Development of multiblock copolymers with novel hydroquinone-based hydrophilic blocks for proton exchange membrane (PEM) applications

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ABSTRACT

Hydrophilic–hydrophobic sequenced multiblock copolymers were synthesized and evaluated for use as proton exchange membranes (PEMs). The multiblock copolymers were prepared by a coupling reaction between fully disulfonated hydroquinone-based hydrophilic oligomers (HQS100) and unsulfonated poly(arylene ether sulfone) hydrophobic oligomers (BPS0). The hydroquinone-based hydrophilic oligomers possess several advantages over previously utilized biphenol-based hydrophilic oligomers (BPS100), including higher hydrophilicity, enhanced nano-phase separation with hydrophobic segments, and lower cost. To maintain the hydrophilic–hydrophobic sequences in the system, the coupling reactions were conducted at low temperature (e.g., 105 °C) to avoid ether–ether exchange reactions. The coupling reaction was solvent sensitive due to a low reactivity of the hydroquinone-phenoxide end-group on the HQS100. All copolymers produced tough ductile films when cast from an NMP or DMF solution. Fundamental membrane parameters including water uptake, proton conductivity, and swelling ratio were investigated along with morphology characterizations by atomic force microscopy (AFM).

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1. Introduction

Over the last decade, a substantial body of research has been devoted to developing novel proton exchange membranes (PEMs) which can replace the state-of-the-art Nafion®. Among a variety of candidates, wholly aromatic high temperature polymers have been considered to be the most promising materials [1–3]. The major advantages for utilizing high temperature polymers for fuel cell applications include their excellent thermal and oxidative stability, as well as the fact that they are economical and easy to produce. The most extensively studied materials are the so-called BPSH-type materials, which are statistical random copolymers based on disulfonated poly(arylene ether sulfone)s [4–6]. BPSH-type copolymer systems utilize 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) as the key monomer, which can facilitate precise control over the degree of sulfonation, and excellent stability of the sulfonic acid moieties [2,7]. Although PEMs based on BPSH-type materials display improved properties over Nafion® under fully hydrated conditions with respect to conductivity, durability, and fuel cross-over, their proton conductivities under partially hydrated conditions have remained somewhat disappointing. This could be due to the fact that the proton conduction channels in sulfonated hydrocarbon-based materials are narrower

than those of Nafion-type materials, which accounts for the significant reduction in conductivity under low humidity conditions [8,9]. A number of strategies have been used to address this problem, including (1) the partial fluorination of the aromatic polymer backbone to form a sharp phase separation [10,11], (2) the incorporation of bulky pendent groups to increase free-volume [12,13], (3) the addition of hydrophilic nano-particles to help retain water [14], and (4) the addition of heteropolyacid (HPA) [15]. Although each of these approaches was somewhat beneficial in increasing proton conductivity under low RH conditions, none of these methods could overcome important fundamental limitations.

Recently, PEMs based on hydrophilic–hydrophobic sequenced multiblock copolymers have been considered as strong candidates for overcoming limited proton conduction under partially hydrated conditions [16–21]. These multiblock copolymers utilize fully disulfonated biphenol-based poly(arylene ether sulfone) as the hydrophilic block (BPSH100), with various engineering materials used as the hydrophobic block. These multiblock copolymer-based PEMs exhibit nano-phase separated morphologies and well-connected ionic hydrophilic phases. As such, they can facilitate high proton conductivity even under low relative humidity conditions, while the well-connected hydrophobic phase can provide dimensional stability [16,22,23]. A number of extensive structure-property studies revealed that property enhancements can be strongly influenced by the length of the hydrophilic and hydrophobic blocks. Generally, proton conductivity and water uptake increase with increasing hydrophilic and hydrophobic block

length by forming long-range co-continuous lamellae morphologies [16,22,24]. Even though the multiblock copolymers based on BPSH100 hydrophilic block were comparable or superior to Nafion with respect to proton conductivity under low humidity conditions, we were unable to achieve even higher conductivity by solely increasing IEC values [22]. Increasing the volume fraction of hydrophilic segments in a system in order to improve IEC values produces a decrease in the hydrophobic segment volume fraction, resulting in poor mechanical properties and excess swelling behavior. In other words, a balancing act is hard to achieve for maintaining both high IEC and advantageous mechanical properties.

