Controlled Disulfonated Poly(Arylene Ether Sulfone) Multiblock Copolymers for Direct Methanol Fuel Cells

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ABSTRACT: Structure−property−performance relationships of disulfonated poly(arylene ether sulfone) multiblock copolymer membranes were investigated for their use in direct methanol fuel cell (DMFC) applications. Multiple series of reactive polysulfone, polyketone, and polynitrile hydrophobic block segments having different block lengths and molecular composition were synthesized and reacted with a disulfonated poly(arylene ether sulfone) hydrophilic block segment by a coupling reaction. Large-scale morphological order of the multiblock copolymers evolved with the increase of block size that gave notable influence on mechanical toughness, water uptake, and proton/methanol transport. Chemical structural changes of the hydrophobic blocks through polar group, fluorination, and bisphenol type allowed further control of the specific properties. DMFC performance was analyzed to elicit the

impact of structural variations of the multiblock copolymers. Finally, DMFC performances of selected multiblock copolymers were compared against that of the industrial standard Nafion in the DMFC system.

KEYWORDS: *direct methanol fuel cells, multiblock copolymers, poly(arylene ether sulfone), proton conductivity, methanol permeability, water uptake*
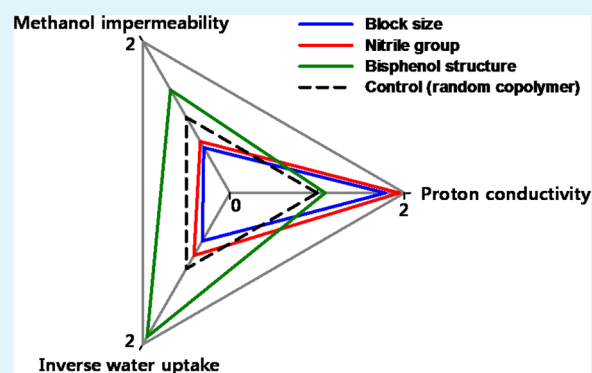
1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are of particular significance for portable power sources with power output ranging up to 50 W. The major advantage of DMFC is the ease of transport of methanol, which has high energy density, yet is a reasonably stable liquid at environmental conditions. Particular barriers of DMFC for large-scale commercialization include: (i) high cost of fuel cell components, catalysts and membranes in particular; (ii) low rate of fuel oxidation and oxygen reduction, especially in the presence of fuel crossover; (iii) questionable performance durability; and (iv) flammability and toxicity of methanol.[1]

Although industrial standard Nafion membranes for DMFC applications have desired properties such as excellent proton conductivity, oxidative stability, and low electrocatalyst poisoning, their high methanol permeability and material cost remain as technical challenges. Since the late 1990s, the development of alternative and economically viable poly(arylene ether) membranes containing a disulfonated arylene ether sulfone moiety has been explored to resolve those issues with Nafion.[2,3]

The first successful DMFC membranes we developed were the biphenol-based disulfonated poly(arylene ether sulfone) random copolymers (i.e., BPSH-x) which were prepared from direct copolymerization of 4,4′-biphenol and disulfonated and unsulfonated dichlorodiphenyl sulfone. The BPSH membranes
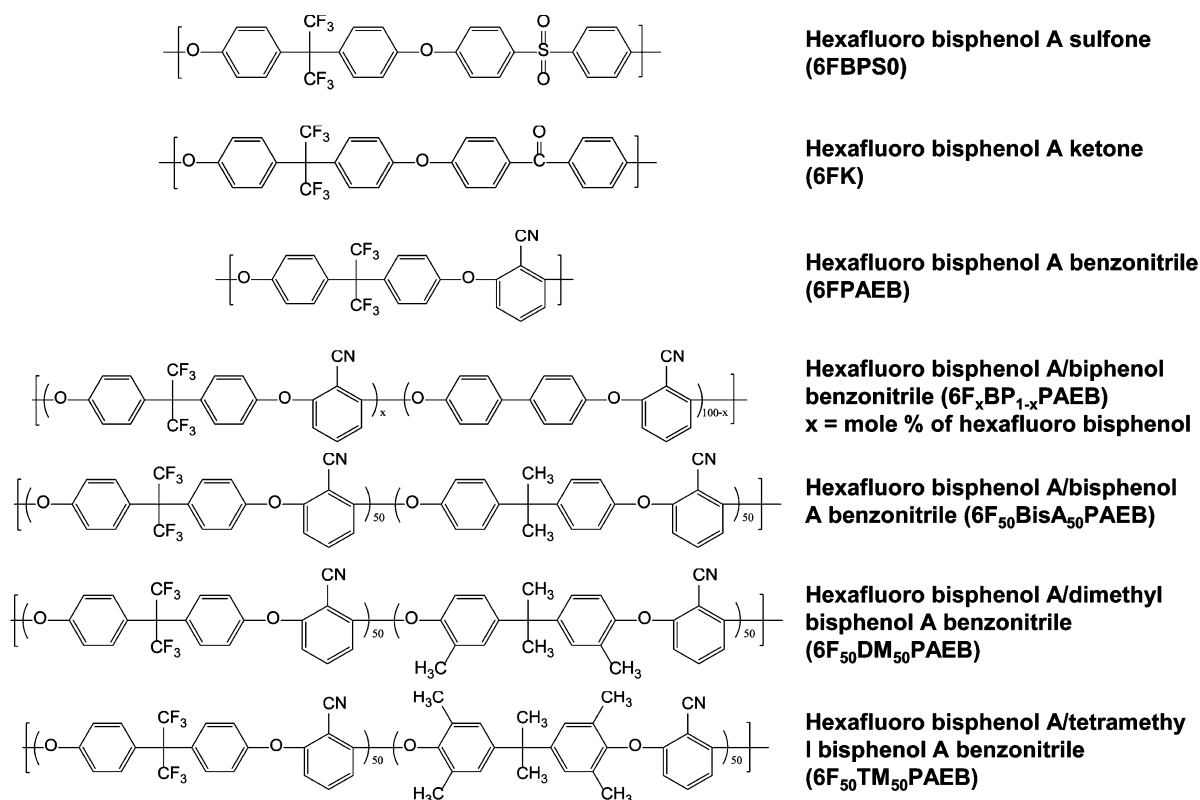
with 30% disulfonation had 5 times lower methanol permeability than Nafion[4] and exhibited promising initial performance under certain DMFC operating conditions.[5] However, notable performance deterioration was observed during extended-term DMFC operations,[6] which was related to the excessive swelling of the BPSH-x membrane that caused the local delamination of the membrane from the Nafion-bonded electrode.[7,8]

A few years later, we prepared another series of promising DMFC membranes, i.e., disulfonated poly(arylene ether benzonitrile) random copolymers (6FCN) from direct copolymerization of 4,4′-hexafluorobisphenol A and mixture of 2,6-dichlorobenzonitrile and disulfonated dichlorodiphenyl sulfone.[9] The 6FCN membranes had two structural differences from the precedent BPSH membranes: (i) partial fluorination and (ii) replacing diphenyl sulfone with benzonitrile group. Those structural changes resulted in improved proton conductivity while reducing water uptake. The 6FCN membranes with 35% disulfonation showed superior DMFC performance to the BPSH membrane with 40% disulfonation[10] and stable performance up to 3000 h of continuous DMFC

