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Hydrophilic–hydrophobic multiblock copolymers based on poly(arylene ether sulfone) via low-temperature coupling reactions for proton exchange membrane fuel cells

Hae-Seung Lee [a], Abhishek Roy [a], Ozma Lane [a], Stuart Dunn [a,b], James E. McGrath [a,*]

[a] *Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States*
[b] *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, United States*

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Abstract

Two series of multiblock copolymers based on poly(arylene ether sulfone)s were developed and evaluated for use as proton exchange membranes (PEMs). The multiblock copolymers were synthesized by a coupling reaction between phenoxide terminated fully disulfonated poly(arylene ether sulfone) (BPSH100) and decafluorobiphenyl (DFBP) or hexafluorobenzene (HFB) end-capped unsulfonated poly(arylene ether sulfone) (BPS0) as hydrophilic and hydrophobic blocks, respectively. The highly reactive nature of DFBP and HFB allowed the coupling reactions to be accomplished under mild reaction conditions (e.g., <105 °C). The low coupling temperatures prevented possible ether–ether exchange reactions which can cause a loss of order due to randomization of the hydrophilic–hydrophobic sequences. The multiblock copolymers produced tough and ductile membranes and their fundamental properties as PEMs were explored. They showed enhanced conductivities under fully hydrated conditions when compared with a random BPSH copolymer with a similar IEC. These copolymers also showed anisotropic swelling behavior, whereas the random copolymers were isotropic. The synthesis and fundamental properties of the multiblock copolymers are reported here and the systematic fuel cell properties and more detailed morphology characterization will be provided elsewhere.

Keywords: Hydrophilic–hydrophobic multiblock copolymers; Sulfonated poly(arylene ether sulfone); Fluoroaromatic endlinking

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1. Introduction

Fossil fuel resources are limited, expensive and combustion engines can contribute to environmental degradation; the need to find alternative energy sources has thus become imperative [1]. Polymer electrolyte membrane fuel cells (PEMFC) are potentially one of the best candidates to replace conventional internal combustion engines in automobiles, stationary power and batteries in portable electronic devices because of their high energy efficiency and environmental friendliness [2].

Nafion® is a perfluorosulfonic acid (PFSA) ionomer manufactured by DuPont which has been fabricated into membranes by both extrusion of a precursor and dispersion casting. It has been the benchmark membrane as a result of its outstanding properties, such as high proton conductivity, stability in the fuel cell environment, mechanical toughness and moderate water uptake [3]. Furthermore, the nature of the poly(tetrafluoroethylene)-like backbone (~87 mol%) and the existence of semi-crystallinity in the main backbone provides excellent chemical and hydrolytic stabilities, as well as good mechanical properties [4]. However, Nafion-type membranes have several disadvantages at higher operation temperatures (e.g., >100 °C) which are desirable for several reasons, including faster electrode kinetics and higher tolerance to CO poisoning. Absorbed water also depresses the glass transition temperature (T_g) and α relaxation of the membranes, resulting in the deterioration of mechanical properties as well as fuel cell performance [5,6]. Although the poor mechanical properties at

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[*] Corresponding author. Tel.: +1 540 231 5976; fax: +1 540 231 8517.
E-mail address: jmcgrath@vt.edu (J.E. McGrath).

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high temperature may be improved by fabrication of composite membranes with Teflon fabric reinforcements [7], the high cost along with high fuel permeability have spurred the development of new PEM materials.

As an alternative to Nafion, sulfonated poly(arylene ether) copolymers have been proposed as one of the most attractive new PEM materials due to their excellent thermal and oxidative stability, good mechanical properties, good processability and exceptional hydrolytic stability [8,9], The direct copolymerization of partially disulfonated poly(arylene ether sulfone) random copolymers (BPSH) was largely developed in our research group [10], and we have intensively explored their performances and properties for PEM applications [11,12]. Although its excellent stability and proton conductivity under fully hydrated conditions makes it a promising and likely lower cost alternative to Nafion, the proton conductivities under low humidity were significantly lower [13].

More recently, we have begun to address this drawback with hydrophilic–hydrophobic multiblock copolymer systems that can have much higher water diffusion coefficients than either the random copolymers or the perfluorosulfonic acid (PFSA) ionomers, which is important for conductivity at lower humidities. Several series of multiblock copolymers were synthesized via coupling reactions of fully disulfonated poly(arylene ether sulfone) hydrophilic blocks (BPSH100) and various types of hydrophobic blocks [14–19]. The multiblock copolymer membranes exhibited unique phase separated morphologies and permitted significantly enhanced proton conductivities under partially hydrated conditions by forming well connected hydrophilic domains [19,20]. One of our most recent research activities was to prepare hydrophilic–hydrophobic multiblock copolymers whose chemical components are similar to that of BPSH random copolymer. We hypothesized that by adopting ordered hydrophilic–hydrophobic sequences in the multiblock copolymers, the proton conductivities can be significantly improved with the same chemical components of BPSH random copolymers.

Unfortunately, conventional approaches to prepare multiblock copolymers (e.g., coupling reactions between two different telechelic oligomers via nucleophilic aromatic substitution) are highly limited since their high reaction temperatures can randomize hydrophilic–hydrophobic sequences by well-known ether–ether exchanges which can take place under nucleophilic step copolymerization conditions. Of the different approaches to prevent the ether–ether exchange reactions, lowering the reaction temperature should be the simplest methodology. For this reason, utilizing perfluorinated small molecules such as decafluorobiphenyl (DFBP) and hexafluorobenzene (HFB) as the linkage groups between the hydrophilic and hydrophobic oligomers is appealing. Their highly reactive nature in nucleophilic aromatic substitution reactions can permit a significantly lower coupling reaction temperature which should minimize side-reactions, including the ether–ether exchange reaction.