A possible solution to this dilemma is utilizing a more hydrophilic (e.g., higher IEC) block for the multiblock copolymer system. When a higher IEC hydrophilic oligomer is used to obtain an IEC multiblock copolymer, the amount of the higher IEC hydrophilic block should be less than that of lower IEC hydrophilic block to obtain the target IEC. Using the same logic, if the feed ratio of the hydrophilic and hydrophobic blocks is fixed, a higher IEC hydrophilic block system will incorporate more sulfonic acid moieties in the multiblock copolymers. As a result, one can increase the IEC values of the multiblock copolymers without scarifying the volume fraction of hydrophobic segments, which plays an important role in producing desirable mechanical properties. In addition, higher IEC hydrophilic blocks can lead a sharper phase separation in the copolymer membrane due to the increased hydrophilic–hydrophobic contrast.

This paper, therefore, describes the synthesis and characterization of a novel multiblock copolymer system with hydroquinone-based hydrophilic oligomers. The fully disulfonated hydroquinone-based poly(arylene ether sulfone) hydrophilic oligomer (HQSH100) has an IEC of 3.89 meq g^{-1}, which is approximately 20% higher than that of BPSH100. A series of multiblock copolymers with HQSH100 hydrophilic blocks was synthesized, and their fundamental membrane properties and morphology will be described.

2. Experimental

2.1. Materials

Monomer grade 4,4′-dichlorodiphenylsulfone (DCDPS), and 4,4′-biphenol (BP) were provided by Solvay Advanced Polymers and Eastman Chemical, respectively, and were dried *in vacuo* at 110 °C prior to use. Hydroquinone (HQ) was purchased from Aldrich and was purified by sublimation under reduced pressure. The sulfonated comonomer 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) was synthesized and purified according to previously reported procedures [7]. The purity of SDCDPS was determined by UV–vis spectroscopy [25]. Hexafluorobenzene (HFB) and potassium carbonate were purchased from Aldrich and used without further purification. N-methyl-2-pyrrolidone (MNP), dimethyl sulfoxide (DMSO), N,N-dimetheylacetamide (DMAc), and toluene were received from Aldrich and were distilled at reduced pressure before use.

2.2. Synthesis of hydroquione-based hydrophilic oligomers (HQS100) with phenoxide telechelic functionality

HQ-based fully disulfonated hydrophilic blocks of different molecular weights were synthesized via step growth polymerization. A sample oligomer synthesis with molecular weight of 3000 g mol^{-1} is as follows: 66.6 mmol of HQ (7.3351 g), 56.3 mmol of SDCDPS (27.6649 g) and 79.9 mmol of potassium carbonate (20 mol% excess) were dissolved in 140 mL of distilled NMP and 70 mL of toluene in a 3-necked flask equipped with a condenser,

a Dean Stark trap, nitrogen inlet and mechanical stirrer. The reaction mixture was heated at 150 °C for 4 h with refluxing toluene to dehydrate the system. The reaction temperature was then slowly increased to 185 °C to remove the toluene and allowed to react for 48 h. The reaction solution was cooled to room temperature and filtered to remove salts. For high molecular weight oligomers, dilution with NMP was necessary to ease the filtration. The oligomer was coagulated in acetone followed by filtration and drying *in vacuo* at 110 °C for 24 h.

2.3. Synthesis of phenoxide-terminated poly(arylene ether sulfone) hydrophobic oligomers (BPS0) and their end-capping with hexafluorobenzene (HFB)

BP based unsulfonated hydrophobic blocks of different molecular weights were synthesized via step growth polymerization. A sample oligomer synthesis with molecular weight of 5000 g mol^{-1} is as follows: 66.5 mmol of BP (13.0210 g), 61.4 mmol of DCDPS (12.0210 g) and 79.8 mmol of potassium carbonate (20 mol% excess) were dissolved in 120 mL of distilled DMAc and 60 mL of toluene in a 3-necked flask equipped with a condenser, a Dean Stark trap, nitrogen inlet and mechanical stirrer. The reaction mixture was heated at 150 °C for 4 h with refluxing toluene to dehydrate the system. The reaction temperature was slowly increased to 175 °C to remove the toluene and allowed to react for 48 h. The dried oligomer was obtained according to procedures used for HQS100 synthesis.

