govern the proton transport, and has been found to increase with increasing block lengths in the case of block copolymers.[9,18] The extent of morphological barrier of water and proton transport is reflected in the self-diffusion coefficient of water: higher self-diffusion coefficient indicates more distinct phase separated morphology. In fact, under partially hydrated conditions, the self-diffusion coefficient scales with the diffusion coefficient of proton for Nafion.[13,19] Hence a clear understanding about the influence of block lengths on self-diffusion coefficient of water is needed.

For the copolymers studied in this work, the self-diffusion coefficient of water was found to increase with increasing block lengths, with the 15 K–15 K sample showing the highest value. Proton conductivity measured under fully hydrated conditions at 30 °C shows a very similar trend. The enhanced nanophase separation in higher block length materials resulted in higher proton conductivity than Nafion and BPSH 35. From Table 2, the 17 K–12 K sample has long block lengths and a modest hydration number while still exhibiting high proton conductivity, making it a desirable proton exchange membrane. Therefore, for these multiblock copolymers, proton conductivity seems to depend more on morphology than on water content.

$$\Psi = \sigma/\lambda \tag{4}$$

Table 1.
Characterizations of BisSF-BPSH multiblock copolymers.

Hydrophobic/Hydrophilic Block Lengths (g/mol)	Molar Feed Ratio	η (dL/g)[a)]	Target IEC	IEC by ^{1}H NMR
5 K:5 K	1:0.59	0.64	1.3	1.31
7 K:5 K	1:0.86	0.92	1.3	1.33
7 K:7 K	1:0.57	0.85	1.3	1.20
15 K:10 K	1:0.84	0.75	1.3	1.25
17 K:12 K	1:0.77	1.00	1.3	1.32
15 K:15 K	1:0.63	1.26	1.3	1.45
20 K:20 K	1:0.60	0.89	1.3	1.41

[a)] Measured at 25 °C in 0.05M LiBr/NMP.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 2.
Electrochemical properties of BisSF-BPSH(*x*:*y*) multiblock copolymers, Nafion, and BPSH-35.

Sample	IEC (meq/g)	water uptake (%)	λ[a)]	σ(S/cm) ($H_2O_{(l)}$, 30 °C)	σ (S/cm) (95 %RH, 80 °C)	D[b)] (10^{-6} cm^2/s) (25 °C)
Nafion	0.9	25	15	0.10	0.11	4.3
5 K:5 K	1.2	31	14	0.10	0.07	2.9
10 K:8 K	1.0	52	29	0.12	0.16	8.6
15 K:10 K	1.3	47	20	0.13	0.17	8.0
17 K:12 K	1.3	38	16	0.15	0.16	7.5
15 K:15 K	1.4	78	33	0.15	0.17	12.0
BPSH-35	1.5	40	15	0.06	0.10	2.2

[a)] Hydration number, # of water molecules per sulfonic acid group.
[b)] Self-diffusion coefficient of water.

A plot of the selectivity against the hydration number (Figure 11) illustrates the structure-property relationships among the BisSF-BPSH copolymers, BPSH-35, and Nafion, where selectivity (Ψ) is defined in Equation 4. Highly selective materials occur at low hydration numbers and high proton conductivity since these are the ideal properties of a polymer electrolyte membrane. BPSH-35 has the same hydration number as Nafion, but lower proton conductivity. From Table 2 and Figure 11 it can be noted that the 17 K–12 K sample is the most selective material, where the high hydrophilic block length provides higher proton conductivity and the high hydrophobic/hydrophilic block length ratio (17/12) may have contributed to its low water uptake. On the other hand, as the fraction of the hydrophilic block length increases the selectivity decreases because the swelling, water uptake, and hydration number increases, which will cause problems in long-term fuel cell stability.

Proton conductivity as a function of relative humidity (RH) was studied and the results are displayed in Figure 12. This should shed light on the effect of morphology on proton conductivity under partially hydrated conditions. For the random copolymer, BPSH-35, 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; however, due to the

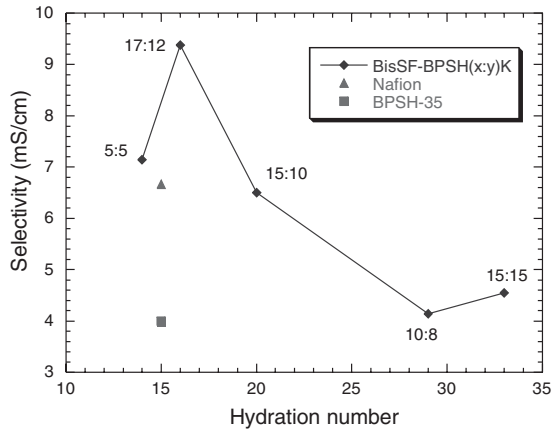

Figure 11.
Selectivity of the BisSF-BPSH multiblock copolymers, BPSH-35, and Nafion.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

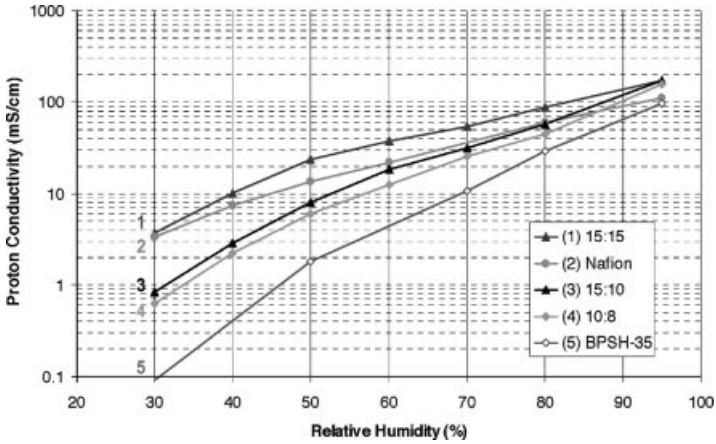

Figure 12.
Proton conductivity of BisSF-BPSH(x:y) multiblock copolymers, BPSH-35, and Nafion as a function of RH.