In this paper we report the synthesis and characterization of segmented sulfonated multiblock copolymers based on poly(arylene ether sulfone) by utilizing DFBP and HFB as linkage groups. The multiblock copolymers were produced by coupling reactions between hydrophilic BPSH100 and DFBP or HFB end-capped hydrophobic BPS0 blocks, respectively. The highly reactive perfluorinated end groups on the hydrophobic blocks allowed the coupling reaction to proceed below 105 °C and prevented potential ether–ether exchange reactions. By the described synthetic routes, two series of multiblock copolymers with different linkage groups were synthesized and characterized. This paper also evaluates the effect of block length on proton conductivity, water uptake and other membrane properties.

2. Experimental

2.1. Materials

Monomer grade 4,4′-dichlorodiphenyl sulfone (DCDPS) and 4,4′-biphenol (BP) were provided by Solvay Advanced Polymers and Eastman Chemical Company, respectively, and dried *in vacuo* at 110 °C prior to use. The enabling comonomer, 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) was synthesized from DCDPS and purified according to a procedure reported elsewhere [21]. Decafluorobiphenyl (DFBP) and hexafluorobenzene (HFB) were used as received from Lancaster and Aldrich, respectively. *N*-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), cyclohexane, and toluene were purchased from Aldrich and distilled from calcium hydride before use. Potassium carbonate, chloroform, acetone, and 2-propanol (IPA) were purchased from Aldrich and used without further purification.

2.2. Synthesis of phenoxide terminated fully disulfonated hydrophilic oligomer (BPSH100)

A series of fully disulfonated poly(arylene ether sulfone) hydrophilic oligomers (BPSH100) was synthesized with different molecular weights. A sample synthesis of 5000 g/mol BPSH100 is as follows: 8.9720 g (48.2 mmol) of BP, 21.0280 g (42.8 mmol) of SDCDPS and 7.9911 g (57.8 mmol) of potassium carbonate were charged to a three-necked 250-mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet, and a mechanical stirrer. Then distilled DMAc (120 mL) and toluene (60 mL) were added to the flask and the reaction was heated at 145 °C with stirring. The solution was allowed to reflux at 145 °C while the toluene azeotropically removed the water in the system. After 4 h, the toluene was removed from the reaction by slowly increasing the temperature to 180 °C. The reaction was allowed to proceed for another 96 h. The resulting viscous solution was cooled to room temperature and diluted with DMAc to facilitate filtration. After filtration, the solution was coagulated in IPA. The oligomer was dried at 120 °C *in vacuo* for at least 24 h.

2.3. Synthesis of phenoxide terminated unsulfonated hydrophobic oligomers (BPS0)

A series of unsulfonated poly(arylene ether sulfone) hydrophobic oligomers (BPS0) was synthesized with different molecular weights. A sample synthesis of 5000 g/mol BPS0 oligomer is as follows: 13.0210 g (66.5 mmol) of BP, 12.0210 g (61.4 mmol) of DCDPS and 11.0245 g (79.8 mmol) of potassium carbonate were charged to a three-necked 250-mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet, and a mechanical stirrer. Distilled DMAc (120 mL) and toluene (60 mL) were added to the flask and the solution was heated at 145 °C with stirring. The solution was allowed to reflux at 145 °C while the toluene azeotropically removed the water in the system. After 4 h, the toluene was removed from the flask by slowly increasing the temperature to 180 °C. The reaction was allowed to proceed for another 48 h. The same isolation and purification process of BPSH100 oligomer was applied for BPS0 oligomers.

2.4. End-capping of phenoxide terminated hydrophobic oligomers with DFBP and HFB

Phenoxide terminated BPS0 oligomers were end-capped with DFBP or HFB via a nucleophilic aromatic substitution reaction. A typical end-capping reaction of 5000 g/mol BPS0 oligomer is as follows: 5.0000 g (1.0 mmol) of BPS0 oligomer, 0.5528 g (4.0 mmol) of potassium carbonate were charged to a three-necked 100-mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet, and a mechanical stirrer. Distilled DMAc (50 mL) and cyclohexane (15 mL) were added to the flask. The solution was allowed to reflux at 100 °C to azeotropically remove the water in the system. After 4 h, the cyclohexane was removed from the system. The reaction temperature was set to 105 °C (DFBP) or 80 °C (HFB). When HFB was used, the nitrogen purge was stopped at this point because of its lower boiling point. Then 2.0047 g (6.0 mmol) of DFBP or 1.1163 g (6.0 mmol) of HFB was added and the reaction was allowed to proceed for 12 h. The solution was then cooled to room temperature and filtered. The filtered solution was coagulated in methanol. The polymer was dried at 110 °C *in vacuo* for 24 h.

2.5. Synthesis of hydrophilic–hydrophobic multiblock copolymers

Two series of multiblock copolymers with different linkage groups were synthesized via a coupling reaction between phenoxide terminated BPSH100 oligomers and DFBP or HFB end-capped BPS0 oligomers. A typical coupling reaction was performed as follows: 5.0000 g (1.0 mmol) of BPSH100 ($\overline{M}_n = 5000$ g/mol), 0.5528 g (4.0 mmol) of potassium carbonate, 100 mL of DMAc, and 30 mL of cyclohexane were added to a three-necked 250-mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet, and a mechanical stirrer. The reaction mixture was heated at 100 °C for 4 h to dehydrate the system with refluxing cyclohexane. After removing the cyclohexane, 5.0000 g (1.0 mmol) of DFBP or HFB end-capped BPS0 ($\overline{M}_n = 5000$ g/mol) was added. The coupling reaction was conducted at 105 °C for 24 h. The resulting yellowish polymer solution was filtered and precipitated in IPA. The copolymer was purified in a Soxhlet extractor with methanol for 24 h and with chloroform for another 24 h. The copolymer was dried at 120 °C *in vacuo* for 24 h.

2.6. Characterization

^{1}H and ^{13}C NMR analyses were conducted on a Varian INOVA 400 MHz spectrometer with DMSO-d_6 to confirm the chemical structures of the oligomers and copolymers. ^{1}H NMR spectroscopy was also used to determine number-average molecular weights of the oligomers via end group analysis. Intrinsic viscosities were determined in NMP containing 0.05 M LiBr at 25 °C using an Ubbelohde viscometer. The thermooxidative stabilities of the acid form membranes were determined by using a TA Instrument TGA Q500. Prior to TGA characterization, the membranes were placed in the TGA furnace at 150 °C in a nitrogen atmosphere for 30 min to remove residual solvent and moisture. The samples were then evaluated over the range of 80–800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The ion exchange capacity (IEC) values of the acid form copolymers were determined by titration with 0.01 M NaOH solution.

2.7. Film casting and membrane acidification

The copolymers in salt form were dissolved in NMP (7% w/v) and filtered through 0.45 μm Teflon® syringe filters. The solutions were then cast onto clean glass substrates. The films were dried for 2 days with an infrared lamp at 45–55 °C for 48 h. The residual solvent was removed by drying in a vacuum oven at 110 °C for 24 h. The membranes in the salt form were converted to acid form by boiling in 0.5 M sulfuric acid for 2 h, followed by boiling in deionized water for 2 h.

2.8. Determination of proton conductivity and water uptake

Proton conductivities under fully hydrated conditions were evaluated in liquid water. The conductivity of the membrane was determined from the geometry of the cell and resistance of the film which was taken at the frequency that produced the minimum imaginary response. A Solartron (1252A + 1287) impedance/gain-phase analyzer over the frequency range of 10 Hz–1 MHz was used for the measurements. The membrane water uptake was determined by the weight difference between dry and wet membranes. The vacuum dried membranes were weighed (W_{dry}), and then immersed in deionized water at room temperature for 24 h. The wet membrane was blotted dry and immediately weighed again (W_{wet}). The water uptake of the membranes was calculated according to the following equation.

$$\text{Water uptake }(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

The hydration number (λ) which can be defined as the number of water molecules absorbed per sulfonic acid unit, was determined from the water uptake and the ion content of the dry membrane according to the following equation.

$$\lambda = \frac{(W_{\mathrm{wet}} - W_{\mathrm{dry}})/\mathrm{MW}_{\mathrm{H_2O}}}{\mathrm{IEC} \times W_{\mathrm{dry}}} \times 1000$$

where $\mathrm{MW}_{\mathrm{H_2O}}$ is the molecular weight of water (18.01 g/mol).

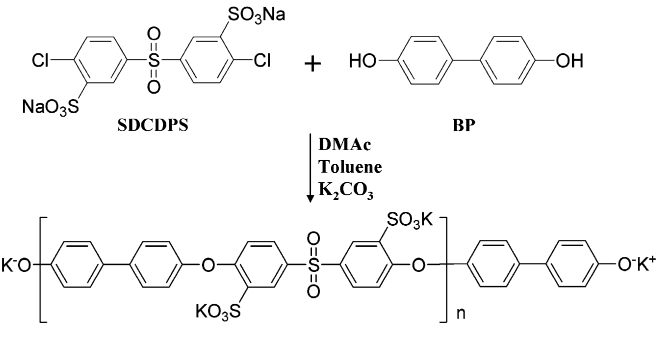
2.9. Determination of swelling ratio

The volume swelling ratios of all of the membranes were determined from the dimensional changes from wet to dry state both in-plane and through-plane. Initially, samples were equilibrated in water and wet dimensions were measured. The dried dimensions were obtained by drying the wet membrane at 80 °C in convection oven for 2 h.

3. Results and discussion

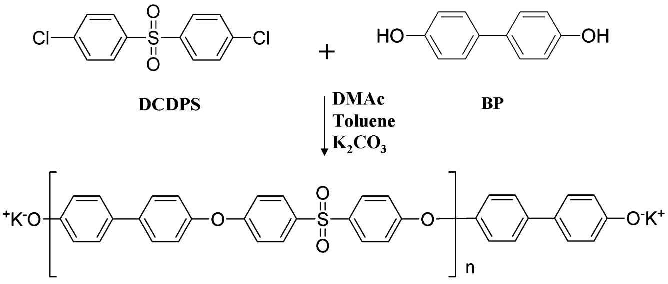
3.1. Synthesis of hydrophilic and hydrophobic oligomers

Fully disulfonated poly(arylene ether sulfone) hydrophilic oligomers (BPSH100) and unsulfonated poly(arylene ether sulfone) hydrophobic oligomers (BPS0) with phenoxide telechelic functionality were synthesized via step growth polymerization (Figs. 1 and 2). The control of the molecular weight and end group functionality was achieved by off-setting the molar ratios of monomers for the synthesis. In all cases, the molar feed ratios of BP over SDCDPS or DCDPS were greater than 1 to produce phenoxide telechelic functionality. The target number-average molecular weights of the oligomers ranged from 3 to 20 kg/mol. The number-average molecular weights of the oligomers were determined by ^{1}H NMR end group analysis. On the ^{1}H NMR spectra of both BPSH100 and BPS0, four small peaks at 6.80, 7.40, 7.05 and 6.80 ppm were assigned to the protons on the BP moieties which are located at the end of the oligomers. Meanwhile, the peaks at 7.1, 7.65 and 7.1, 7.9 were assigned to the protons on the BP moieties in the middle of the main chain of BPSH100 and BPS0, respectively (Figs. 3 and 4). By comparing the integrations of the end group BP and the main chain BP, the number-average molecular weights of oligomers were determined. The determined molecular weights and measured intrinsic viscosities of the oligomers are summarized in Table 1. When a log–log plot between the intrinsic viscosities and the number-average molecular weights was made, it showed a linear relationship, confirming successful control of molecular weight for both hydrophilic and hydrophobic block series (Fig. 5).



Fully Disulfonated Hydrophilic Oligomer (BPSH 100)

Fig. 1. Synthesis of a fully disulfonated hydrophilic oligomer with phenoxide telechelic functionality.



Unsulfonated Hydrophobic Oligomer (BPS0)

Fig. 2. Synthesis of an unsulfonated hydrophobic oligomer with phenoxide telechelic functionality.

3.2. End-capping of the hydrophobic oligomers

Since both the BPSH100 and BPS0 oligomers have the same telechelic functionality (e.g., phenoxide end group), a modification of one of the oligomers is necessary to facilitate a coupling reaction for producing multiblock copolymers. In the research, BPS0 hydrophobic blocks were end-capped with HFB or DFBP to produce fluorine-terminated end group functionality (Fig. 6). The amounts of the end-capping reagents used in the reaction were 200% molar excess. Due to the high reactivity of DFBP and HFB, the end-capping reactions were completed in 12 h under mild conditions. The end-capping reaction temperatures were 105 and 80 °C for DFBP and HFB, respectively. To prevent a loss of low-temperature boiling HFB (e.g., 80 °C) during the reaction, the temperature was chosen not to exceed its boiling temperature without a nitrogen purge. On the ^{1}H NMR spectra of the end-capped oligomers, the disappearance of the phenoxide bearing BP peaks at 6.80, 7.40, and 7.60 ppm confirmed that all of the phenoxide groups reacted with the end-capping reagents (Fig. 7). Although the disappearance of the end group peaks in the NMR spectra is an evidence of the end-capping reaction, there is still possibility of inter-oligomer coupling between the BPS0 oligomers since DFBP and HFB are multi-functional. If there was a significant degree of the inter-oligomer coupling, the intrinsic viscosities after end-capping should be much higher than the initial values. This possibility was excluded by comparing the intrinsic viscosities of BPS0 oligomers before and after the end-capping reaction. Table 2 shows the intrinsic viscosity change before and after the end-capping reaction. Slight increases in the intrinsic viscosity were observed for the end-capped BPS0. However, these increases are not due to the inter-oligomer coupling reaction but the chain length extension by the end-capping reagents. This conclusion was also confirmed by conducting the

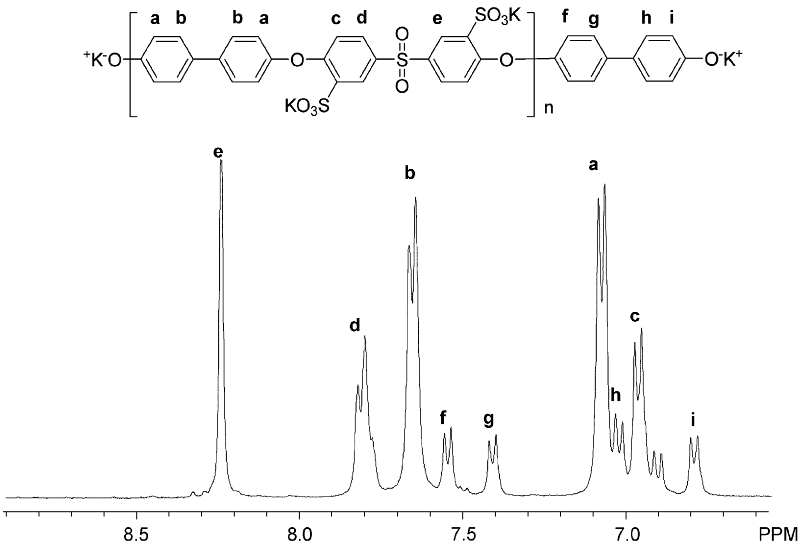


Fig. 3. ^{1}H NMR spectrum of phenoxide terminated BPSH100 hydrophilic oligomer.

end-capping reaction with various amounts of end-capping reagents (Fig. 8). Even with 400% molar excess of the end-capping agents, slight increases in intrinsic viscosity were observed, but no further increases were observed until 200% molar excess was used. Then, the increases were significantly enlarged at a molar excess of less than 100% due to the inter-oligomer coupling reactions. Therefore, a molar excess of 200% is sufficient for preventing inter-oligomer coupling.

3.3. Synthesis of BPSH–BPS multiblock copolymers

Two series of multiblock copolymers were synthesized by a coupling reaction between phenoxide terminated BPSH100 oligomers and DFBP or HFB end-capped BPS0 oligomers (Fig. 9). Hereafter, an acronym of the multiblock copolymer BPSHx–BPSy will be used where the BPSH and BPS imply the used BPSH100 and BPS0 while x and y denote the molecular weight of the reacted oligomers, respectively. The coupling reactions were conducted between the fluorine on the hydrophobic oligomers and the phenoxide end groups on the hydrophilic oligomers. The disappearance of the phenoxide end group peaks from the hydrophilic oligomer confirmed that the coupling reaction was successful (Fig. 10). As we hypothesized earlier, the low temperature of the coupling reaction minimized the ether–ether chain exchange reaction as confirmed by the ^{13}C NMR spectra. Fig. 11 is a comparison of the ^{13}C NMR of the BPSH35 random copolymer and BPSH10–BPS10 multiblock copolymer. As can be seen, each peak

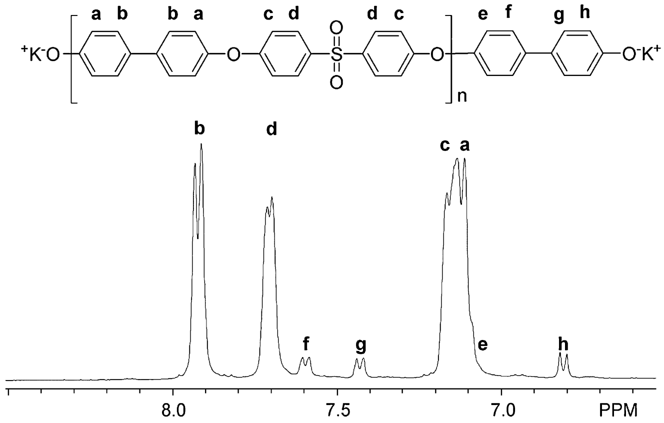


Fig. 4. ^{1}H NMR spectrum of phenoxide terminated BPS0 hydrophobic oligomer.

Table 1
Characterization of hydrophilic and hydrophobic telechelic oligomers

Target	Hydrophilic blocks		Hydrophobic blocks	
M_n (g mol^{-1})	M_n[a] (g mol^{-1})	IV[b] (dL g^{-1})	M_n[a] (g mol^{-1})	IV[b] (dL g^{-1})
3000	3190	0.12	3160	0.19
5000	4790	0.17	5020	0.24
10,000	9180	0.28	9130	0.38
15,000	15,290	0.37	13,900	0.49
20,000	20,000	0.46	–	–

[a] Determined by ^{1}H NMR.

[b] In NMP with 0.05 M LiBr at 25 °C.

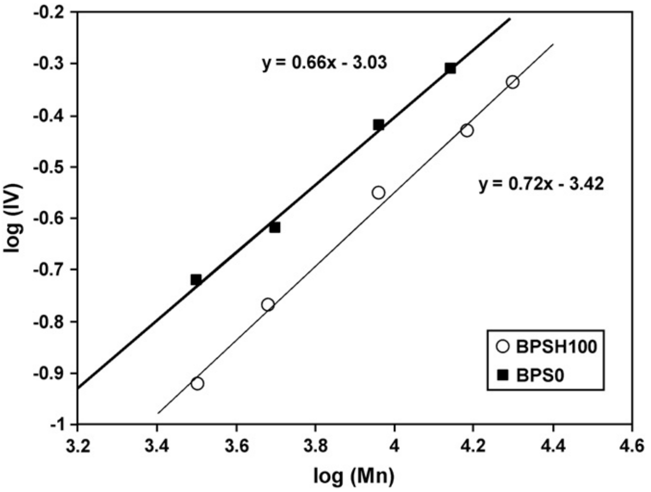


Fig. 5. Double logarithmic plot of [η] versus M_n of hydrophilic (BPSH100) and hydrophobic (BPS0) oligomers.

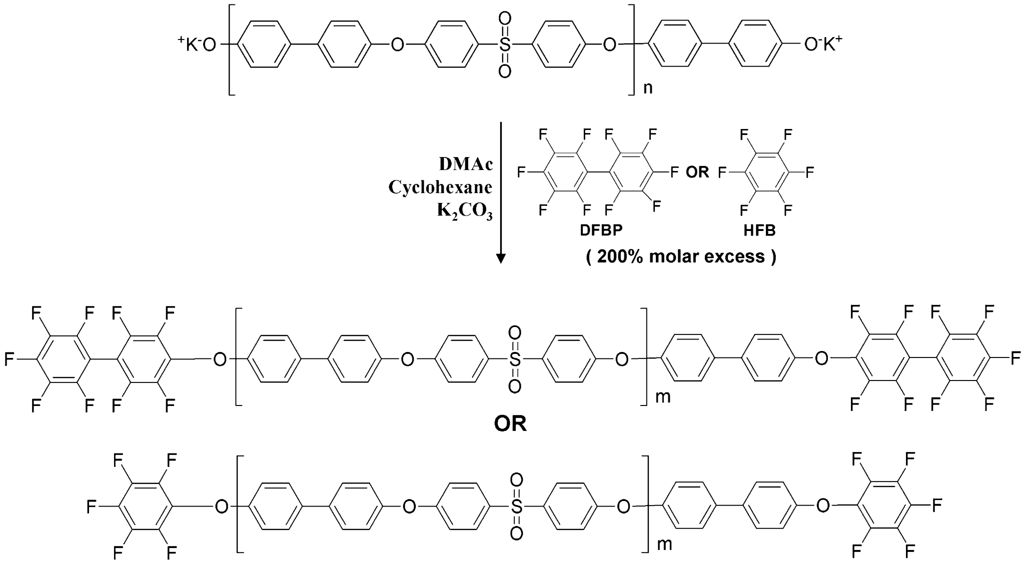


Fig. 6. End-capping of BPS0 hydrophobic oligomer with DFBP or HFB.

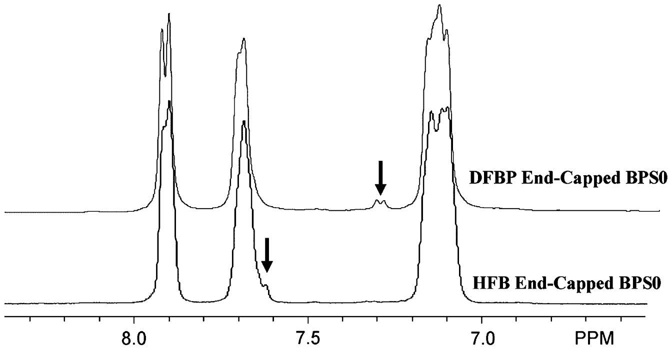


Fig. 7. ^{1}H NMR spectra of BPSH and HFB end-capped BPS0 hydrophobic oligomers. Black arrows indicate the peaks from the end-capped BP moieties.

from the random copolymer shows multiplet, suggesting a random sequence of sulfonated moieties on the main chain. On the other hand, the multiblock copolymer showed sharp narrow peaks, explaining the ordered sequences in the copolymer and confirming the prevention of randomization during the reaction.

3.4. Characterization of membrane properties of BPSH–BPS multiblock copolymers

One of the primary objectives in the preparation of this copolymer series was to keep the IEC fixed by varying hydrophilic and hydrophobic block lengths. To synthesize the fixed IEC copolymers, equal block lengths of hydrophilic–hydrophobic blocks were used with 1:1 stoichiometry (e.g., BPSH3–BPS3, BPSH5–BPS5 etc.). The other objective was to make higher IEC copolymers by using longer hydrophilic blocks than hydrophobic blocks with 1:1 stoichiometry (e.g., BPSH10–BPS5, BPSH15–BPS10 etc). The developed copolymers and their fundamental properties are summarized in Table 3. BPSH35 random copolymer was put in the table as a control. The determined IEC values by titration were close to the theoretical values. For the equal block length copolymers, the IEC values ranged from 1.28 to 1.40 meq/g and were slightly lower than BPSH35 random copolymer value of 1.50 meq/g. However, even with lower IECs, the proton

Table 2
Intrinsic viscosities of BPS0 hydrophilic blocks before and after end-capping

M_n[a] ($g\ mol^{-1}$)	Initial IV[b] ($dL\ g^{-1}$)	IV after end-capping[b] ($dL\ g^{-1}$)	
		DFBP	HFB
3160	0.19	0.23	0.22
5020	0.24	0.29	0.26
9130	0.38	0.44	0.39
13,900	0.49	0.56	0.50

[a] Determined by ^{1}H NMR.
[b] In NMP with 0.05 M LiBr at 25 °C.

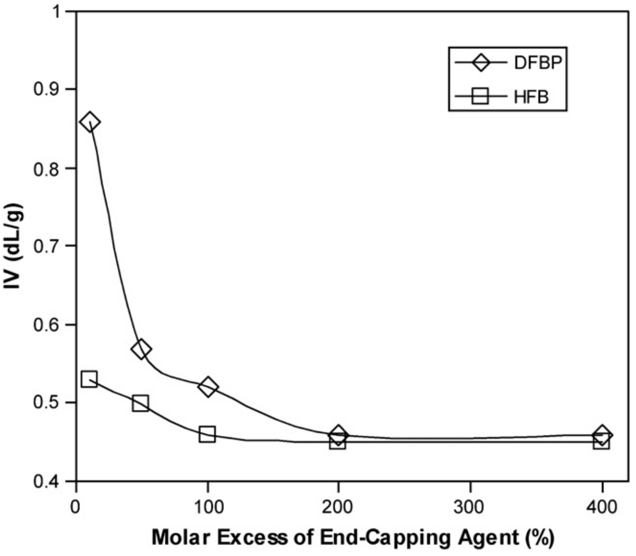


Fig. 8. Changes in intrinsic viscosity of the end-capped BPS0 hydrophobic oligomer as a function of the molar excess of end-capping reagent. The initial intrinsic viscosity of the oligomer was 0.41 dL/g.

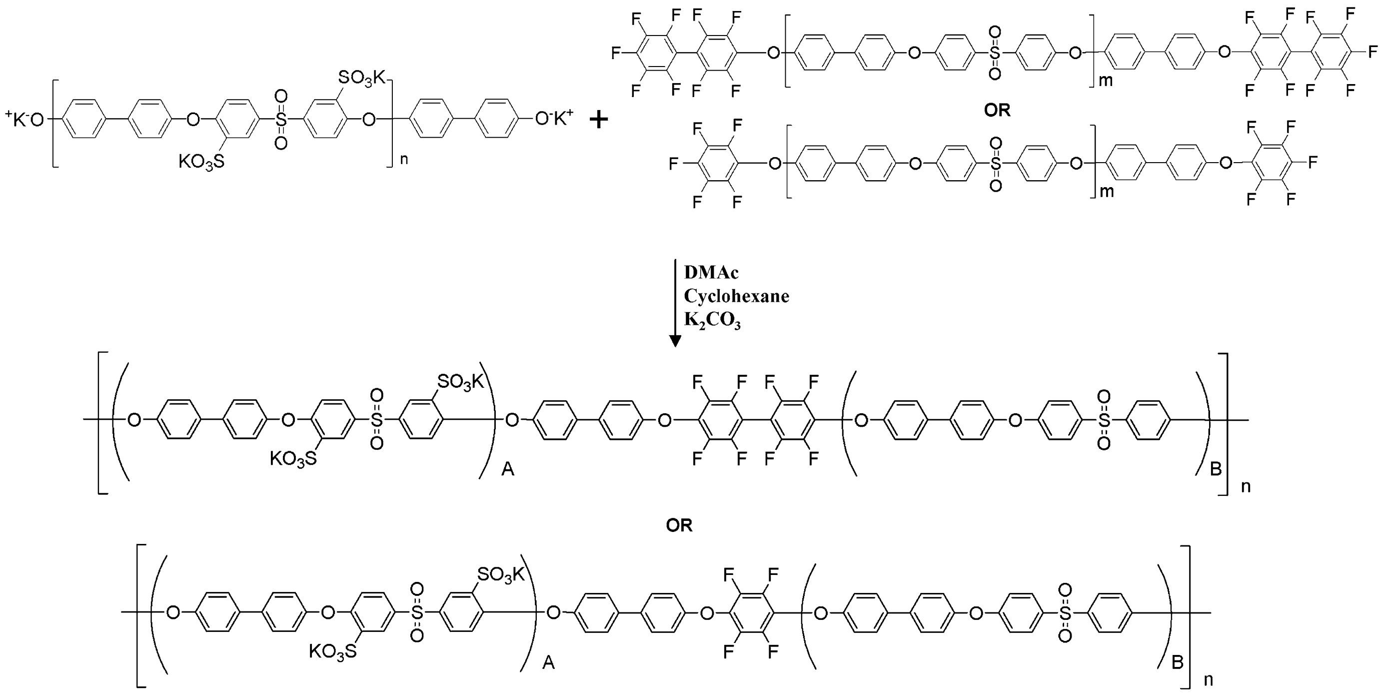


Fig. 9. Synthesis of segmented sulfonated multiblock copolymers (BPSH–BPS) with different linkage groups.

conductivity values of the BPSH–BPS copolymers ranged from 0.065 to 0.120 S/cm, which are comparable or even higher than that of BPSH35. It is interesting to observe the effect of block length on the proton conductivity and water uptake. Multiblock copolymers based on hydrophilic and hydrophobic blocks are known to have an ability to form phase separated morphologies [14,19,20,22]. It has also been reported that the degree of phase separation increases with increasing block lengths and that the developed phase separated morphologies enhances proton conductivity by forming a well connected hydrophilic domain. This trend was confirmed in BPSH–BPS with equal block length copolymers. For example, with DFBP linkage group, as the block length increases from 3 to 15 kg/mol, the proton conductivities also increase from 0.065 to 0.120 S/cm. The water uptake of the multiblock copolymers revealed the similar trend of the proton conductivities and increased with increasing block lengths with the equal block lengths. For higher IEC copolymers with unequal block lengths, their proton conductivities were exceptionally high and reached up to 0.160 S/cm with an IEC of 1.83 meq/g. Except for the higher water uptake and hydration number values which were observed in the HFB linked copolymers, no significant differences were noticed between DFBP and HFB linked systems. A systematic explanation of the relationship between IECs, water uptake and proton conductivity will be provided in a separate article.

Fig. 12 shows the swelling ratios of BPSH–BPS with the DFBP linkage group. The *x*, *y* represent the in-plane swelling and *z* represents the through-plane swelling. All multiblock copolymers showed anisotropic swelling behaviors in comparison to BPSH35 and Nafion (NRE211). Although all the multiblock copolymers showed similar in-plane swelling, the through-plane swelling increased along with block length. The increase in water uptake and through-plane swelling with increasing block length may suggest the formation of ordered hydrophilic domains within the copolymer. Also the

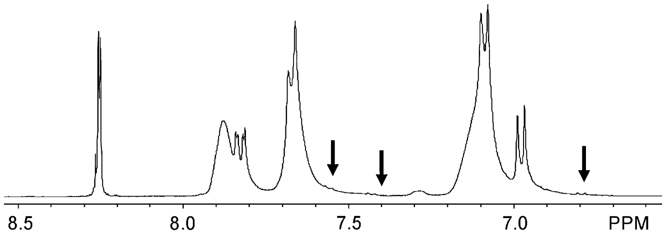


Fig. 10. ^{1}H NMR spectrum of BPSH5–BPS5 with DFBP linkage. Black arrows indicate the disappearance of the end groups on the hydrophilic blocks after the coupling reaction with fluorine-terminated hydrophobic blocks.

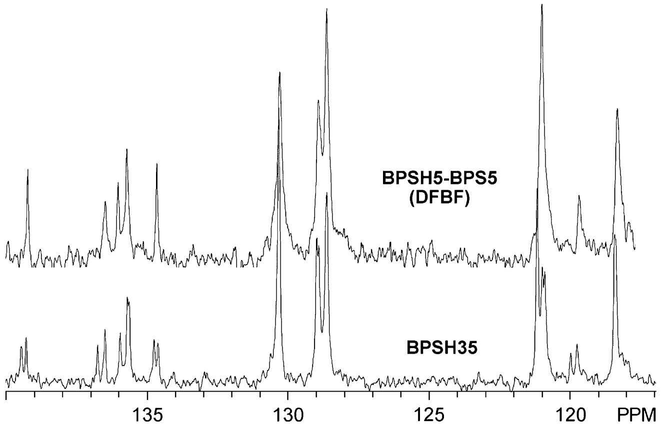


Fig. 11. ^{13}C NMR spectra of BPSH35 random copolymer and BPSH5–BPS5 multiblock copolymer with DFBP linkage.

Table 3
Properties of BPSH–BPS multiblock copolymers in the sulfonic acid form

Copolymers	Linkage	Calculated IEC (meq g^{-1})	Experimental IEC[a] (meq g^{-1})	Intrinsic viscosity[b] (dL g^{-1})	Water uptake (%)	Conductivity[c] (S cm^{-1})	Hydration number (λ)
Nafion 112	–	–	0.90	–	25	0.090	15.0
BPSH35	–	1.53	1.50	0.70	36	0.070	13.3
BPSH3–BPS3	DFBP	1.42	1.33	0.78	30	0.065	12.5
BPSH5–BPS5	DFBP	1.46	1.39	1.01	33	0.088	13.2
BPSH10–BPS10	DFBP	1.57	1.28	0.68	60	0.095	25.6
BPSH15–BPS15	DFBP	1.67	1.33	0.94	74	0.120	30.9
BPSH10–BPS5	DFBP	1.97	1.83	0.94	100	0.160	30.3
BPSH15–BPS10	DFBP	1.86	1.71	0.97	90	0.140	29.2
BPSH20–BPS15	DFBP	1.79	1.71	1.12	70	0.120	22.7
BPSH5–BPS5	HFB	1.55	1.30	0.62	52	0.090	22.2
BPSH10–BPS10	HFB	1.57	1.38	0.76	79	0.100	31.8
BPSH15–BPS15	HFB	1.66	1.40	0.94	79	0.090	31.3
BPSH10–BPS5	HFB	2.08	2.06	1.01	158	0.120	43.1
BPSH15–BPS10	HFB	1.98	1.83	0.85	139	0.120	42.2
BPSH20–BPS15	HFB	1.88	1.91	0.85	107	0.140	31.1

[a] Determined by titration with NaOH.
[b] In NMP with 0.05 M LiBr at 25 °C.
[c] Measured in deionized water at 30 °C.

in-plane swelling measurements for the higher block length materials were lower than that of NRE211. This is considered as an important property in addressing the durability issue under low relative humidity cycling operation.

Thermal and oxidative stabilities of the copolymers in their acid form were investigated by TGA (Fig. 13). All films displayed a two-step degradation profile. The initial weight loss was observed at 270 °C and was assigned to the decomposition of the sulfonic acid groups on the BPSH100 block. The second decomposition, which started at 500 °C, was attributed to main-chain polymer degradation. For BPSH3–BPS3 and BPSH5–BPS5 which have relatively short block lengths, their initial 5% weight loss temperatures ranged from 300 to 313 °C and were similar to the 5% weight loss temperature 313 °C of the BPSH35 random copolymer. However, BPSH10–BPS10 and BPSH15–BPS15 showed much higher temperatures that ranged from 357 to 367 °C. This might be another block length effect on the thermal stability of the copolymers.

In this study, the various properties of BPSH–BPS copolymers using both DFBP and HFB linkage groups have been characterized. Assuming that two copolymers, which feature the same hydrophilic and hydrophobic blocks but with different linkage groups, do not have significantly different properties, HFB is the preferred linkage group due to its commercial availability and cost. According to the Chemical Abstracts Service (CAS) database, only HFB is available in a kilogram-scale quantity at a tenth of the cost of DFBP. When we consider that the molecular weight of DFBP is almost twice that of HFB, the molar cost of HFB is far more affordable.

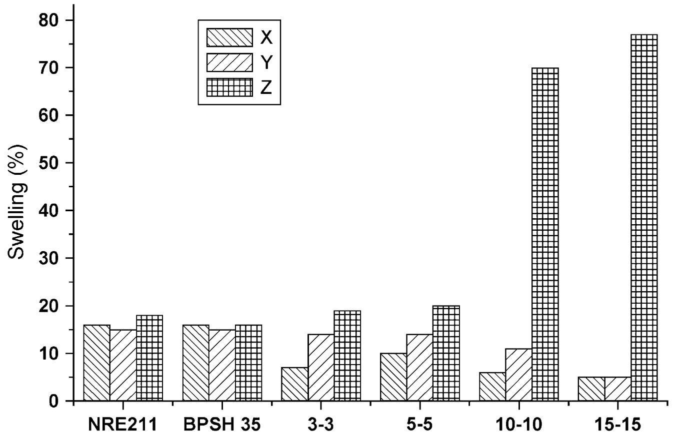


Fig. 12. Comparison of swelling ratios of random copolymer and BPSH–BPS multiblock copolymers with DFBP linkage.

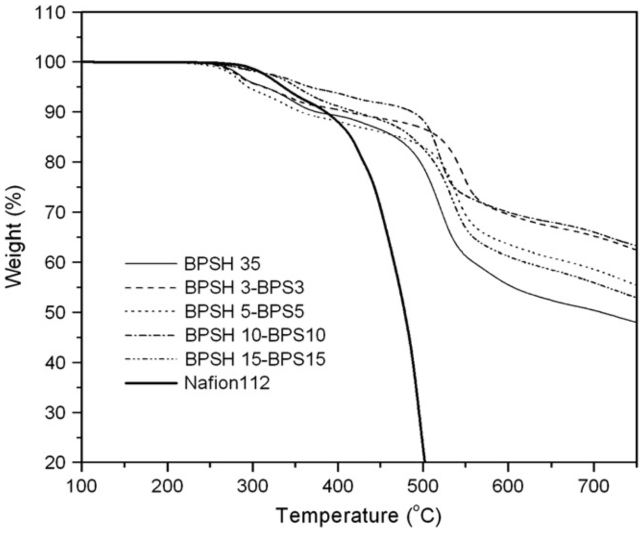


Fig. 13. TGA thermograms of BPSH35, Nafion 112 and BPSH–BPS multiblock copolymers with different block lengths.

4. Conclusion

Hydrophilic–hydrophobic multiblock copolymers based on poly(arylene ether sulfone) were developed and characterized. The multiblock copolymers were synthesized utilizing highly reactive DFBP and HFB as the linkage groups to lower the coupling reaction temperatures. The mild reaction conditions prevented possible ether–ether exchange reactions which can randomize the hydrophilic–hydrophobic sequences. The multiblock copolymers showed ordered sequences which were confirmed by ^{13}C NMR. Transparent and ductile membranes were prepared from NMP by solvent casting. Their proton conductivities and water uptake values were influenced by block lengths at similar IEC values. As the block length increased, the proton conductivity and water uptake increased. The proton conductivities of the multiblock copolymers were comparable or even higher than that of BPSH random copolymers with similar IECs which supports the existence of well connected hydrophilic domains in the system. Further characterization will be reported elsewhere.

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References

[1] de Bruijn F. Green Chemistry 2005;7:132.

[2] Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Chemical Reviews (Washington, DC, United States) 2004;104:4587.

[3] Banerjee S, Curtin DE. Journal of Fluorine Chemistry 2004;125:1211.

[4] Mauritz KA, Moore RB. Chemical Reviews (Washington, DC, United States) 2004;104:4535.

[5] Kim YS, Dong L, Hickner MA, Glass TE, Webb V, McGrath JE. Macromolecules 2003;36:6281.

[6] Savadogo O. Journal of Power Sources 2004;127:135.

[7] Bahar B, Cavalca C, Cleghorn S, Kolde J, Lane D, Murthy M, et al. Journal of New Materials for Electrochemical Systems 1999;2:179.

[8] Wang S, McGrath JE. Synthetic methods in step-growth polymers; 2003. p. 327.

[9] Rose JB. Polymer 1974;15:456.

[10] Wang F, Hickner M, Ji Q, Harrison W, Mecham J, Zawodzinski TA, et al. Macromolecular Symposia 2001;175:387.

[11] Kim YS, Hickner MA, Dong L, Pivovar BS, McGrath JE. Journal of Membrane Science 2004;243:317.

[12] Harrison WL, Hickner MA, Kim YS, McGrath JE. Fuel Cells (Weinheim, Germany) 2005;5:201.

[13] Kim YS, Wang F, Hickner M, McCartney S, Hong YT, Harrison W, et al. Journal of Polymer Science, Part B: Polymer Physics 2003;41:2816.

[14] Wang H, Badami AS, Roy A, McGrath JE. Journal of Polymer Science, Part A: Polymer Chemistry 2006;45:284.

[15] Ghassemi H, Ndip G, McGrath JE. Polymer 2004;45:5855.

[16] Yu X, Roy A, Dunn S, Yang J, McGrath JE. Macromolecular Symposia 2006;245/246:439.

[17] Lee H-S, Roy A, Badami AS, McGrath JE. Macromolecular Research 2007;15:160.

[18] Li Y, Roy A, Badami AS, Hill M, Yang J, Dunn S, et al. Journal of Power Sources 2007;172:30.

[19] Lee H-S, Badami AS, Roy A, McGrath JE. Journal of Polymer Science, Part A: Polymer Chemistry 2007;45:4879.

[20] Roy A, Hickner MA, Yu X, Li Y, Glass TE, McGrath JE. Journal of Polymer Science, Part B: Polymer Physics 2006;44:2226.

[21] Sankir M, Bhanu VA, Harrison WL, Ghassemi H, Wiles KB, Glass TE, et al. Journal of Applied Polymer Science 2006;100:4595.

[22] Kim YS, Einsla ML, Hawley M, Pivovar BS, Lee H-S, Roy A, et al. ECS Transactions 2007;11:49.