The isolated BPS0 oligomers were then end-capped with HFB via a nucleophilic aromatic substitution reaction. A sample end-capping reaction of the 5000 g mol^{-1} oligomer is as follows: 50,000 g (1.0 mmol) of BPS0 oligomer and 0.5528 g (4.0 mmol) of potassium carbonate were charged to a 3-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 by distillation. The reaction temperature was decreased to 80 °C and the nitrogen purge was stopped to avoid the possible loss of low-temp boiling HFB (b.p. = 80 °C). Afterwards, 1.1163 g (6.0 mmol) of HFB was added and the reaction was allowed to proceed for 12 h.

2.4. Synthesis of hydrophilic–hydrophobic multiblock copolymers (HQSH-BPS)

Multiblock copolymers with various lengths of hydrophilic and hydrophobic blocks were synthesized. A sample coupling reaction is as follows: into a 100 mL 3-necked flask equipped with a mechanical stirrer, nitrogen inlet and a Dean Stark trap, 3.0000 g of hydrophilic oligomer (M_n = 3000 g mol^{-1} 1.0 mmol), 0.5528 g of K$_2$CO$_3$ (4.0 mmol), 20 mL of cyclohexane and 40 mL of DMSO were added and dehydrated at 100 °C for 4 h. The cyclohexane was then removed by distillation and 50,000 g of hydrophobic oligomer (M_n = 5000 g mol^{-1} 0.1 mmol) was added. The coupling reaction was conducted at 105 °C for 24 h. The obtained brown polymer solution was coagulated in isopropyl alcohol. The resulting polymer was filtered and dried in a vacuum oven at temperatures up to 110 °C.

2.5. Characterization

The chemical structures of the oligomers and copolymers were confirmed by ^{1}H NMR analyses on a Varian INOVA 400 MHz spectrometer with DMSO-d_6. In addition, ^{1}H NMR spectroscopy was utilized for end-group analyses of the oligomers to determine their $\overline{M}_n$. Intrinsic viscosities were determined in NMP containing 0.05 M

LiBr at 25 °C using an Ubbelohde viscometer. Ion exchange capacity (IEC) values were determined by titration with a 0.01 M NaOH solution.

2.6. Film casting and membrane acidification

The starting membranes were cast in their salt form by solution casting. The salt form copolymers was dissolved in NMP or DMF (7%, w/v) and filtered with syringe filters (0.45 μm Teflon®). The filtered solutions were then cast onto clean glass substrates. The films were dried under an IR ramp at 60 °C for 1 day and followed by drying *in vacuo* at 110 °C for 24 h. The acid-form membranes were obtained by boiling in a 0.5 M sulfuric acid aqueous solution for 2 h, followed by boiling in deionized water for 2 h. The membranes were kept in deionized water at room temperature for 24 h for further characterization.

2.7. Determination of proton conductivity and water uptake

Proton conductivity measurements were performed on membranes after being soaked in deionized water for 24 h at 30 °C. An impedance spectrum was recorded from 1 MHz to 10 Hz using a Solartron (1252A + 1287) impedance/gain-phase analyzer. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the membrane was taken at the frequency which produced the minimum imaginary response. All impedance measurements were performed under fully hydrated conditions. The proton conductivity was taken as the reciprocal of the resistance and reported in units of Siemens per centimeter (S cm^{-1}). 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.

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

2.8. Atomic force microscopy (AFM)

Tapping mode AFM was performed using a Veeco Multimode Atomic Force Microscope. Samples were equilibrated at 30% relative humidity (RH) at room temperature for at least 24 h and sealed before imaging.

3. Results and discussion

3.1. Synthesis of controlled molecular weight hydrophilic blocks (HQS100)

Different number–average molecular weight hydrophilic oligomers were synthesized via the step growth polymerization of SDCDPS and HQ (Fig. 1). We were able to precisely control molecular weight and end-group functionality via a stoichiometric imbalance of the monomers. All oligomers were designed to be terminated with phenoxide end-groups by using an excess amount of HQ. The target molecular weights for hydrophilic blocks ranged from 3000 to 15,000 g mol^{-1}. Earlier, the synthesis was attempted in DMAc at 175 °C for 96 h. However, the poor solubility of HQS100 in DMAc resulted in premature precipitation within just a few hours. As a result, it was impossible to control both molecular weight and end-group functionality. It has been suggested that the insolubility of the oligomers may stem from the formation of
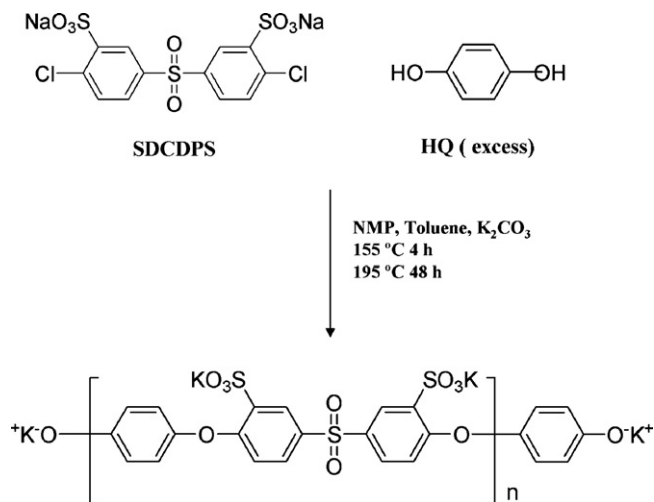

Fig. 1. Synthesis of a phenoxide-terminated fully disulfonated poly(arylene ether sulfone) hydrophilic oligomer based on hydroquinone (HQS100).

crystallites from the HQ moieties on the main chain backbone [26]. To maintain homogeneous conditions during synthesis, DMSO was also used as the reaction solvent. Although it provided both good solubility and rapid reaction kinetics (i.e., the reaction can be completed in 48 h at 180 °C), the resulting product was not pure enough to be used for the coupling reaction due to unidentified side reactions. On the one hand, although undesirable side reactions could be avoided when the reactions were conducted at fairy low temperatures (e.g., 135 °C), the reaction time was significantly prolonged (e.g., ~200 h). On the other hand, when we conducted the reaction in NMP at 195 °C for 48 h, we were able to avoid any side reactions. Thus, we used the latter reaction conditions for preparing the HQS100 oligomers used in this research [27]. End-group analyses of selected peaks via ^{1}H NMR spectra were used to determine the number–average molecular weight of the oligomers (Fig. 2). On the NMR spectrum of the HQS100, two small peaks, **e** and **f**, at 6.75 and 6.83 ppm, respectively, were assigned to the protons on the HQ moieties, located at the end of the chain. Calculating the integration ratios between one of these peaks and one of the other main peaks (**a**–**d**) was used to determine the number–average molecular weight of the oligomers. Table 1 lists the characterization data for the HQS100 hydrophilic telechelic oligomers used in this study.
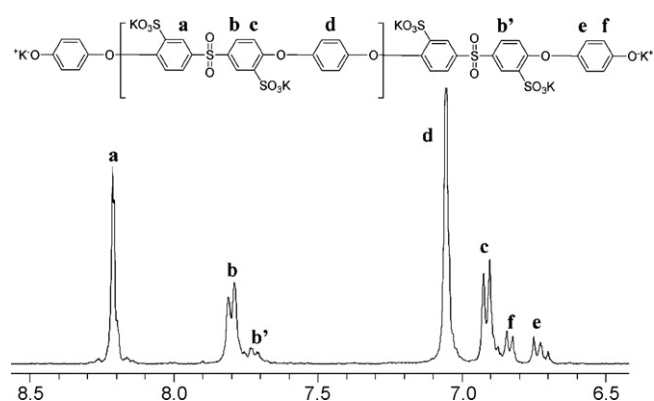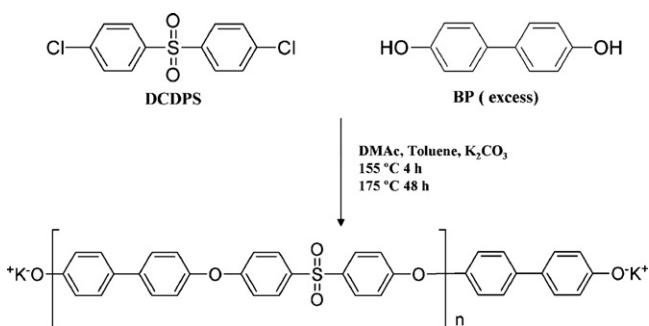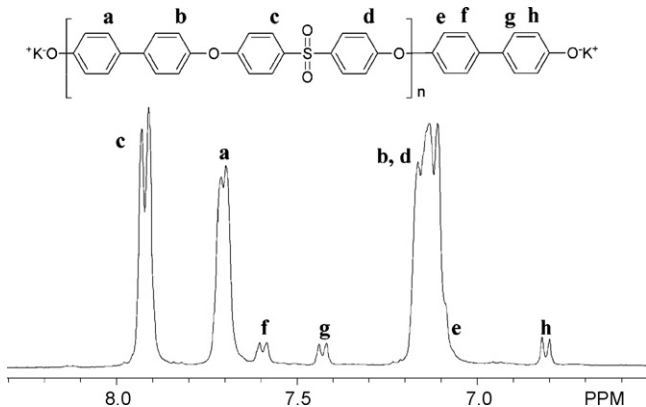

Fig. 2. ^{1}H NMR spectrum of HQS100 with a molecular weight of 3000 g mol^{-1}.

Table 1
Characterization of HQS100 hydrophilic telechelic oligomers.

Target M_n (g mol^{-1})	M_n (g mol^{-1})[a]	IV (dL g^{-1})[b]
3,000	3,200	0.12
5,000	4,700	0.14
6,000	5,500	0.16
9,000	9,100	0.22
10,000	10,700	0.23
12,000	12,900	0.24
15,000	14,800	0.29

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

Fig. 3. Synthesis of a phenoxide-terminated undisulfonated poly(arylene ether sulfone) hydrophobic oligomer based on biphenol (BPS0).

**Fig. 4.** ^{1}H NMR spectrum of BPS0 with a molecular weight of 3000 g mol^{-1}.

3.2. Synthesis of controlled molecular weight hydrophobic blocks (BPS0) and their end-capping with hexafluorobenzene (HFB)

Unsulfonated poly(arylene ether sulfone) oligomers based on biphenol (BPS0) with varying molecular weights were synthesized as hydrophobic blocks (Fig. 3). Control of molecular weight and end-group functionality was achieved by upsetting the feed ratios of the monomers. ^{1}H NMR spectroscopy of the BPS0 hydrophobic oligomers showed that the oligomers possessed phenoxide end-group functionality as intended, and we were able to determine number–average molecular weight via end-group analyses (Fig. 4). Molecular weight and intrinsic viscosity data for the BPS0 are summarized in Table 2. When log–log plots were made between number average molecular weight and intrinsic viscosity, linear relationships for both the hydrophilic and hydrophobic oligomers were identified, thereby confirming successful molecular weight control (Fig. 5).

The synthesized hydrophilic and hydrophobic oligomers possessed the same phenoxide end-groups, making them unsuitable for the coupling reaction needed to produce multiblock copolymers since they are not reactive with each other (i.e., both end-groups

Table 2
Characterization of BPS0 hydrophobic telechelic oligomers.

Target M_n (g mol^{-1})	M_n (g mol^{-1})[a]	IV (dL g^{-1})[b]
3,000	3,200	0.19
5,000	5,200	0.26
10,000	10,400	0.35
15,000	14,700	0.46
20,000	20,800	0.51
25,000	24,400	0.54

[a] Determined by ^{1}H NMR.
[b] In NMP with 0.05 M LiBr at 25 °C.
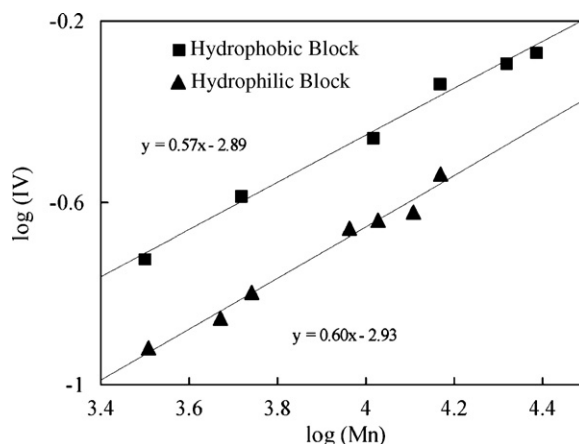
Fig. 5. Double logarithmic plot of [η] versus M_n of hydrophilic (HQS100) and hydrophobic (BPS0) oligomers.

are nucleophiles). Thus, it was necessary to modify the end-group functionality of either hydrophilic or hydrophobic block to facilitate the coupling reaction. For this research, we chose to modify the BPS0 hydrophilic blocks, which were end-capped with hexafluorobenzene (HFB) (Fig. 6). In doing so, we could convert the nucleophilic BPS0 oligomers into elecrophilic, fluorine-terminated BPS0 oligomers, which would facilitate a coupling reaction with the HQS100 oligomers. As shown in Fig. 7, the end-group peaks for the terminal BP moieties completely disappeared and a new peak appeared at 7.65 ppm. This peak corresponds to the same protons on the terminal BP moieties but was attached to HFB. Although NMR spectra comparisons before and after end-capping reaction confirmed that all the phenoxide end-groups had reacted with HFB, the formation of high molecular weight BPS0 oligomers via an inter-oligomer coupling reaction was still possible due to the multifunctionality of the HFB. To prevent this from occurring, a large excess of HFB was used. Specifically, the molar ratio between the BPS0 and HFB was 1:6. In addition, intrinsic viscosity studies of the BPS0 oligomers before and after end-capping showed that there was little, if any, inter-oligomer coupling, as evidenced by the less than 0.02 dL g^{-1} increase with the end-capped oligomers. This implies that the end-capping reaction was successful without any significant inter-oligomer coupling, and that high molecular weight BPS0 oligomers had formed.

3.3. Synthesis of multiblock copolymers by a coupling reaction of hydrophilic and hydrophobic oligomers

Multiblock copolymers of varying hydrophilic and hydrophobic block lengths were synthesized via a coupling reaction (Fig. 8). This reaction is a simple nucleophilic aromatic substitution reaction between the phenoxide and the fluorine end-groups on the HQS100 and the BPS0 oligomers, respectively. Although expected to be fairly straightforward, this coupling reaction turned out to be solvent sensitive. Specifically, when the coupling reactions were
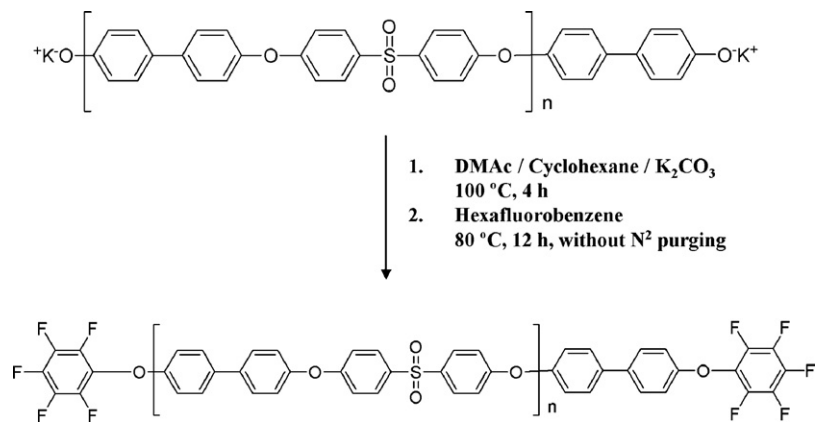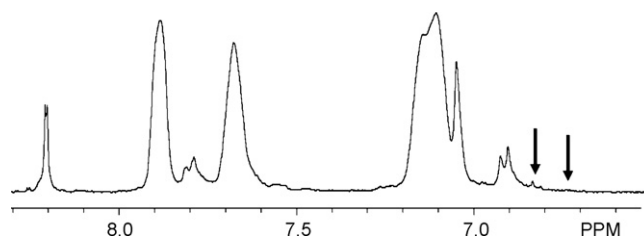
Fig. 6. End-Capping of the phenoxide-terminated hydrophobic oligomer (BPS0) with HFB. This procedure transforms the nucleophilic telechelic oligomer into an electrophilic telechelic oligomer.
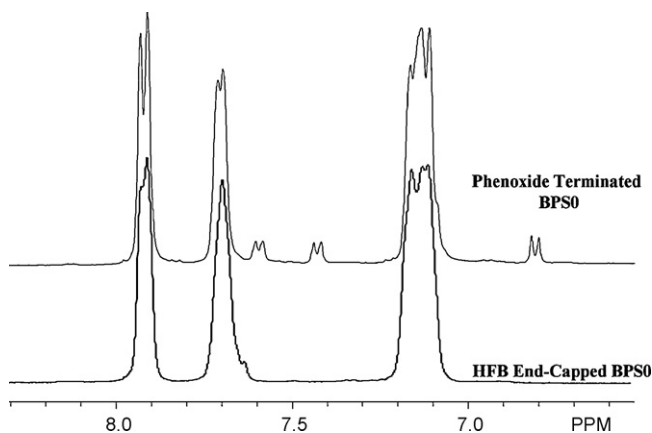
Fig. 7. BPS0 hydrophobic oligomer ^{1}H NMR spectra comparison before and after the end-capping reaction with HFB.

Fig. 9. ^{1}H NMR spectrum of HQSH3-BPS5. Black arrows indicate the disappearance of the end-groups on the hydrophilic blocks after the coupling reaction with fluorine-terminated hydrophobic blocks.

conducted in NMP, the resulting intrinsic viscosity and IEC values for the multiblock copolymers were always lower than expected. Similar problems were observed with either DMAc or DMF. However, the low reactivity between the hydrophilic and hydrophobic oligomers was significantly enhanced when DMSO was used. As shown on the ^{1}H NMR spectrum in Fig. 9, the end-group peaks associated with the hydrophilic oligomer disappeared, confirming that the coupling reaction was successful. One possible explanation for the solvent sensitivity of the coupling reaction is that the reactivity

of the phenoxide group on the HQ moieties could have been influenced by the polarity of the solvents. In other words, DMSO might have solvated the potassium ion more effectively than the other solvents with a higher dielectric constant, thereby increasing the reactivity of the phenoxide anion toward the fluorine electrophile of the BPS0 oligomers. Although the use of DMSO helped us to avoid solvent sensitivity, we did encounter another problem—namely the poor solubility of the BPS0 oligomers in DMSO, which became even more apparent when high molecular weight BPS0 oligomers were used (e.g., >10,000 g mol^{-1}). This difficulty was addressed by reducing the oligomer concentration during the coupling reaction to 3–4 (w/v) %. All multiblock copolymers used in this study were synthesized through a coupling reaction in DMSO.

We also studied another strategy to overcome a low degree of coupling. Since poor reactivity seems to stem from the low
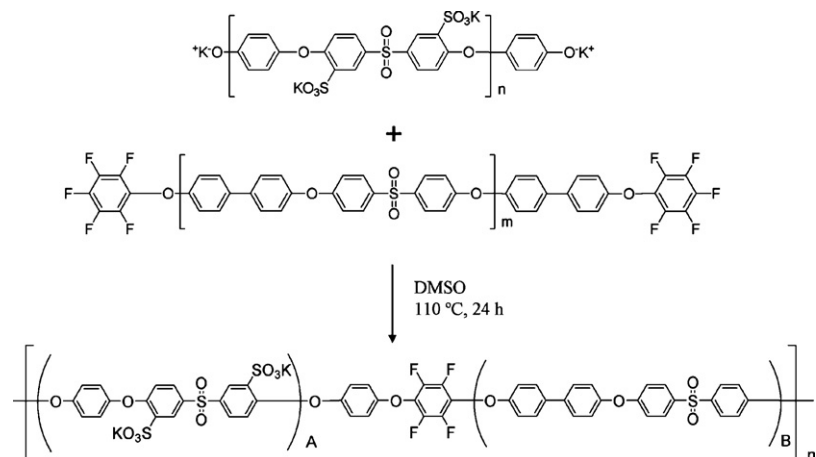
Fig. 8. Synthesis of segmented sulfonated multiblock copolymers via a coupling reaction.

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

| Copolymers	Calculated IEC (meq g^{-1})	Experimental IEC (meq g^{-1})[a]	Intrinsic viscosity (dL g^{-1})[b]	Water uptake (%)	Conductivity (S cm^{-1})[c]
Nafion 112	–	0.90	–	25	0.090
BPSH 35	1.53	1.50	0.70	36	0.070
HQSH 3–BPS 5	1.44	1.32	0.56	27	0.04
HQSH 6–BPS 10	1.31	1.21	0.60	18	0.03
HQSH 9–BPS 15	1.45	1.20	0.68	13	0.03
HQSH 12–BPS 20	1.45	1.37	0.68	17	0.04
HQSH 3–BPS 3	1.89	1.79	0.52	112	0.13
HQSH 5–BPS 5	1.79	1.88	0.51	183	0.17
HQSH 10–BPS 10	1.91	1.78	0.98	156	0.21
HQSH 15–BPS 15	1.90	1.67	0.99	145	0.16

[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.