Hexafluoro bisphenol A sulfone
(6FBPS0)

Hexafluoro bisphenol A ketone
(6FK)

Hexafluoro bisphenol A benzonitrile
(6FPAEB)

Hexafluoro bisphenol A/biphenol
benzonitrile (6F$_x$BP$_{1-x}$PAEB)
x = mole % of hexafluoro bisphenol

Hexafluoro bisphenol A/bisphenol
A benzonitrile (6F$_{50}$BisA$_{50}$PAEB)

Hexafluoro bisphenol A/dimethyl
bisphenol A benzonitrile
(6F$_{50}$DM$_{50}$PAEB)

Hexafluoro bisphenol A/tetramethy
l bisphenol A benzonitrile
(6F$_{50}$TM$_{50}$PAEB)

Figure 1. Chemical structure and code name of the hydrophobic block segments.

operation.[8] Guiver et al. also developed low swelling poly-(arylene ether) nitrile copolymer membranes with a higher content of nitrile groups[11−14] and reported excellent DMFC performance.[15,16]

Although the BPSH and 6FCN membranes having statistical random copolymer architecture showed some promising results for the use in DMFCs, multiblock copolymers have drawn attention for H$_2$/air fuel cells because of their improved proton conductivity under low relative humidity (RH) conditions. Disulfonated poly(arylene ether) multiblock copolymers prepared via a coupling reaction between hydrophilic and hydrophobic oligomers with phenoxide and halide telechelic functionalities[17,18] exhibited improved H$_2$/air fuel cell performance compared to statistical random copolymers at a reduced RH.[19] Nonetheless, the benefit of using multiblock copolymers for DMFC applications is arguable because DMFC is typically operated under fully hydrated conditions.

In this research, we investigated the structure-property-performance relationships of disulfonated poly(arylene ether) multiblock copolymers for their use in DMFC applications. Several series of disulfonated poly(arylene ether) multiblock copolymers having different hydrophilic/hydrophobic block lengths and hydrophobic block structure were prepared via a coupling reaction between a disulfonated poly(arylene ether sulfone) hydrophilic oligomer and various hydrophobic oligomers. The controlled synthesis allowed us to systematically explore the effects of hydrophilic/hydrophobic block length, polar group (e.g., sulfone, ketone, and nitrile), degree of fluorination, and bisphenol type. Water uptake, density, and weight-based ion exchange capacity (IEC$_W$) of the multiblock copolymers were directly measured from stand-alone membranes and converted to the volume based properties in order to explain the property differences between the multiblock

copolymers. Proton conductivity and methanol permeability were obtained from high frequency resistance (HFR) measurement and methanol crossover limiting current of single cell DMFC hardware, respectively. The conductivity and methanol permeability along with the selectivity, i.e., the ratio of proton conductivity to methanol permeability, were used to correlate the membrane properties with DMFC performance. Finally, DMFC performance of selected multiblock copolymers was compared and discussed in terms of benefits of multiblock copolymers over the industrial standard Nafion membranes.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Multiblock Copolymers. We prepared several series of disulfonated poly(arylene ether) multiblock copolymers via a coupling reaction of phenoxide terminated fully disulfonated poly-(arylene ether sulfone) (BPS100) and fluorine-terminated hydrophobic segments. To prevent the randomization of the multiblock copolymers by possible ether−ether interchange reactions, we utilized mild reaction conditions for each multiblock copolymer. Detailed synthetic procedures and structural characterization for each multiblock copolymer were reported in the previous literatures.[20−22] Figure 1 shows the chemical structure and code name of the hydrophobic segments of the multiblock copolymers.

2.2. Membrane Preparation and Acidification. The sulfonated copolymers in their salt form were dissolved in dimethylacetamide (DMAc) (∼7%, w/v) and filtered through a 0.45 μm Teflon syringe filter. The filtered solution was then cast onto a clean glass substrate and dried for 24 h under an infrared lamp at ∼45°C. The membranes were then annealed by drying in a vacuum oven at 220°C for 12 h. All of the membranes were converted from salt form to acid form by boiling in 0.5 M sulfuric acid solution for 2 h, followed by boiling in deionized water for 2 h. The prepared membranes were dried using a vacuum table at 60°C for 1 h before use. The range of membrane thickness was 25 to 60 μm, which was controlled by the amount of cast solution.

2.3. Membrane Characterization. Intrinsic viscosities (IV) of multiblock copolymers were obtained from a size exclusion chromatography (SEC) equipped with a Waters 1515 isocratic HPLC pump, a Waters autosampler, a Waters HR5-HR4-HR3 column set, a Waters 2414 refractive-index detector, and a Viscotek 270 viscometric detector. NMP (containing 0.05 M LiBr) at 50 °C was used as the mobile phase.

Mechanical properties were measured by dynamic mechanical thermal analyzer (TA A800-RH). The temperature and RH was precisely controlled in an environment chamber. The tensile properties were measured using 10 mm × 30 mm rectangular test strips at a load ramp of 0.5 MPa min^{-1} at 80°C. The stress-strain behavior of the membranes was measured after obtaining equilibrium RH of 10 and 90% for 60 min.

The cross-sectional morphology was examined using a TEM after microtoming. Samples were stained with 0.5 M lead acetate for 1 h in order to enhance the phase contrast between hydrophilic and hydrophobic components of the copolymers.

Water uptake (WU) was measured after drying the membrane in acid form at 100°C under vacuum overnight. The dried membrane was immersed in water at 30 °C and periodically weighed on an analytical balance until a constant weight was obtained. The density of the copolymers was measured from the membrane dimensions and weight after drying at 75°C for 2 h. The volume-based water uptake was calculated from the density of copolymer and the density of water, 1 g/cm^3.

Weight-based ion exchange capacity (IEC$_W$) was determined by titration with 0.01 M NaOH. A volume-based dry IEC (IEC$_{V\,(dry)}$) was obtained by multiplying the dry membrane density by the weight-based (IEC$_W$), which was estimated from the copolymer structure. An IEC$_{V\,(wet)}$ was then calculated from IEC$_{V\,(dry)}$, the membrane WU, and the density of water.

Proton conductivity of the copolymers was determined in a window cell geometry[23] using a Solartron 1252 + 1287 impedance/gain-phase analyzer over the frequency range of 10-1 MHz following the literature procedures.[24] For determining proton conductivity in liquid water, the membranes were equilibrated at 30°C in deionized water for 24 h prior to testing.

2.4. Preparation of Membrane Electrode Assembly. Membrane electrode assemblies (MEAs) using multiblock copolymers were prepared either by catalyst coated membrane (CCM) or gas diffusion electrode (GDE). For CCM, standard LANL catalyst ink formulation was prepared using PtRu black (HiSPEC® 6000 Pt:Ru 50:50 atomic %, Johnson Matthey) and Pt black (HiSPEC 1000, Johnson Matthey) catalysts and commercially available 5% Nafion dispersion (1100 equiv weight, Ion Power Inc.).[10] The Pt loadings for PtRu anode and Pt cathode catalyst layers were 6 and 4 mg/cm^2, respectively. The catalyst inks were prepared by ultrasonically mixing appropriate amounts of catalyst powders with de-ionized water (Millipore, 18 MΩ cm) and 5% Nafion suspension for 90 seconds. Subsequently, the catalyst inks were hand-painted onto the copolymer membranes, followed by drying at 80 °C for 60 min. The MEAs were assembled with single-(anode) and double-(cathode) sided hydrophobic carbon cloths (ELAT, E-TEK Inc.). For GDE, 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 Pt loadings for PtRu anode and Pt cathode catalyst layers were 2.7 and 2 mg/cm^2, respectively. The geometric active cell area was 5 cm^2.

2.4. Characterization of Membrane Electrode Assembly. DMFC polarization curves and high frequency resistance (HFR) were obtained using a fuel cell test station equipped with internal AC impedance analyzer (Fuel Cell Technology Inc.). Cell performance was obtained after ∼3 h break-in under H$_2$/air conditions at a cell voltage of 0.7 V at 80°C (CCM) and 75°C (GDE). For DMFC mode operations, 0.5, 1, and 2 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 the 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. Proton conductivity of membranes was estimated from HFR measured at 0.5 M methanol fed concentration and known membrane thickness.

Extended-term DMFC test was performed under 80 °C, 2 M methanol, and air fed conditions. The current density and HFR changes of the single cells were monitored every 10 min for 100 h at a constant cell voltage (0.45 V). Polarization curves after 100 h were taken for comparing with initial performance. The data presented in this work were selected from a single membrane sample after confirming a good reproducibility with multiple samples. MEAs using commercially available Nafion membranes were also tested for comparison.

Methanol crossover of MEAs was evaluated from the measurement of limiting methanol crossover currents of single cells; Methanol solutions of 0.5, 1, and 2 M were fed to one side of the cell, while humidified nitrogen at 500 sccm and ambient pressure were supplied to the other side.[10,15] The methanol permeation flux was determined from the limiting current density resulting from transport-controlled methanol electro-oxidation at the other side of the cell using a potential-step experiment. Methanol permeability of membranes was estimated from the methanol limiting current at 0.5 M methanol feed concentration. Methanol crossover of MEAs as a function of current density was determined by the CO$_2$ measurement.[25,26] The CO$_2$ from cathode exhaust was measured using a gas analyzer (ZRE NDIR, California Analytical Instruments, Inc.) after removing water. Both HFR measurements and limiting methanol crossover current densities exhibited experimental reproducibility of approximately ±5%.

3. RESULTS AND DISCUSSION

Several series of hydrophilic−hydrophobic multiblock copolymers varying in block length were synthesized via coupling reactions of phenoxide terminated fully disulfonated arylene ether sulfone (BPS100) and fluorine-terminated arylene ether oligomers. For purposes of comparison, random copolymers with similar weight-based IEC (IEC$_W$) were synthesized by controlling the feeding ratio of sulfonated to non-sulfonated monomers. Table 1 summarizes the hydrophilic and hydrophobic block lengths, intrinsic viscosity (IV) and IEC$_W$ of the copolymers. The IEC$_W$ ranges from 1.45−1.74 mequiv/g. The intrinsic viscosity of multi-block copolymers increases with the hydrophilic and hydrophobic block lengths. This is probably attributed that multiblock copolymers having greater block lengths tend to form bigger aggregates in the solution.

3.1. Effect of Hydrophilic−Hydrophobic Block Lengths. Unlike random copolymers, multiblock copolymers are composed of sequences of oligomeric building blocks. Figure 2 shows the schematic illustration of random and multiblock copolymers as a function of block length. The length of oligomeric blocks plays an important role in forming a self-assembled microstructure which impacts the membrane properties. Therefore, exploring the microstructure of multiblock copolymers as a function of block length is essential to understanding the membrane properties. In this section, we discuss the morphological features of multiblock polymers as a function of block length, followed by the mechanical and other key membrane properties. The DMFC performance differences derived from the property difference are discussed.

3.1.1. Microstructure and Mechanical Properties. Figure 3 compares the TEM images of random and multiblock copolymers as a function of block length. In those images, nonstained hydrophobic domains appear brighter, whereas hydrophilic domains appear darker because of the higher electron density obtained by lead neutralization. The random copolymer showed a featureless image indicating the absence of

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Table 1. Hydrophilic and Hydrophobic Block Lengths, Intrinsic Viscosity, and IEC_W of Copolymers

copolymer	block length (kg/mol)		IV (dL/g)[a]	IEC_W (meq/g)
	hydrophobic	hydrophilic		
6FBPS0-BPSH	random		0.65	1.45
	7	7	0.82	1.53
	11	11	1.03	1.55
	15	15	1.25	1.56
6FK-BPSH	random		0.85	1.52
	7	7	1.08	1.55
	11	11	1.03	1.50
	15	15	1.10	1.56
6FPAEB-BPSH	random		0.62	1.46
	7	7	0.61	1.55
	11	11	0.61	1.55
	15	15	1.01	1.55
$6F_{100}BP_0PAEB$-BPSH	10	10	0.82	1.53
$6F_{75}BP_{25}PAEB$-BPSH	10	10	0.91	1.55
$6F_{50}BP_{50}PAEB$-BPSH	10	10	1.12	1.55
$6F_{25}BP_{75}PAEB$-BPSH	10	10	1.14	1.50
$6F_{50}BisA_{50}PAEB$-BPSH	10	10	NA[b]	1.74
$6F_{50}DM_{50}PAEB$-BPSH	10	10	0.85	1.65
$6F_{50}TM_{50}PAEB$-BPSH	10	10	0.58	1.50

[a]measured at 30°C. [b]NA: not available.

Hydrophobic component M_W: 435–534 g/mol

Hydrophilic component M_W: 520 g/mol
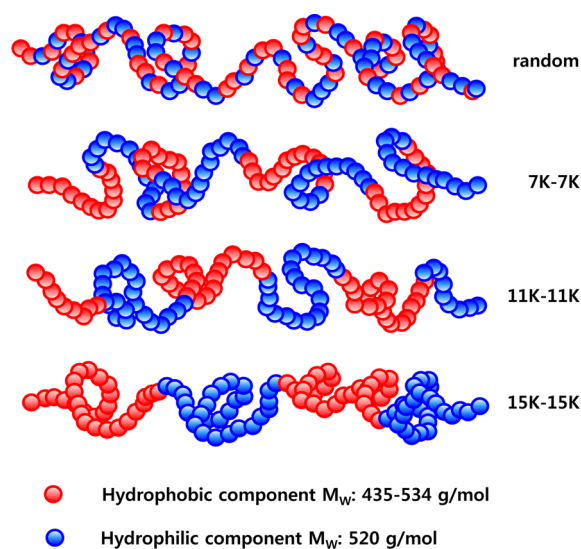
Figure 2. Schematic illustration of polymer architecture of random and multiblock copolymers having the block length of 7K-7K, 11K-11K, and 15K-15K.

large-scale morphological order because of the statistical chain compositions. In contrast, the multiblock copolymer membranes showed a self-assembled "fingerprint-type" structure. As the block length increased from 7 to 15 kg/mol, the large-scale phase separated structure became more prominent with increased inter-domain distance and domain continuity. Similar morphological changes with increasing block length were also observed with other multiblock copolymers[20−22] where X-ray
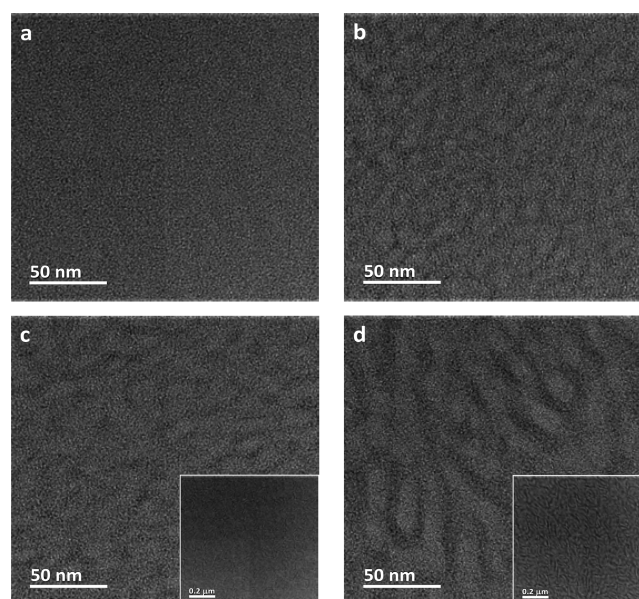
Figure 3. TEM cross-sectional morphology of 6FPAEB-BPSH random and multiblock copolymers: hydrophobic−hydrophilic block length: (a) random, (b) 7K-7K, (c) 11K-11K, and (d) 15K-15K.

scattering analysis further identified this self-assembled structure as lamella morphology.

The morphological differences may impact the mechanical properties of the membranes. Figure 4 compares the stress-
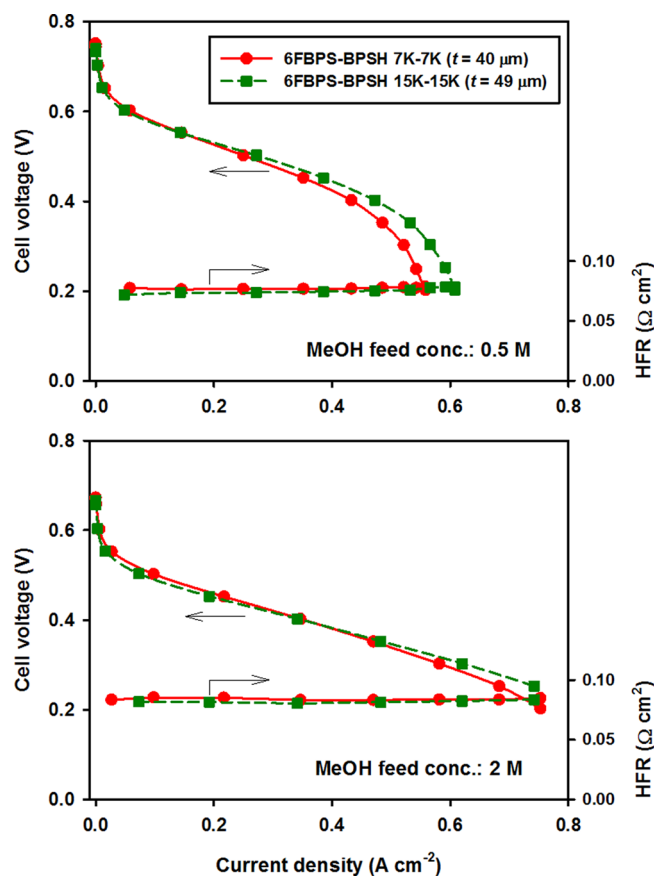
Figure 4. Comparison of stress−strain curves of the 6FPAEB-BPSH random and multiblock copolymers at 10 and 90% RH.

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strain behaviors of the random and multiblock copolymers at 80°C under controlled RH conditions. At 10% RH, the multiblock copolymers show substantially higher strain than the random copolymer; and the strain increases with block length. The substantially increased strain results in improved membrane toughness (calculated from the area of the stress strain curves) from 1.0 (random) to 8.4 (7K-7K) and 15.0 MPa (15K-15K). The increased strain of multiblock copolymers is due to the increased elasticity originated from the distinct phase separations between hydrophilic soft domain and hydrophobic hard domains. At 90% RH, the strain of all copolymers, in particular of the random copolymer, substantially increases, whereas the strength and modulus decrease. As a result, less difference in the toughness between the copolymers decreases although the multiblock copolymers still exhibit a superior toughness. The mechanical property change under high RH conditions is due to the plasticization effect of the absorbed water.

3.1.2. Properties and DMFC Performance. Table 2 compares water uptake (WU), methanol permeability (P),

Table 2. Water uptake (WU), methanol permeability (P), proton conductivity (σ), and selectivity of the 6FBPS-BPSH, 6FK-BPSH, and 6FPAEB-BPSH copolymers

copolymer (hydrophobic/ hydrophilic block lengths)	WU (wt %)	$P \times 10^{-6}$ (cm^2/s)	σ (mS/cm) SA	σ (mS/cm) HFR	selectivity[a] $\times 10^6$
6FBPS0-BPSH (random)	38	NA	130	NA	NA
6FBPS0-BPSH (7K/7K)	50	1.8	170	51	28
6FBPS0-BPSH (11K/ 11K)	55	2.2	180	64	29
6FBPS0-BPSH (15K/ 15K)	60	2.5	190	67	27
6FK-BPSH (random)	35	NA	70	NA	NA
6FK-BPSH (7K/7K)	54	1.8	140	54	30
6FK-BPSH (11K/11K)	50	1.9	140	57	30
6FK-BPSH (15K/15K)	55	2.9	170	74	26
6FPAEB-BPSH (random)	30	NA	80	NA	NA
6FPAEB-BPSH (7K/7K)	42	1.6	140	53	33
6FPAEB-BPSH (11K/ 11K)	42	1.8	140	64	36
6FPAEB-BPSH (15K/ 15K)	46	2.2	150	73	33

[a]selectivity was estimated using the conductivity from the single cell. NA: not available.

proton conductivity (σ), and selectivity of random and multiblock copolymers. The proton conductivity values measured from single cell high frequency resistance (HFR) is only about 35% of those from stand-alone (SA) membranes. There may be multiple reasons for this, including: (i) in-plane (SA) vs. through plane conductivity (HFR), (ii) pure water (SA) vs. aqueous methanol solution (HFR), (iii) liquid equilibrated (SA) vs. vapor equilibrated (HFR) at the cathode, and (iv) membrane only (SA) vs. electronic and interfacial contribution (HFR) for the resistance measurement. In spite of the notable difference, the conductivity measured from single cell reflects SA membrane conductivity fairly well. The multiblock copolymers exhibit higher water uptake, methanol permeability and proton conductivity than the random copolymer and those properties increase with block length. It is speculated that more prominent domain structure and

greater phase continuity obtained with increased block length are responsible for the greater water uptake and higher methanol/proton transports. Although the methanol permeability and proton conductivity increased linearly with block length, the selectivity differences between copolymers were similar, with a notably higher selectivity observed with a block length of 11K. Previous studies using poly(arylene ether) random copolymers indicated that a maximum selectivity was typically obtained at the vicinity of a percolation threshold where hydrophilic phase became continuous due to the increased water uptake.[27] This result suggests that the maximum selectivity obtained with 11K block length is originated from a threshold connectivity of hydrophilic domains structures. This result indicates that the multiblock copolymers with the block length of ~11K may have a potential to exhibit better DMFC performance although the difference should be rather small.

The DMFC performance of multiblock copolymers having 7K-7K and 15K-15K block length is compared under 0.5 and 2 M methanol feed concentrations (Figure 5). At 0.5 M methanol
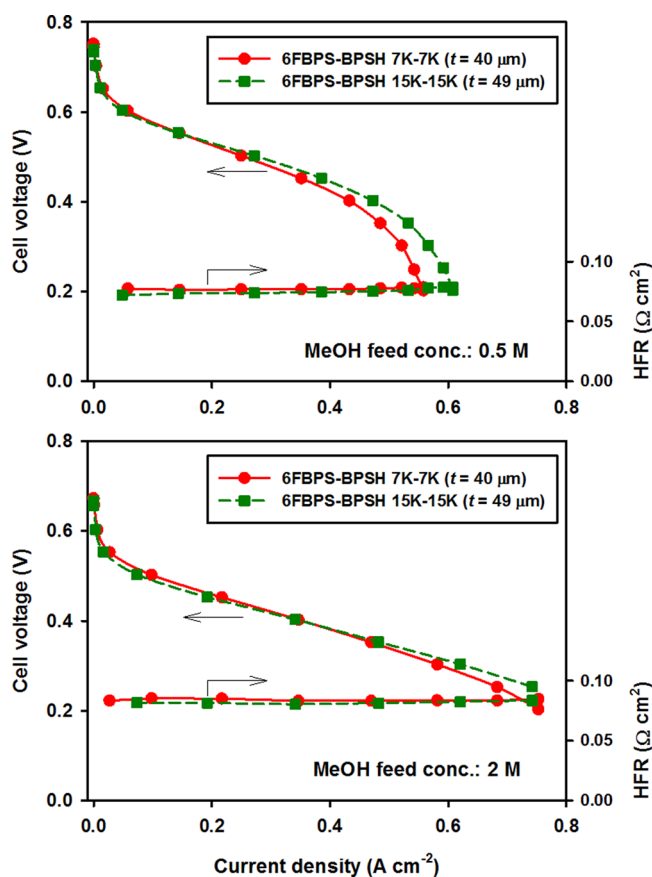

Figure 5. Comparison of DMFC performance using 6FBPS0-BPSH 7K-7K and 15K-15K at 0.5 and 2 M methanol feed concentration; membrane thickness (*t*) was specified; anode, Pt−Ru black 6 mg/cm^2; cathode, Pt black 3 mg/cm^2; cell temperature = 80°C.

feed, the multiblock copolymer with the block length of 15K exhibits slightly better performance at high current density than the copolymer with the block length of 7K. This is attributed that the HFR of the cell using 15K-15K had slightly lower resistance ca. 0.077 vs. 0.074 Ω cm^2 at 0.5 V with minimal methanol crossover effects at the low methanol feed concentration. At 2 M methanol feed, on the other hand, the

copolymer with the shorter block length exhibits slightly better performance with the exception of the high current density range, ca. >0.5 A/cm^2. It is likely that the substantial methanol crossover at the methanol feed conditions adversely impacts the performance. The methanol crossover limiting currents of the cell using 6FBPS0-BPSH 7K-7K is lower than that of the cells using 6FBPS0-BPSH 15K-15K (i.e., 377 vs. 550 mA/cm^2, respectively) at the methanol feed conditions in spite of slightly greater thickness of the 6FBPS0-BPSH 15K-15K membrane. However, the difference of DMFC performance using these copolymers is negligible and one should expect that the performance difference may be even less with further adjusting membrane thickness. In principle, identical fuel cell performance is anticipated with membranes having the same selectivity through control of the membrane thickness. For example, if "A" membrane has 10-times higher conductivity and methanol permeability than "B" membrane, identical DMFC performance should be obtained with 10-times thinner "B" membrane if there is no interfacial or non-uniformity issue. Therefore, the actual benefit of using long block length multiblock copolymers should be discussed in light of membrane thickness restraints if the membrane selectivity is comparable. In practical DMFC operations, a minimum thickness is required to meet the fuel efficiency target and membrane robustness. Further increase in membrane thickness is undesirable due to the resultant voltage efficiency loss and material cost increase. For these reasons, relatively thick version of Nafions such as Nafion 115 and much thinner polyaromatic random copolymer membranes have been suggested to use.[28] Because multiblock copolymers have higher proton conductivity and methanol permeability than random copolymers, DMFC performance using thicker multiblock copolymers should have comparable performance to that of using thinner random copolymers for optimum conditions. Using a thicker membrane has an obvious benefit in light of DMFC durability. Greater toughness of multiblock copolymers may increase the mechanical stability. In fact, typical minimum thickness of poly(arylene ether) random copolymers for mechanical integrity was limited to ~50 μm, but often ~30 μm thick multiblock copolymers were used without disintegration of membrane robustness. Therefore, the major advantage of using highly conductive and more methanol permeable multiblock copolymers is mechanical robustness, which allows using a thinner membrane for DMFC applications. Although the effect of block length on selectivity is small, multiblock copolymers with the block length of 11K may give additional performance improvement.

3.2. Effect of Chemical Structure of Hydrophobic Block.
In this section, the chemistry effect of hydrophobic block is discussed. For a systematic approach, the chemical structure of hydrophobic blocks was controlled, yet the hydrophilic block component and the block lengths were fixed to 10K. The effects of polar group (i.e., sulfone, ketone, and nitrile), degree of fluorination and bisphenol type on membrane properties are discussed and correlated with DMFC performance.

3.2.1. Polar Groups. Figure 6 displays the chemical structural variations of polar group in the fluorinated hydrophobic block segment. The hydrophobic telechelic oligomers with the molecular weight of 10 kg/mol were synthesized via nucleophilic substitution reactions using hexafluoro bisphenol A and dihalide diphenyl sulfone, diphenyl ketone or benzonitrile monomers.
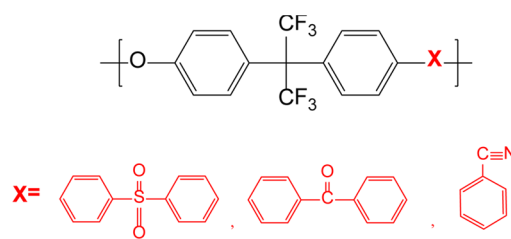
Figure 6. Chemical structural variation of polar group in the hydrophobic block segment.

Table 2 in the previous section shows the properties of multiblock copolymers that contain sulfone, ketone and nitrile groups in the hydrophobic block segments. It was noted that while the polysulfone and polyketone multiblock copolymers showed similar membrane properties at the given block length, the polynitrile multiblock copolymers exhibited notably lower WU, methanol permeability, and proton conductivity. The selectivity of the polynitrile copolymers was slightly better. Volumetric parameter analysis[30] may give further insight for understanding property differences.[29] Table 3 displays the

**Table 3. Volume-Based Parameters of the 6FBPS0-BPSH, 6FK-BPSH, and 6FPAEB-BPSH Copolymers**

copolymer (hydrophobic/hydrophilic block lengths)	density (g/cm^3)	WU (vol %)	IEC$_{V(dry)}$ (cm^3/mequiv)	IEC$_{V(wet)}$ (cm^3/mequiv)
6FBPS0-BPSH (random)	1.58	60	2.29	1.43
6FBPS0-BPSH (7K/7K)	1.29	65	1.97	1.20
6FBPS0-BPSH (11K/11K)	1.36	75	2.11	1.21
6FBPS0-BPSH (15K/15K)	1.25	75	1.95	1.11
6FK-BPSH (random)	1.28	45	1.95	1.34
6FK-BPSH (7K/7K)	1.27	69	1.97	1.17
6FK-BPSH (11K/11K)	1.31	66	1.97	1.19
6FK-BPSH (15K/15K)	1.27	70	1.98	1.17
6FPAEB-BPSH (random)	1.44	43	2.10	1.47
6FPAEB-BPSH (7K/7K)	1.29	54	2.00	1.30
6FPAEB-BPSH (11K/11K)	1.38	58	2.14	1.35
6FPAEB-BPSH (15K/15K)	1.34	62	2.08	1.28

membrane density and IEC$_V$ under dry and wet conditions of each copolymer. The multiblock copolymers having sulfone and ketone groups have comparable density, WU, and IEC$_V$. This indicates that the contributions of the polar groups to membrane properties are similar. The multiblock copolymers having nitrile group, on the other hand, have slightly greater density and lower WU which produced greater IEC$_{V (wet)}$. This may be attributed that the multiblock copolymers containing nitrile groups are more intensively packed than other multiblock copolymers[30] and sulfone and ketone groups can hold more water molecules via hydrogen bonding structure.[31] The slightly higher IEC$_{V (wet)}$ obtained with the block length of 11K is consistent with the previous result that the maximum IEC$_{V (wet)}$ value was obtained at the percolation threshold[29] and again with the selectivity behavior demonstrated in Table 2.

Because the selectivity of the nitrile containing copolymers is higher (~10%) than those of the polysulfone and polyketone multiblock copolymers, slightly better DMFC performance is expected when an optimum thickness was employed. Furthermore, better DMFC durability may be expected with polynitrile multiblock copolymers because relatively lower water uptake can prevent interfacial failure with Nafion-bonded

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electrode.[6−8] Figure 7 compares the DMFC performance using the 6FBPS0-BPSH and 6FPAEB-BPSH membranes with the
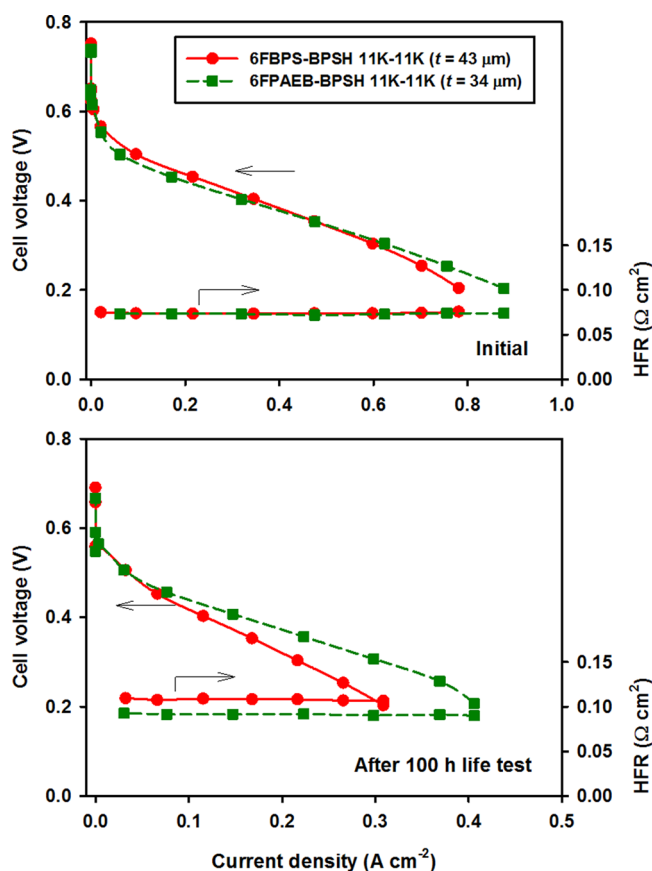
Figure 7. DMFC performance using the 6FBPS0-BPSH and 6FPAEB-BPSH membranes with block length of 11K-11K at 2 M methanol feed concentration before and after 100 h extended-term test; membrane thickness (t) was specified; anode, Pt−Ru black 6 mg/cm^2; cathode, Pt black 3 mg/cm^2; cell temperature = 80°C.

block length of 11K-11K before and after 100 h extended-term test. Since the proton conductivity of nitrile containing multiblock copolymers was 16% lower, slightly thinner membrane for the polynitrile multiblock copolymer was selected for the performance comparison. The initial DMFC performance of the cell of the polysulfone and polynitrile multiblock copolymers is comparable with slightly better methanol blocking but higher resistance characteristics for nitrile containing polymer. After 100 h of DMFC operations, the DMFC performance of both cells decreases substantially. This is probably attributed to the interfacial delamination between the electrode and membrane[6] as evidenced by the increased cell HFR and the Ru crossover that contaminates the cathode.[32] The cell using the polysulfone multiblock copolymer membrane exhibit more substantial performance loss than the cell using the polynitrile multiblock copolymer. The increased cell HFR for the cell with the polysulfone multiblock copolymer suggests that more substantial interfacial delamination between membrane and electrode occurred during the extended test.

3.2.2. Degree of Fluorination. The effect of degree of fluorination was investigated by replacing hexafluoro bisphenol A (6F) with biphenol (BP) in the hydrophobic polynitrile block segment. The structural variation is shown in Figure 8. The
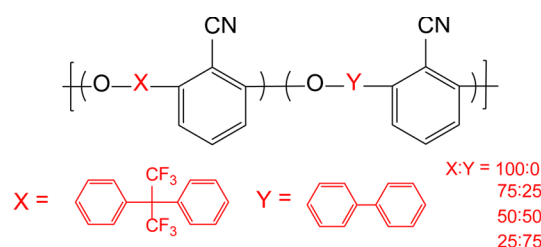
Figure 8. Chemical structural variation of degree of fluorination in the hydrophobic block segment.

properties and DMFC performance of highly fluorinated perfluorosulfonic acid, Nafion, is also compared in this section in order to see further extension of the fluorination effect.

Table 4 shows clear trend in property changes of the multiblock copolymers with increasing degree of fluorination:

Table 4. Properties of the 6FxBP(100-x)PAEB-BPSH100 (10K-10K) copolymers

6F content	WU (wt %)	$P \times 10^{-6}$ (cm^2/s)	(σ mS/cm) SA	HFR	selectivity
100	45	2.0	140	60	30
75	44	1.9	140	61	32
50	52	1.8	130	60	35
25	54	1.5	130	64	43
Nafion	20	3.1	120	66	21

(i) lower water uptake, (ii) higher methanol permeability, (iii) similar proton conductivity, and (iv) lower selectivity. Comparison of the properties with Nafion suggests that this trend can be extended to highly fluorinated Nafion which has the lowest WU and selectivity yet the highest methanol permeability. The reason for lower water uptake upon fluorination was ascribed to the higher density of fluorine as well as the increased hydrophobicity of the copolymer.[33]

Table 5 shows the membrane density and IEC$_V$ of each copolymer. Note that the density of multiblock copolymers

Table 5. Volume based parameters of the 6F$_x$BP$_{(100-x)}$PAEB-BPSH100 (10K-10K) copolymers

6F to BP ratio	density (g/cm^3)	WU (vol %)	IEC$_{V(dry)}$ (cm^3/meq)	IEC$_{V(wet)}$ (cm^3/meq)
100	1.35	61	2.07	1.28
75	1.25	55	1.94	1.25
50	1.20	63	1.86	1.15
25	1.05	57	1.58	1.01
Nafion	2.0	40	1.84	1.31

increases with degree of fluorination. Consequently, the volume-based water uptake becomes comparable. This is attributed to the fact that the volume of fluorine (i.e., van der Waals radii of F: 1.47 Å) is only 18% greater than the volume of hydrogen (i.e., van der Waals radii of hydrogen: 1.2 Å), whereas the atomic weight of fluorine is 19 times to that of hydrogen. The increased density of fluorinated copolymers causes higher IEC$_{V(wet)}$ values. Due to the opposite trend of weight-based water uptake and IEC$_{V(wet)}$, the proton conductivity becomes comparable regardless of the fluorination level including Nafion. On the other hand, the methanol permeability, the other key parameter for selectivity, increases with fluorination. The high methanol permeability with fluorinated proton

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exchange membranes is a well-known fact from the comparative studies of Nafion and wholly aromatic copolymers.[4,34] The fluorine incorporation in hydrophobic components increases the phase contrast between hydrophobic and hydrophilic phase domains. Consequently, polar molecules such as water (or methanol) in fluorinated systems are less bound and water (or methanol) transport in wholly aromatic copolymers (ca. bigger water domain) becomes slower. Because of the increased methanol permeability with degree of fluorination, the selectivity of fluorinated multiblock copolymers and Nafion is higher than nonfluorinated one.

Figure 9 compares the DMFC performance using $6F_{75}BP_{25}$ and $6F_{25}BP_{75}$ multiblock copolymers and Nafion membranes at
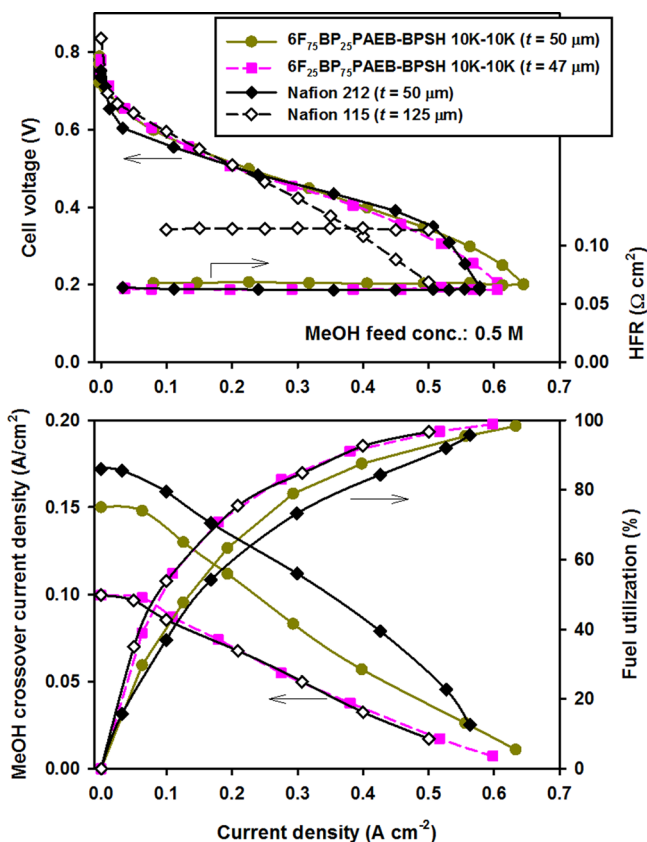
Figure 9. Comparison of DMFC performance using $6F_{75}BP_{25}PAEB$-BPSH 10K-10K, $6F_{25}BP_{75}PAEB$-BPSH 10K-10K, Nafion 212, and Nafion 115 at 0.5 M methanol feed concentration; membrane thickness (t) was specified; anode, Pt−Ru black 6 mg/cm^2; cathode, Pt black 3 mg/cm^2; cell temperature = 80 °C.

0.5 M methanol feed conditions. The DMFC performance using the two multiblock copolymers and Nafion 212 ($t = 50$ μm) shows comparable polarization behaviors. The performance using Nafion 115 ($t = 125$ μm), however, is much inferior. As mentioned above; this is attributed to the cell resistance effect that is predominant at 0.5 M methanol feed conditions. However, the methanol crossover and fuel utilization of these cells as a function of current density shows that cells using Nafion 212 and $6F_{75}BP_{25}PAEB$-BPSH suffer from low fuel utilization caused by notably higher methanol crossover. The fuel utilization of the cell using $6F_{25}BP_{75}PAEB$-BPSH reaches 77 and 95% at 0.5 V and peak power, which are significantly higher than the cell using Nafion 212 (i.e., 62 and 90% at 0.5 V and peak power, respectively) and are comparable to the cell using Nafion 115 (i.e., 75 and 88% at 0.5 V and peak power, respectively). Considering the polarization behavior and fuel utilization, the performance of $6F_{25}BP_{75}PAEB$ and $6F_{75}BP_{25}PAEB$ are better than those of Nafion-based systems. This is consistent with the selectivity result shown in Table 4.

3.2.3. Bisphenol Structure. Effect of bisphenol structure was investigated by replacing biphenol (BP) with bisphenol A (Bis A), dimethyl bisphenol A (DM), and tetramethyl bisphenol A (TM) in the $6F_{50}X_{50}PAEB$ hydrophobic block segment with the level of fluorination was fixed to 50% (Figure 10).