scattered hydrophilic domains in the membranes, they lack the connectivity among sulfonic acid groups for proton transport under partially hydrated conditions. With the multiblock copolymers, on the other hand, as the block length increases the performance under partially hydrated conditions also increases. This suggests the presence of long, co-continuous channels through which protons can be transported along the sulfonic acid groups and water molecules, and this is related to the self-diffusion coefficient of water. On account of enhanced nanophase separation, the BisSF-BPSH(15 K:15 K) multiblock copolymer exhibited higher proton conductivity than Nafion at all RH values. Taking into account the generic fuel cell operating conditions ranging from 80% to 100 % RH, 17 K–12 K and 15 K–10 K would also perform better than Nafion under these conditions (data for 17 K–12 K is not shown in Figure 12 because it essentially overlaps with the curve for 15 K–10 K).

Conclusions

Hydrophilic-hydrophobic poly(arylene ether) multiblock copolymers, BisSF-BPSH, with fully disulfonated and highly fluorinated blocks, were synthesized by the coupling reactions of fluorinated BisSF oligomers and hydrophilic BPSH oligomers. The copolymers' structures, as well as the existence of sequence lengths, were confirmed by ^{1}H and ^{19}F NMR. High molecular weight copolymers were obtained even when large molar excesses of hydrophobic oligomers were used, indicating that perfect stoichiometry is not as important as in the polymerization of small molecules.

The sequence lengths of the copolymers seem to dominate their proton conductivity both in liquid water and under partially hydrated conditions; the IEC seems relatively insignificant. Water uptake generally increases with the increase of block lengths, but at similar IECs, the ratio of hydrophobic to hydrophilic block length, besides the absolute values, can also play a role. The proper combination of IEC, hydrophilic and hydrophobic sequence lengths, which can be readily controlled by synthesis, have proved to yield materials that are more selective than Nafion 112.

Under partially hydrated conditions, multiblock copolymers with higher block lengths showed better performance with regard to proton conductivity as a function of relative humidity, presumably due to their more distinct nanophase separation and better connectivity among the ionic domains. The self-diffusion coefficients of

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

water, measured by NMR using the PGSE technique, followed the same trend as the conductivity and may be used as a measure of proton transport under partially hydrated conditions.

Acknowledgements: The authors would like to thank the Department of Energy (DEFG 36-06G016038), UTC Fuel Cell (No. PO3561) and Nissan Motor for their support.

[1] M. S. Whittingham, R. F. Savinell, T. Zawodzinski, *Chem. Rev.* **2004**, *104*, 4243.
[2] M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, *104*, 4245.
[3] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587.
[4] J. A. Kerres, *J. Membr. Sci.* **2001**, *185*, 3.
[5] K. A. Mauritz, R. B. Moore, *Chem. Rev.* **2004**, *104*, 4535.
[6] W. L. Harrison, F. Wang, J. B. Mecham, V. A. Bhanu, M. Hill, Y. S. Kim, J. E. McGrath, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 2264.
[7] F. Wang, M. Hickner, Q. Ji, W. Harrison, J. Mecham, T. A. Zawodzinski, J. E. McGrath, *Macromol. Symp.* **2001**, *175*, 387.
[8] F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, J. E. McGrath, *J. Membr. Sci.* **2002**, *197*, 231.
[9] A. Roy, M. A. Hickner, X. Yu, Y. Li, T. Glass, J. E. McGrath, *J. Polym. Sci. Part B: Polym. Phys.* **2006**, *44*, 2226.
[10] X. Yu, A. Roy, J. E. McGrath, *Div. Fuel Chem.* **2005**, *50*(2), 577.
[11] X. Yu, A. Roy, J. E. McGrath, *PMSE Preprints* **2006**, *95*, 141.
[12] M. Sankir, V. A. Bhanu, W. L. Harrison, H. Ghassemi, K. B. Wiles, T. E. Glass, A. E. Brink, M. H. Brink, J. E. McGrath, *J. Appl. Polym. Sci.* **2006**, *100*, 4595.
[13] T. A. Zawodzinski, M. Neeman, L. O. Sillerud, S. Gottesfeld, *J. Phys. Chem.* **1991**, *95*, 6040.
[14] T. E. Springer, T. A. Zawodzinski, M. S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* **1996**, *143*, 587.
[15] P. Y. Ghi, D. J. T. Hill, A. K. Whittaker, *Biomacromolecules* **2002**, *3*, 554.
[16] T. A. Zawodzinski, T. E. Springer, M. Neeman, L. O. Sillerud, *Isr. J. Chem.* **1992**, *32*, 281.
[17] Y. S. Kim, F. Wang, M. Hickner, S. McCartney, Y. T. Hong, W. Harrison, T. A. Zawodzinski, J. E. McGrath, *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 2816.
[18] A. Roy, X. Yu, A. Badami, J. E. McGrath, Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26–30, 2006, PMSE-111.
[19] K. D. Kreuer, *Solid State Ionics* **2000**, *136*, 149.

Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim