



Multiblock Copolymers Based upon Increased Hydrophobicity Bisphenol A Moieties for Proton Exchange Membranes

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Increasing hydrophobicity multiblock copolymers were synthesized by altering the copolymer composition of the hydrophobic segments. A series of nitrile-containing hydrophobic oligomers consisting of bisphenol A (Bis A), dimethylbisphenol A (DMBPA), and tetramethylbisphenol A (TMBPA) moieties were reacted with a disulfonated poly(arylene ether sulfone) hydrophilic segment to form the multiblock copolymer series. ¹H and ¹⁹F NMR spectroscopy were used to monitor the progress of the copolymerization reactions and confirm the desired compositions. Membranes cast from the resultant multiblock copolymers had high molecular weight as measured by size-exclusion chromatography (SEC), and showed strong mechanical properties. As the hydrophobicity of the polymers increased from the Bis A, to the DMBPA, and to the TMBPA systems, the membranes showed a corresponding decrease in water uptake. The reduced water uptake and limited fluorine content produced membranes with significantly reduced methanol permeabilities over that of Nafion or other similar multiblock copolymer membranes. Electrochemical testing showed that the more hydrophobic TMBPA systems showed improved performance at higher methanol concentrations.

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Wholly aromatic polymeric materials have been extensively shown to be viable candidates for use as proton exchange membranes (PEMs) in polymer electrolyte fuel cells (PEMFCs) due to their high proton conductivity, strong mechanical properties, and excellent thermal, chemical and oxidative stability.¹⁻⁷ The major focus of these studies has been based upon sulfonated poly(arylene ether sulfone)s (SPAESs) and sulfonated poly(ether ether ketone)s (SPEEKs).⁸⁻¹⁰ The use of a pre-sulfonated monomer allowed these materials to be synthesized quickly without the need to post-sulfonate the resultant membranes. Copolymers produced from this pre-sulfonation method were found to be more stable plus the low methanol permeability of these wholly aromatic membranes made these materials even more attractive in direct methanol fuel cells (DMFCs), as low methanol permeability increases fuel efficiency and cell performance.¹¹⁻¹³ High fuel crossover is a critical problem associated with the highly fluorinated Nafion and similar poly(perfluorosulfonic acid) membranes, which are traditionally used as the PEMs in DMFCs.

Recently, sulfonated poly(arylene ether) copolymers containing nitrile groups have been shown to further improve performance by reducing membrane swelling compared to analogous copolymers that have similar ion-exchange capacities (IECs).¹⁴⁻²⁰ The membrane electrode assemblies (MEAs) of these copolymer membranes showed superior performance to both Nafion and the biphenol based SPAES statistical copolymer (BPSH-40) membranes. The reduction in water uptake caused by the introduction of the nitrile group has been proposed to allow for better interfacial adhesion between the PEM with Nafion-bonded electrodes, decreasing the high frequency resistance (HFR) and increasing the performance of the MEAs.^{18,21,22} Additionally, studies conducted on the non-fluorinated systems suggested that elimination of the fluorine moiety caused delamination between the membrane and the Nafion.^{23,24}

While nitrile-containing copolymer systems showed promising electrode compatibility and low methanol permeability with statistical copolymer architecture, further improvement can be made with multiblock copolymers.²¹ Two major advantages were expected with multiblock copolymers: i) enhanced proton conductivity and ii) better mechanical properties. Enhanced proton conductivity arises due to the self-assembled morphology of the multiblock copolymer, with the increases in conductivity allowing for the use of a less resistant membrane.²⁵ The less resistant multiblock copolymer membranes

then consequently reduce cell resistance. Additionally, improved mechanical properties due to hydrophilic-hydrophobic phase separations can allow for the use of higher IEC membranes (high IEC membranes are usually less mechanically stable) as well as improve fuel cell stability. Our previous results showed that the cell using high IEC multiblock copolymers exhibited substantially reduced cell resistance that had been hard to obtain with the cell using statistical copolymers. However, using high IEC multiblock copolymer membranes often require further structure control since membranes with higher IEC absorb more water.²⁶⁻³² One approach taken to attempt to control the water uptake and mechanical properties of these multiblock copolymers is by control of the hydrophobic segment in the design of the multiblock copolymer. Investigation of SPEAS using different sized hydrophobic components and varying block lengths in the multiblock copolymer have been reported.^{32,33} However, very little research has been explored involving a change in hydrophobic nature via chemical structure control of the non-sulfonated segment.

In this work we report novel multiblock copolymers that have extremely low water uptake. The multiblock copolymer series was synthesized with a SPAES hydrophilic phase and a poly(arylene ether benzonitrile) hydrophobic phase. A partial mole percent of the fluorinated monomer was replaced with a series of non-fluorinated bisphenol A moieties with increasing hydrophobicity as a result of added benzyl methyls. The electrochemical properties of these copolymers were examined to elucidate the structural effect on membrane properties. Further DMFC testing and performance will be discussed in a second corresponding publication.

Experimental

Materials.— 2,6-Difluorobenzonitrile (DFBN), *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), cyclohexane, and toluene were purchased from Sigma-Aldrich. DFBN and toluene were reagent grade and used as received, NMP and DMAc were distilled from calcium hydride before use. 4,4'-Hexafluoroisopropylidenediphenol (6F-BPA), received from Ciba, was sublimated and then recrystallized twice from toluene. Monomer grade 4,4'-biphenol (BP) was provided by Eastman Chemical Company, and dried under vacuum at 80°C prior to use. Monomer grade 3,3'-disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS) was received from Akron Polymer Systems and dried under vacuum at 150°C for 3 days prior to use. A previously reported method was used to determine purity of the SDCDPS monomer from UV-Vis spectroscopy.³⁴ 2,2-Bis(4-hydroxy-3-methylphenyl)propane

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(dimethyl bisphenol A, DMBPA), and 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol A, TMBPA) were both reagent grade, purchased from TCI America and used as received. 4,4'-(Propane-2,2-diyl)diphenol (Bisphenol A, Bis A) was kindly provided by Solvay and recrystallized from toluene prior to use. Reagent grade potassium carbonate (K_2CO_3), acetone, and methanol were purchased from Fisher Scientific. Potassium carbonate was dried under vacuum at 180°C prior to use, while acetone and methanol were used without further purification.

Synthesis of the nitrile-containing hydrophobic oligomers.— All oligomers were synthesized via nucleophilic aromatic substitution with different block lengths being achieved by using a molar excess of the benzonitrile monomer. An example synthesis of a hydrophobic oligomer with a targeted 10,000 g/mol molecular weight (M_n) is as follows: 6FBPA (5.14 g, 15.29 mmol), Bis A (3.49 g, 15.29 mmol) and DMAc (70 mL) were placed into a three neck round bottom flask equipped with a stir bar, condenser, nitrogen inlet, and Dean-Stark trap. The mixture was heated to 140°C and stirred until 6FBPA was completely dissolved. Once a transparent solution was obtained, K_2CO_3 (4.86 g, 35.17 mmol) and toluene (35 mL) were added into the flask. The reaction was allowed to reflux at 140°C for 4 h to azeotropically remove water from the system, and then slowly heated to 170°C to remove toluene. The reaction temperature was decreased to 80°C and DFBN (4.42 g, 31.79 mmol) was added to the flask (added after dehydration to prevent any possible DFBN monomer loss). The reaction was allowed to proceed for 8 h at 125°C (in a closed system to prevent loss of DFBN monomer), then cooled to room temperature and filtered to remove any excess K_2CO_3 or by-product salts. The oligomer was precipitated in methanol (1000 mL), stirred overnight, filtered and then dried in vacuo at 110°C for 48 h. All other hydrophobic oligomers were synthesized in the same fashion.

Synthesis of hydrophobic-hydrophilic multiblock copolymers.— All multiblock copolymer systems were synthesized with equal block lengths of the hydrophobic and hydrophilic segments to form a series of multiblock copolymers. The hydrophilic oligomers (BPS100) was synthesized as reported previously.^{26,30,35,36} An example synthesis of the multiblock copolymer is as follows: BPS100 (4.500 g, 0.500 mmol), K_2CO_3 (0.150 g, 1.087 mmol), and NMP (45 mL) were added to a three-necked 100-mL flask equipped with a mechanical stirrer, condenser, nitrogen inlet and Dean-Stark trap. The reaction bath was heated to 120°C, then cyclohexane (15 mL) was added and refluxed for 6 h to remove water from the system. After removing cyclohexane, the reaction bath was cooled to 90°C, and the hydrophobic oligomer (4.600 g, 0.510 mmol) was added. The bath temperature was raised to 135°C and kept at this temperature for 48 h. The reaction mixture was precipitated into isopropanol (1000 mL) and stirred for 12 h. The product was filtered then washed in deionized (DI) water at 90°C for 12 h, filtered again and then dried in vacuo at 150°C for 24 h. The copolymers based upon the different hydrophobic segments were synthesized in the same fashion as the procedure stated above.

Synthesis of a hydrophobic-hydrophilic statistical copolymer 6FTMPAEB-BPS-50.— A statistical copolymer was synthesized with similar molar ratios to the hydrophobic-hydrophilic multiblock copolymers. 6F-BisA (1.681 g, 5.000 mmol), 2,6-DCBN (1.720 g, 10.000 mmol), TMBPA (1.422 g, 5.000 mmol), SDCDPS (5.039 g, 10.000 mmol), BP (1.862 g, 10.000 mmol) and NMP (50 mL) were added to a three-necked 100 mL flask equipped with a mechanical stirrer, condenser, nitrogen inlet and Dean-Stark trap. The reaction bath was heated to 150°C, then K_2CO_3 (3.870 g, 28.000 mmol) and toluene (25 mL) were added and refluxed for 3 h to dehydrate the system. Toluene was drained from the system and the reaction was heated to 190°C and maintained at this temperature for 72 h. The viscous solution was hot filtered using an aspirator to remove salts, and then precipitated dropwise in isopropanol (1600 mL) and stirred overnight. The fibrous white solid was filtered using an aspirator,

washed with additional isopropanol and then dried in vacuo at 150°C for 24 h.

Membrane preparation and acidification.— The potassium salt form segmented block copolymers were dissolved in DMAc (~7% w/v), after drying at 150°C for 24 h, and filtered through a 0.45 μ m Teflon syringe filter. The solutions were cast onto a dry, clean glass substrate and dried for 24 h under an infrared lamp at ~80°C. Additionally, the membranes were annealed under vacuum at 220°C, about 30°C higher than the T_g of the nitrile based hydrophobic blocks. The membranes were converted to the acid form by boiling in 0.5 M sulfuric acid for 2 h, followed by boiling in DI water for 2 h.

Characterization.— 1H , ^{19}F , and ^{13}C NMR analyzes were conducted on a Varian Unity Plus spectrometer operating at 400 MHz (376 MHz for ^{19}F). The spectra of the BPS100 hydrophilic oligomers along with their corresponding block copolymers were obtained from a 10% (w/v) 1 mL solution in DMSO- d_6 . The spectra of the hydrophobic oligomers were obtained from a solution in $CDCl_3$. ^{13}C NMR analyzes were conducted on a Varian Unity spectrometer, operating at 100.58 MHz with DMSO- d_6 as the solvent. Weight average molecular weights (M_w s) of all block copolymers were obtained via a multi-detector size-exclusion chromatography (SEC) using NMP with 0.05 M LiBr as the mobile phase (50°C) with 3 PLgel 10 μ m mixed-B 300 \times 7.5 mm columns in series with a Wyatt Viscostar II Viscometer, a Wyatt Heleos II multi angle light scattering detector, and a Wyatt T-rex refractive index detector. M_w s were reported for these systems as this is an accurate measured value using this technique. Polydispersities are assumed to be approximately two, which is expected for polycondensation polymers.

Tensile testing.— Uniaxial load tests were performed using an Instron 5500R universal testing machine equipped with a 200-lb load cell. The crosshead displacement rate was 5 mm/min and the gauge length was 26.5 mm. The tensile test specimens were prepared with dimensions of 50 mm length and a minimum width of 4 mm per ASTM D638-03. Prior to testing, acid form membrane specimens were dried in vacuo at 100°C and tested at room temperature. All specimens were mounted in pressure locking pneumatic grips.

Proton conductivity and water uptake.— Proton conductivities of the multiblock copolymer membranes in the fully hydrated state were determined at 30°C in liquid water. Measurements were made in-plane with a four electrode configuration. Before the measurement, the membranes were equilibrated in DI water at 30°C for 24 h. A Solartron (1252 + 1287) impedance/gain-phase analyzer over the frequency range of 10 Hz to 1 MHz was used for the measurements following a previously reported method.³⁷ The conductivity was calculated by using equation 1.

$$\sigma = \frac{L}{R \cdot S} \quad [1]$$

Where σ (S/cm) is proton conductivity, L (cm) is the distance between the two electrodes, R (Ω) is the resistance of the membrane and S (cm^2) is the surface area available for proton transport through the membrane. The water uptake of all membranes was determined gravimetrically. The membranes were equilibrated in DI water at room temperature for 2 days after acidification. Wet membranes (in acid form) were removed from DI water, blotted dry to remove surface droplets, and quickly weighed. The membranes were dried at 120°C under vacuum for 24 h and re-weighed. The water uptake of the membranes was calculated according to equation 2, where W_{dry} and W_{wet} refer to the mass of the dry and wet membrane, respectively.

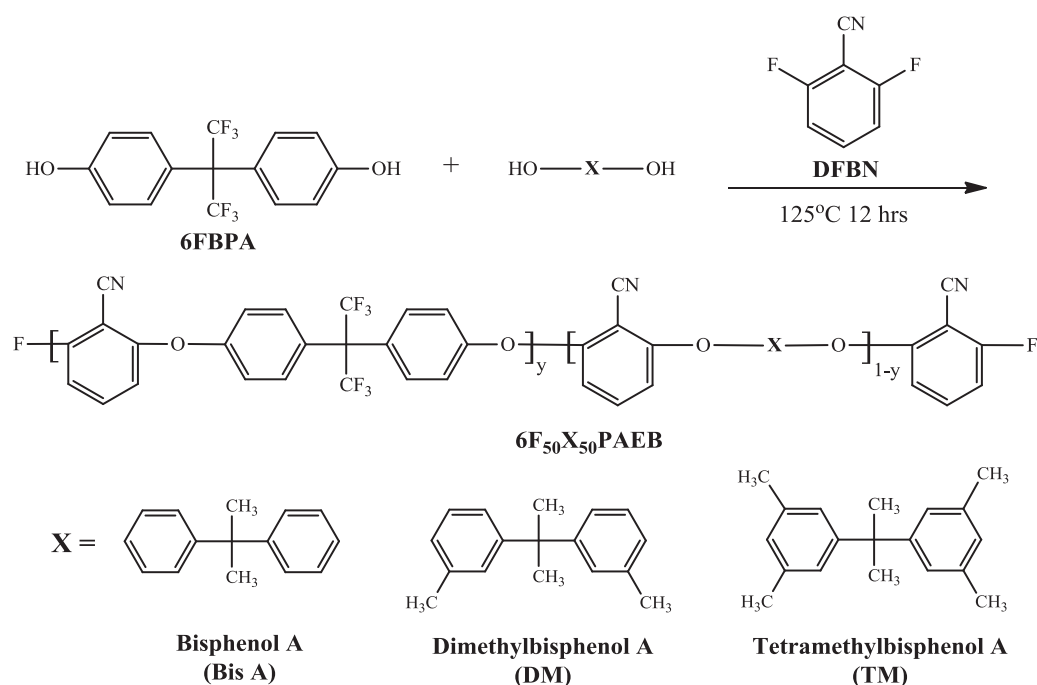
$$\text{Water Uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad [2]$$

Membrane electrode assembly and fuel testing.— Membrane electrode assemblies (MEAs) using multiblock copolymers were prepared

by using the gas diffusion electrode (GDE) method. For GDE method, commercial GDEs with carbon-supported PtRu (75% metal loading, HiSPEC 12100, Johnson Matthey) and Pt (60% metal loading, HiSPEC 9100, Johnson-Matthey) were used for anode and cathode catalyst layers, respectively. The catalyst loading for the anode and cathode are 2.7 and 2 mg/cm², respectively. Multiblock copolymer membranes were inserted between anode and cathode GDE with a glass fiber reinforced Teflon gasket to assemble the MEAs. H₂/air and DMFC polarization curves with high frequency resistance (HFR) were obtained using a fuel cell test station equipped with an internal AC impedance analyzer (Fuel Cell Technology Inc). Cell performance was obtained after 3 h break-in under H₂/air conditions at a cell voltage of 0.7 V at 75°C. For DMFC mode operations, 0.5, and 1 M aqueous methanol solutions were supplied to the anode with a flow rate of 1.8 mL/min; fully humidified air was supplied at 500 sccm without back pressure (high humidification and stoichiometry were used to minimize ohmic and mass transfer effects). HFR was measured by applying a sinusoidal wave perturbation of 2 kHz where capacitive contributions to cell impedance were found to be minimized.

Morphology.— The membranes were tested in the potassium salt form after annealing at 220°C using the same method as listed for the membrane preparation. Additionally the membranes were dried in a vacuum oven at 100°C for 12 h prior to being tested to ensure that no water was present in the membranes. SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu K α). The q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 hour. All the SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated SAXS intensity versus scattering vector q, where $q = (4\pi/\lambda) \sin(\theta)$, where θ is one half of the scattering angle and λ is the wavelength of the X-ray. Interdomain distance (d_x) was calculated from the scattering vector peaks (q_x) based on equation 3, which was derived from Bragg's law.

$$d_x = \frac{2\pi}{q_x} \quad [3]$$



Results and Discussion

Synthesis of fluorine terminated nitrile-containing hydrophobic oligomers.— Figure 1 shows the synthesis scheme used for the fabrication of the fluorine terminated hydrophobic oligomers. For each of the oligomers the difluorobenzonitrile (DFBN) monomer was used in excess according to the Carothers equation in order to obtain a targeted number average molecular weight (M_n) of approximately 10 kg/mol.³⁸ In each of the oligomers synthesized equal molar amounts were used of the fluorinated and non-fluorinated phenolic monomers to afford statistical copolymer oligomers with a 50/50 ratio. The oligomers were denoted as 6F₅₀X₅₀PAEB where X referred to either bisphenol A (Bis A), dimethyl bisphenol A (DM), or tetramethyl bisphenol A (TM) monomers.

The progress of the reactions was monitored by ¹H NMR spectroscopy, where the completion of the reaction was judged by the disappearance of the phenyl protons next to the phenoxide endgroups. Molecular weight of the hydrophobic oligomers were then determined by ¹⁹F NMR spectroscopy by comparing the ratio of the fluorines on the benzonitrile terminated chain to the fluorines on the backbone of the main chain. Figure 2 shows the ¹⁹F spectra with the peak at -64 ppm attributed to the backbone and -105 ppm to the endgroups. Molecular weights of 10 kg/mol were achieved for each of the hydrophobic oligomers.

Synthesis of BPS100 hydrophilic oligomers and corresponding multiblock copolymers.— Synthesis of the disulfonated hydrophilic oligomer, (BPS100), has been well established and was performed according to previous reported procedures.^{26–30,35,36} Phenol terminated oligomers of 10 kg/mol were synthesized for the BPS100 hydrophilic segments, which were then reacted with the different activated halide terminated hydrophobic segments (also 10 kg/mol) to form a series of 10 K-10 K (K is used to represent kg/mol) multiblock copolymers with increasing hydrophobicity. The hydrophobicity was increased via the introduction of methyl groups on the bisphenol A based diol monomer. Addition of two methyl groups on the bisphenol A unit afforded the dimethyl multiblock copolymer, while the four methyl groups gave the tetramethyl multiblock copolymer. Nomenclature for the multiblock copolymers was referred to as 6F₅₀X₅₀PAEB-BPS100 when in the potassium salt form, and 6F₅₀X₅₀PAEB-BPSH when in

Figure 1. Synthesis of the fluorine terminated benzonitrile-containing hydrophobic oligomers.

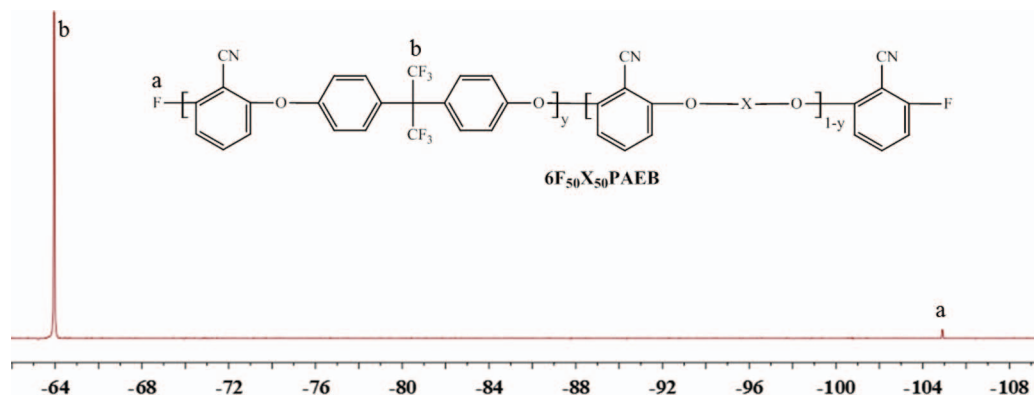


Figure 2. ^{19}F NMR of benzonitrile terminated hydrophobic oligomer.

the acid form. Figure 3 shows the synthesis scheme for the multiblock copolymers. Similar to the previous multiblock copolymers produced in our group, relatively mild reaction temperatures were used in order to reduce any possible ether-ether interchange reactions, which have been shown to occur at elevated temperatures.³⁹ By using this method an alternating multiblock copolymer composition was achieved and confirmed by ^{13}C NMR spectroscopy. Figure 4 shows the region of the ^{13}C spectrum associated with the carbons of ether bonds in the multiblock copolymers and the structures of the multiblock versus the statistical copolymer. The top three spectra represent the multiblock copolymers while the bottom is a statistical copolymer with the same composition as the tetramethyl containing multiblock copolymer. The top three spectra show sharp and clearly defined peaks associated with the ether bonds of the three different multiblock copolymers, while the bottom statistical spectrum shows many jagged and uneven peaks. This is because the statistical copolymer has many more possible ether bonds in its structure. The comparison of the ^{13}C spectrums indicate that ether-ether interchange reactions were minimized for the reactions and that an alternating multiblock copolymer morphology was maintained.

Additionally to gauge the progress of the reaction a small mole percent excess of the hydrophobic oligomer was used and the disap-

pearance of the phenyl protons next to the phenoxide endgroups was followed by ^1H NMR spectroscopy (Fig. 5). After 48 hours the viscosity of the reactions significantly increased and showed no presence of the biphenol endgroup moieties in the spectra, thus the reactions were deemed complete. The ratio between the hydrophilic and hydrophobic peaks in the ^1H NMR spectrum was used to calculate the resulting IEC of the multiblock copolymers. To calculate this, the ratio between the peak at 8.3 ppm, which corresponds to the proton adjacent to the sulfonated group, and the bisphenol A bridging methyl groups at 1.7 ppm were used for all of the multiblock copolymers.

Characterization of membrane properties for 6F₅₀X₅₀PAEB-BPSH series.— The series of multiblock copolymer membranes were characterized in regards to ion-exchange capacity, water uptake, and proton conductivity. These membrane properties are listed in Table I as a function of polymer structure. All membranes listed in Table I were annealed at 220°C, a temperature between the glass transitions of the hydrophobic and hydrophilic segments, which has been shown to facilitate the formation of phase-separated morphological structure and reduce water swelling.^{28–30} The T_g of the hydrophilic phase appears as a very broad transition around 250°C and can be hard to distinguish, as shown in previous publications.²⁹ However, the glass

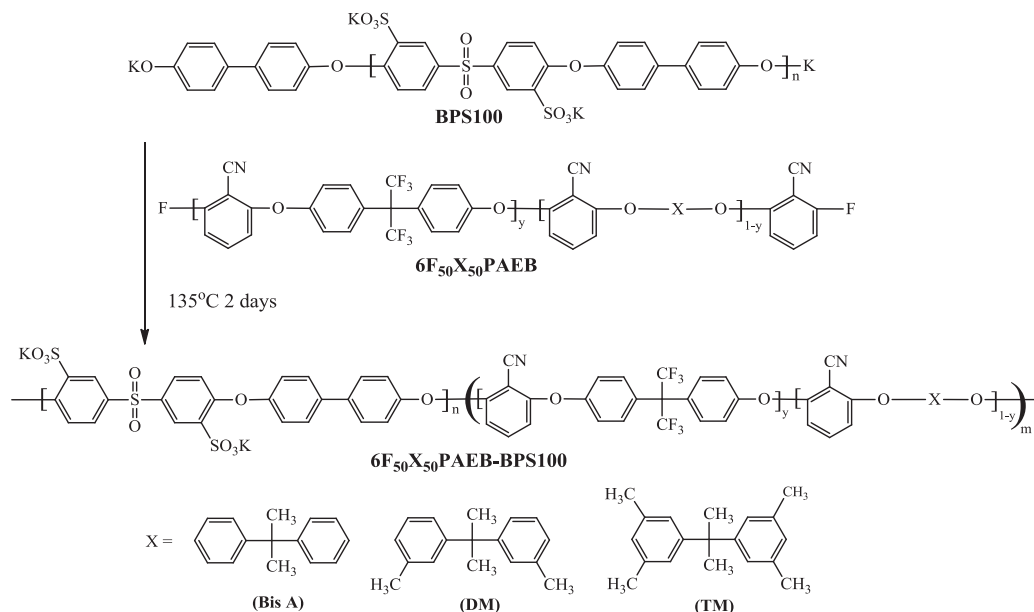


Figure 3. Synthesis scheme for benzonitrile-containing hydrophilic-hydrophobic multiblock copolymers.

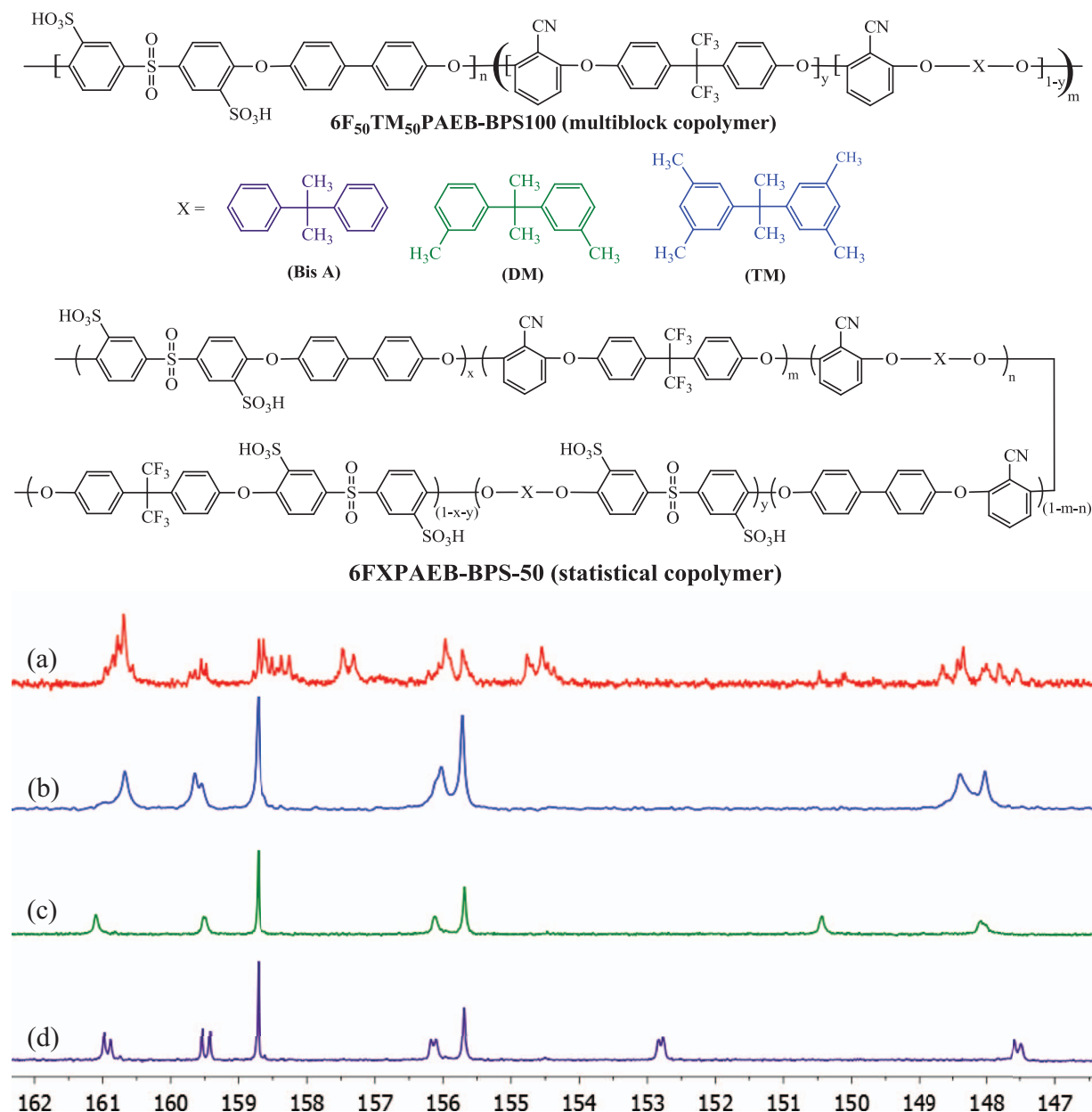


Figure 4. ^{13}C NMR and structures of multiblock copolymers 6F₅₀X₅₀PAEB-BPS100 and random copolymer 6FTMPAEB-BPS-50 focused in the ether region of the spectrum: (a) statistical copolymer 6FTMPAEB-BPS-50, (b) 6F₅₀TM₅₀PAEB-BPS100, (c) 6F₅₀DM₅₀PAEB-BPS100, and (d) 6F₅₀BisA₅₀PAEB-BPS100.

transition temperatures (T_g s) of the hydrophobic oligomers can be seen in Figure 6, which indicate that 220°C is in between the T_g of the hydrophilic and hydrophobic phase for the multiblock copolymers. All multiblock copolymers tested were of equal block length between the hydrophobic and hydrophilic segments to enhance consistency between different compositions. Block lengths of 10 kg/mol were chosen to provide long enough lengths to allow for phase-separation between the two segments. Fifty mole percent of the fluorinated monomers were replaced with the various bisphenols for each of the PEMs in order to reduce the methanol permeability and to gauge the effect of the different comonomers. Fluorination level has been shown to have a direct effect on methanol permeability, however only fifty percent was replaced due to previous studies in which pure non-fluorine containing membranes were found to be incompatible with the Nafion bounded electrodes.^{14,15}

As seen in Table I the inclusion of increasingly hydrophobic bisphenol moieties had a drastic effect on the properties of the multi-

block copolymers. Notably, the water uptake of the membranes were decreased as the comonomer was changed to dimethyl and tetramethyl bisphenols. The lower IEC and M_w of the tetramethyl membrane indicates a slightly lower degree of hydrophilic block incorporation in the segmented multiblock copolymer. Although the IEC for the tetramethyl was less than the other two systems, the ratio for the drop in water uptake was much greater than the ratio for the decrease in the IEC. This indicates that the four pendant benzylic methyl groups are responsible for the stark decline in water uptake in the PEMs. This was most evident from the change to the dimethyl to tetramethyl bisphenol with a decrease from 35 to only 20 percent water uptake for the membranes. To further quantify this point the volume based parameters are presented in Table II. The values from IEC_v wet and dry were calculated according to a previous reported procedure.⁴⁰ As was the case for the weight based values, the tetramethyl system had a lower volume water uptake which resulted in less of a drop in IEC_v going from the dry to wet state. The dimethyl

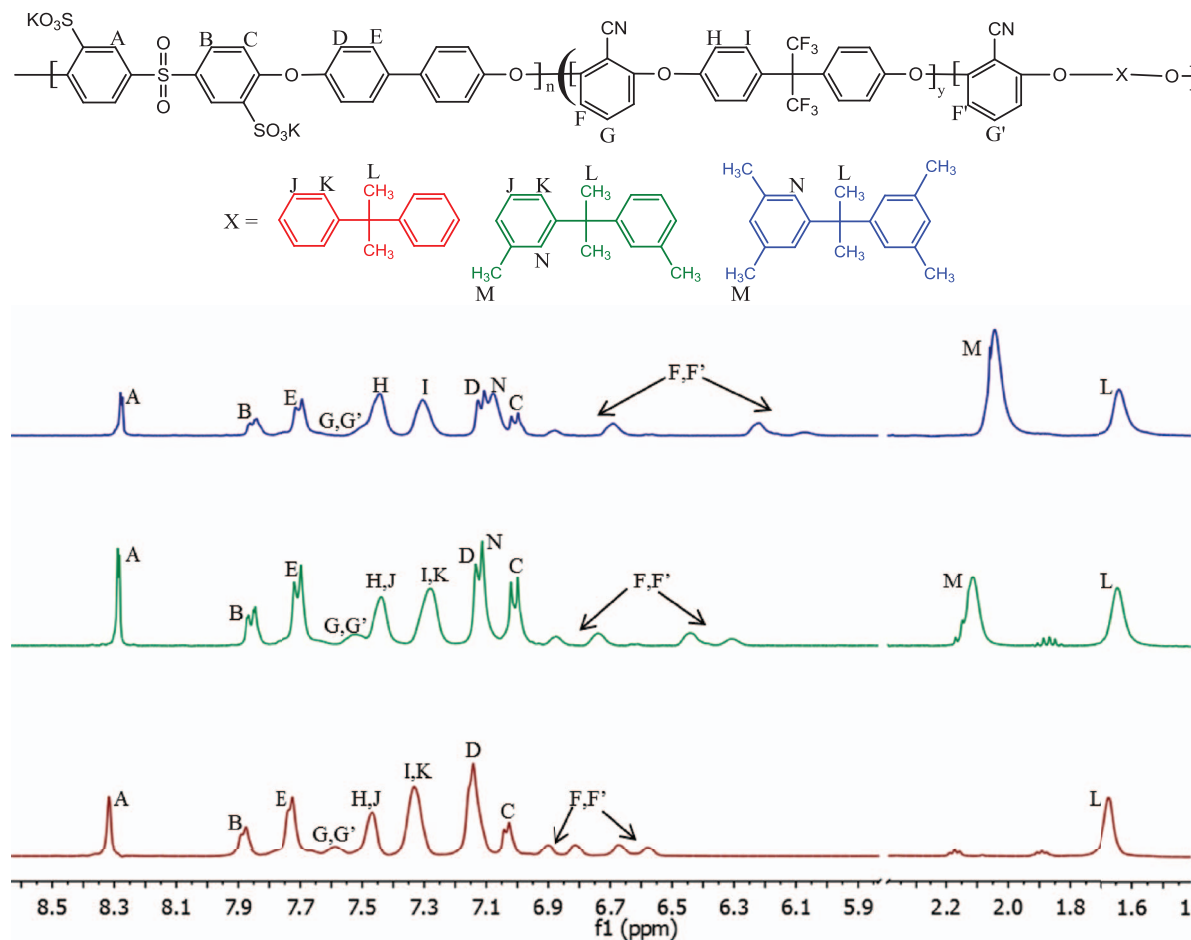


Figure 5. ^1H NMR of $6\text{F}_{50}\text{X}_{50}\text{PAEB-BPSH}$ series: top spectra tetramethyl bisphenol A, middle dimethyl bisphenol A, and bottom bisphenol A.

Table I. Properties of 10 K-10 K $6\text{F}_{50}\text{X}_{50}\text{PAEB-BPSH}$ PEMs (1.0 M MeOH).

$6\text{F}_{50}\text{X}_{50}$ PAEB-BPSH	IEC (meq/g) ^a	IEC (meq/g) ^b	M_w (kg/mol)	Water Uptake (wt%)	Proton Conductivity (S/cm)	Methanol Permeability (cm^2/s) ^c	Relative Selectivity ^d
TM	1.50	1.50	50	20	0.10	$1.28 \text{ E-}07$	1.4
DM	1.65	1.75	80	35	0.15	$1.50 \text{ E-}07$	1.8
Bis A	1.74	1.65	75	40	0.12	$1.38 \text{ E-}07$	1.6
Nafion 212	1.00	–	–	22	0.12	$2.20 \text{ E-}07$	1.0

^aMeasured from ^1H NMR

^bMeasured by titration with 0.01 M NaOH

^cMeasured from limiting current method using fuel cell hardware in 1.0 M MeOH

^dSelectivity = proton conductivity/methanol permeability, relative selectivity is normalized with Nafion selectivity

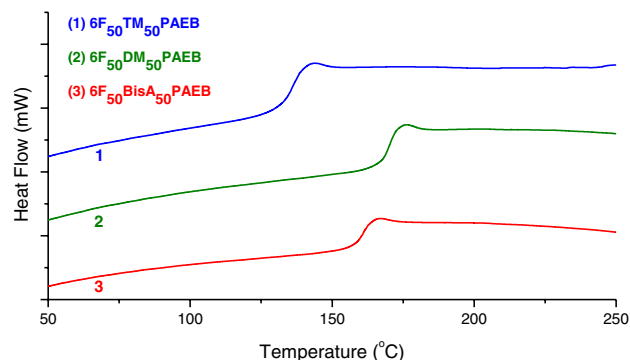


Figure 6. DSC of hydrophobic oligomers.

membrane had a swelling characteristic comparable to that of the Nafion membrane, while the tetramethyl was considerably less than the other membranes.

Even with the lower water uptake and IEC, the tetramethyl system still had a respectable proton conductivity in liquid water of 0.10 S/cm.

Table II. Volume Based Properties for Multiblock Copolymers.

$6\text{F}_{50}\text{X}_{50}\text{PAEB-BPSH}$	Density (g/cm^3)	Water Uptake (vol%)	IEC _v (dry) (cm^3/meg)	IEC _v (wet) (cm^3/meg)
TM	1.21	24	1.82	1.46
DM	1.24	43	2.05	1.43
Bis A	1.24	50	2.16	1.44
Nafion 212	2.0	40	1.84	1.31

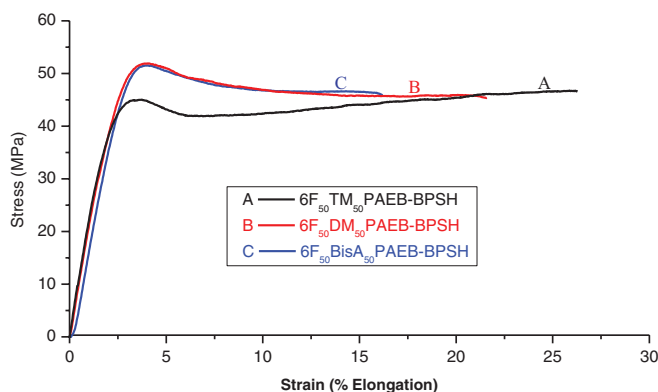


Figure 7. Stress-strain curves for acid form membranes, samples dried prior to testing with rate of 5 mm/min: (a) 6F₅₀BisA₅₀PAEB-BPSH, (b) 6F₅₀DM₅₀PAEB-BPSH, and (c) 6F₅₀TM₅₀PAEB-BPSH.

Thus, the tetramethyl system produced the most desirable system due to the very low water adsorption of the membrane. The conductivity range for the membranes was from 0.10–0.15 S/cm, which is in the expected range for the disulfonated poly(arylene ether sulfone) multiblock copolymers. In addition all of the membranes showed greatly reduced methanol permeability in 1 M MeOH as compared to Nafion 212, with the tetramethyl based membrane having once again the lowest value in the membrane series. Due to this reduction in methanol adsorption, the bisphenol based multiblock copolymers also exhibited greater relative selectivity than the persulfonic acid based membrane. These results suggest that the synthesized membranes would have excellent performance in fuel cell operation and may allow for higher methanol concentrations.

SEC and tensile testing confirmed that multiblock copolymer structures were formed, and the molecular weights of the copolymers are sufficient to provide transparent ductile membranes when cast from DMAc solution. Weight average molecular weights (M_w s), shown in Table I, were between 50 kg/mol and 80 kg/mol. The stress-strain behavior of the membranes verified that ductile materials were acquired, with mechanical properties very representative of SPAESs (Fig. 7). The stress-strain performance of the bis A and dimethyl multiblock copolymers were very similar to each other, with the dimethyl system having a longer elongation at break. The yield stress for the tetramethyl system was less than that of the other two multiblock copolymers, but it exhibited the longest elongation at break of the membranes.

SAXS was performed in order to investigate the effects of bisphenol A methyl substitution on the morphological features of multiblock copolymer membranes (Fig. 8). All of the SAXS profiles showed a

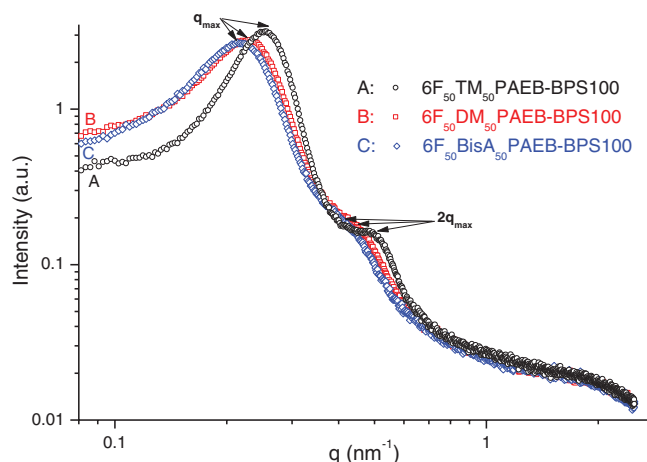


Figure 8. SAXS profiles of bis A based multiblock copolymers.

Table III. Interdomain Distance for SAXS Profiles.

Sample	D-spacing q_{\max} (nm)	FWHM (q_{\max})	χ_{eff}
6F ₅₀ TM ₅₀ PAEB-BPS100	24.5	0.090	0.283
6F ₅₀ DM ₅₀ PAEB-BPS100	27.3	0.114	0.541
6F ₅₀ BisA ₅₀ PAEB-BPS100	28.2	0.107	0.701

primary peak at q_{\max} (Table III) and also a secondary peak at $2q_{\max}$, which is consistent with a lamellar organization of the phase-separated domains in these multiblock copolymers.⁴¹ The most significant difference between these profiles was the smaller domain spacing (larger q_{\max}) observed for the tetramethyl multiblock copolymers. In addition, the primary SAXS peak for the tetramethyl series was found to be significantly sharper compared to the dimethyl and bisphenol A based multiblock copolymers (see FWHM, Table III). Similarly, the secondary peak for the tetramethyl series was also observed to be more prominent and well-resolved. This scattering behavior suggests that the phase separated morphology of the tetramethyl based multiblock copolymers exhibits a more refined order in comparison to the dimethyl and bisphenol A based multiblock copolymers.

Based upon self-consistent mean-field theory (SCFT), the Bragg spacing for the primary scattering peak (d_1) for a lamellar phase-separated block copolymer may be correlated to the effective segment-segment interaction parameter (χ_{eff}) by the following relationship:

$$d_1 = 1.10aN^{2/3}\chi_{\text{eff}}^{1/6} \quad [4]$$

where a is the statistical segment (Kuhn) length, and N is the number of Kuhn segments within a diblock sequence.^{42,43} For the multiblock copolymers studied here, the statistical segment length was approximated using the Kuhn segment length of polycarbonate, with $a = 2.94$ nm and the Kuhn length of each multiblock assumed to be identical based on studies of bisphenol A and tetramethyl bisphenol A polycarbonates.⁴⁴ The value for N was computed by considering the segment length to correspond to two adjacent polycarbonate monomers, resulting in a value of $N = 29$ segments within a single 10 K-10 K AB diblock sequence.⁴⁵ These assumptions have been used for simplicity due to the structural similarity between each multiblock copolymer considered. Following these calculations, the observed increase in q_{\max} with increasing methyl group content corresponds to a decrease in the effective interaction parameter between the blocks of the multiblock copolymers (Table III). With increasing hydrophobicity (and likely an increase in steric constraints) imposed by the addition of methyl substituents, the driving force for phase separation increases, leading to a more ordered phase separated morphology. This increase in lamellar organization of the highly hydrophobic tetramethyl multiblock copolymers may also be a factor in the observed increase in elongation over that of the bis A and dimethyl systems (Figure 7). Future studies will focus on morphological transformations during in-situ tensile/SAXS experiments. Similarly the more ordered morphology could have restricted the swelling of the hydrophilic domain, thus contributing to the observed reduction in water uptake of the multiblock copolymer membranes.

Fig. 9 shows the polarization curves of MEAs using the multiblock copolymers. The MEAs were prepared using similar thickness membranes (~ 30 μm thick) and Nafion-bonded electrodes. Under H₂/air conditions, all three MEAs exhibited a comparable performance (Fig. 9a). The MEAs using 6F₅₀DM₅₀PAEB-BPSH and 6F₅₀BisA₅₀PAEB-BPSH exhibited notably reduced high frequency resistance (HFR), ca. ~ 0.05 Ω cm² compared to the MEA using 6F₅₀TM₅₀PAEB-BPSH. This is consistent with the conductivity of the stand-alone membranes shown in Table I. Under 0.5 M methanol feed conditions, all MEAs exhibited comparable performance. In the low methanol feed conditions, the amount of crossover methanol is minimal and the samples performed comparably, similar to the H₂/air fuel cell. Under 1 M methanol feed conditions, on the other hand, the MEA using 6F₅₀TM₅₀PAEB-BPSH showed better performance

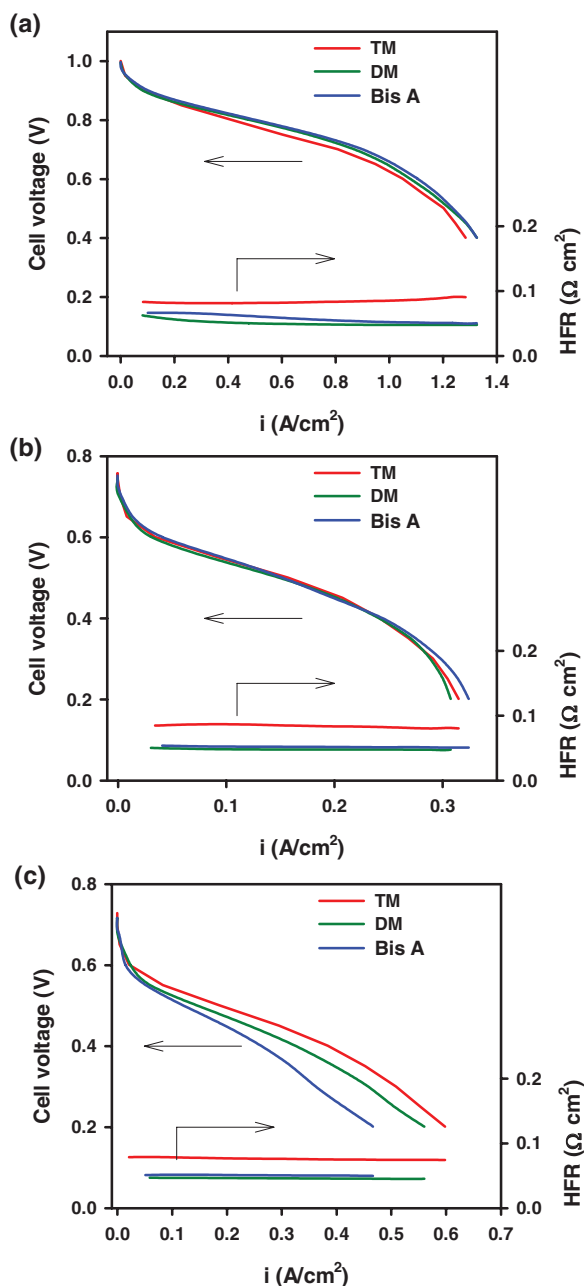


Figure 9. i-V polarization curves (a) H₂/air (b) 0.5 M DMFC and (c) 1 M DMFC at 80°C; Membrane thickness: 6F₅₀TM₅₀PAEB-BPSH: 28 μm, 6F₅₀DM₅₀PAEB-BPSH: 31 μm and 6F₅₀BisA₅₀PAEB-BPSH: 25 μm.

than the other MEAs. The relatively low methanol permeability of 6F₅₀TM₅₀PAEB-BPSH likely contributed to the better performance, as the measured methanol limiting current for this cell was 0.2 A/cm² which is ~ 50% lower than the other MEAs.

Conclusions

A series of multiblock copolymers were synthesized with a disulfonated hydrophilic phase and a partially fluorinated hydrophobic phase. Fifty mole percent of the fluorine was removed in the hydrophobic segments and replaced with a series of biphenol A moieties with increasing amount of benzylic methyl groups. The characterization results showed that, there is a strong correlation between the addition of the methyl groups and the phase separation, the resulting morphology, and the membrane properties. It is hypothesized that

the addition of the methyl groups results in higher hydrophobicity of the otherwise comparable membranes and this is the driving force leading to increased phase separation and improved MEA membrane properties. Addition of the methyl groups on the corresponding multi-block copolymers effectively reduced the IEC, resulting in lower water adsorption, and a decreased interdomain distance. This was most evident in the tetramethyl system, which had a water adsorption nearly half that of the dimethyl and Bis A PEMs. As expected when fabricated into MEAs the tetramethyl system showed the lowest methanol permeability and cross-over current, even over that of the Nafion 212 membrane. The lower methanol permeability was the reason attributed to the improved performance of the tetramethyl membrane over the other two block copolymers at higher methanol concentration conditions. The control over backbone structure along with the reduction in fluorine content should allow for PEMs with superior performance and reduced methanol permeability at higher methanol concentrations in DMFC applications.

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