Table 6 shows the properties of these multiblock copolymers. The most remarkable property change observed with bisphenol

Table 6. Properties of the $6F_{50}BP_{50}PAEB$-BPS, $6F_{50}BisA_{50}PAEB$-BPSH, $6F_{50}DM_{50}PAEB$-BPSH, and $6F_{50}TM_{50}PAEB$-BPSH (10K-10K) Copolymers

bisphenol type	WU (wt %)	$P \times 10^{-6}$ (cm^2/s)	σ (mS/cm) SA	HFR	selectivity
BP	52	1.8	130	60	35
Bis A	40	1.3	120	49	38
DM	35	1.4	150	61	44
TM	20	1.1	100	41	37

type is the membrane WU which is decreased from 52% (BP) to 40% (Bis A) to 35% (DM) to 20% (TM). The substantial decrease in WU observed in the DM- and TM-based multiblock copolymers is perhaps attributed to the increased hydrophobicity from the pendent benzylic methyl groups. The relatively high proton conductivity over methanol permeability of the DM multiblock copolymer makes this copolymer have the highest selectivity among all multiblock copolymers tested in this study.
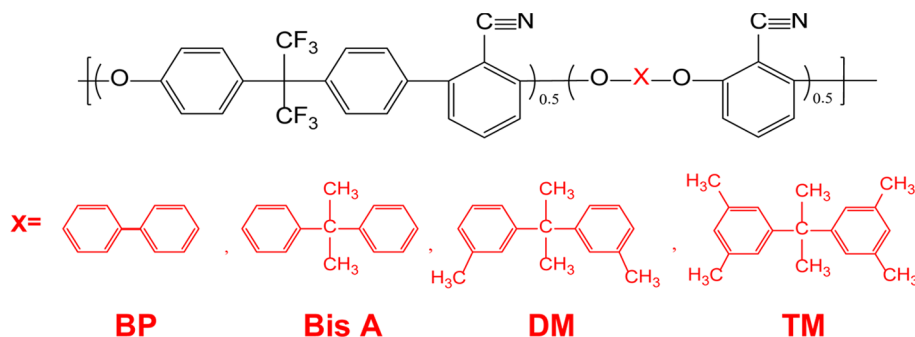
**Figure 10.** Chemical structural variation of bisphenol type in the hydrophobic block segment.

Table 7 shows the density and IEC_V of these multiblock copolymers. Relatively high $IEC_{V(wet)}$ values were obtained with

Table 7. Volume-Based Parameters of the $6F_{50}BP_{50}PAEB$-BPSH, $6F_{50}BisA_{50}PAEB$-BPSH, $6F_{50}DM_{50}PAEB$-BPSH, and $6F_{50}TM_{50}PAEB$-BPSH (10K-10K) Copolymers

bisphenol type	density (g/cm^3)	WU (vol %)	$IEC_{V(dry)}$ (cm^3/mequiv)	$IEC_{V(wet)}$ (cm^3/mequiv)
BP	1.20	62	1.86	1.15
Bis A	1.24	50	2.16	1.44
DM	1.24	43	2.05	1.43
TM	1.21	24	1.82	1.46

Bis A, DM and TM multiblock copolymers. Although the notably high IEC_V(wet) of Bis A copolymer is due to its higher IEC_W (see Table 1), the high $IEC_{V(wet)}$ values for DM and TM multiblock copolymers mainly originate from their low water swelling characteristics, as noted that the WU of DM and TM multiblock copolymers is comparable to or even lower than that of Nafion.

Figure 11 compares the DMFC performance of the cell using Bis A and DM- and TM-based multiblock copolymers at 1 M methanol feed concentration. The cell using the TM based multiblock copolymer outperforms both the Bis A and DM
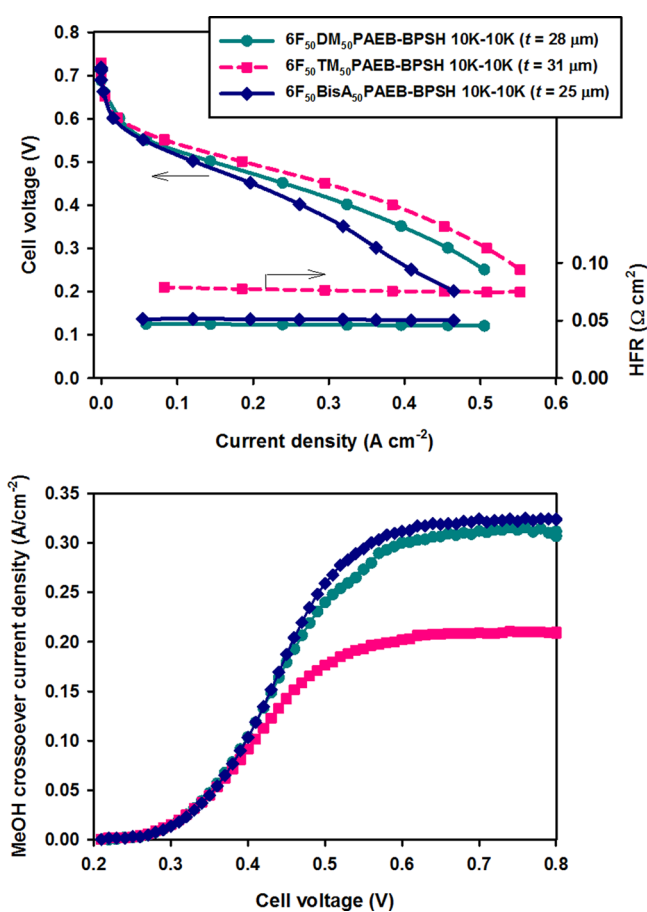
Figure 11. Comparison of DMFC performance and methanol crossover limiting current of cells using multiblock copolymers with different bisphenol structures in the PAEB hydrophobic block; membrane thickness (t) was specified; methanol feed concentration, 1 M; anode, Pt−Ru black 2.7 mg/cm^2; cathode, Pt black 2 mg/cm^2; cell temperature = 75°C.

multiblock copolymers in spite of its slightly higher HFR. This is attributed to the relatively low methanol crossover of the cell using TM-based copolymer which helps to minimize the cathode overpotential from crossovered methanol. Although the cell using DM-based copolymers exhibit very low cell resistance, high mixed potential due to the substantially high methanol crossover could not be overcome. Although further membrane thickness control for the DM-based multiblock copolymer needs to be done for the optimized performance, we believe that TM-based multiblock copolymers have potential to have better DMFC durability since these have much lower water uptake. Longer-term durability testing using this membrane is on-going and will be reported in the future.

4. CONCLUSIONS

Several series of multiblock copolymers were prepared to investigate the structure-property-performance relationships for their use in DMFC applications. Multiblock copolymers have distinctive large scale morphological order which is enhanced with block length. The mechanical properties of multiblock copolymers increases with block length due to the well-developed phase separation. The membrane properties of multiblock copolymers are strongly dependent upon the block length and chemistry of hydrophobic blocks, which in turn impact the DMFC performance as summarized below:

1. Proton conductivity, methanol permeability, and water uptake increased with block length. Slightly higher selectivity was obtained at the block length of 11K. DMFC performance improvement using multiblock copolymers was relatively small because of the similar selectivity. However, improved conductivity and mechanical properties of multiblock copolymers should be considered as potential benefits because these make it possible to fabricate more robust or conductive MEAs.
2. Multiblock copolymers containing nitrile groups in the hydrophobic block showed lower water uptake, which improves DMFC durability.
3. Water uptake of multiblock copolymers decreased with degree of fluorination in the hydrophobic block, which may be beneficial for DMFC durability. However, methanol permeability was substantially increased with degree of fluorination, which adversely impacted the DMFC performance. Superior DMFC performance of a less fluorinated multiblock copolymer to a highly fluorinated multiblock copolymer and Nafion was demonstrated.
4. Bisphenol type structure exerted a substantial influence on water uptake of multiblock copolymers. TM based multiblock copolymer showed the least water uptake and methanol permeability. High selectivity of the multiblock copolymer allowed this copolymer to demonstrate excellent DMFC performance.

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Notes
The authors declare no competing financial interest.

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