reactivity of the HQ-phenoxide moieties, we tried to avoid using HQ-phenoxide end-group on the hydrophilic oligomer for the coupling reaction. First, we end-capped phenoxide-terminated HQS100 oligomers with HFB in DMSO. Since DMSO facilitates both good solubility and high reactivity, end-capping the HQS100 oligomers was successful with no complications. The HFB end-capped HQS100 can then typically be reacted with phenoxide-terminated BPS0 oligomers in NMP or DMAc. In this case, the nucleophile is the BP phenoxide moiety which is strong enough to attack the fluorine end-groups on the HQS100 in either NMP or DMAc. By adopting this strategy, the coupling reaction can be successfully conducted without reducing oligomer concentrations. As mentioned earlier, the main reason for employing highly reactive HFB for the coupling reaction is to prevent hydrophilic–hydrophobic sequence randomization via transetherification by reducing the coupling reaction temperature. To confirm that the synthesized multiblock copolymers maintained the sequences, their ^{13}C NMR spectra were compared with that of a random copolymer that had been synthesized from the same monomers (Fig. 10). As expected, the multiblock copolymer showed sharp singlet or doublet peaks while the random copolymer exhibited complicated mutiplet peaks, thereby confirming that the multiblock copolymer possessed well-defined sequences in the system.

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

A series of multiblock copolymers with varying hydrophilic and hydrophobic block lengths was synthesized, and subsequently examined to determine their potential fuel cell applications. Their fundamental membrane properties are summarized in Table 3. The copolymers are categorized into three groups. The first group
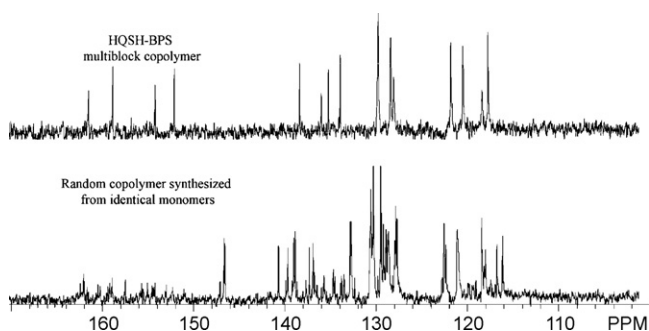
Fig. 10. ^{13}C NMR spectra comparison of HQSH3-BPS5 multiblock copolymer and a random copolymer synthesized from the identical monomers.

includes Nafion 112 and BPSH35, which were used as controls. The second and third groups include the multiblock copolymers with different block lengths. Although varying length of hydrophilic and hydrophobic oligomers were used for the multiblock copolymer synthesis, target IEC values were set to approximately 1.4 and 1.9 meq g^{-1} for the second and the third group, respectively. To obtain the target IEC value of 1.4 meq g^{-1} for the second group, the composition ratio between hydrophilic and hydrophobic blocks was set to 3:5. For the third group, a composition ratio of 1:1 was used to attain the target IEC of 1.9. All polymerization feed ratios were calculated based on a 1:1 molar ratio between hydrophilic and hydrophobic oligomers to attain high molecular weight. The acronym developed for these multiblock copolymers is HQSHx-BPSy, where the HQSH and BPS refer to the use of HQSH100 and BPS0 oligomers, while x and y denote the molecular weight in kg mol^{-1} unit of the oligomers, respectively.

All multiblock copolymers displayed high intrinsic viscosities ranging from 0.51 to 0.99 dL g^{-1}, and could form tough, ductile membranes from solvent casing. IEC values, which were determined by titration, were close to target values, indicating a high degree of coupling. It should be noted that original design of this study involved the preparation of 1.4 meq g^{-1} multiblock copolymers in order to compare their properties with a similar IEC random copolymer (e.g., BPSH35). We predicted that the HQSH-BPS multiblock copolymer with a sequenced architecture would outperform the BPSH35 random copolymer. Our results, however, were unexpected. The multiblock copolymers displayed much lower water uptake and proton conductivity, with IEC values ranging from 1.2 to 1.4 meq g^{-1}, water uptake of 20%, and a proton conductivity of 0.04 S cm^{-1}. These results were significantly lower compared with those of random copolymers with similar IEC values. We were able to explain these results using subsequent AFM characterization.

Fig. 11(a) shows an AFM phase image of the HQSH12-BPS20. The bright and dark regions in the images correspond to hard hydrophobic and soft hydrophilic segments, respectively. As shown in the picture, the dark hydrophilic segments are completely isolated by the hydrophobic segments. This type of morphology would suggest low water uptake and proton conductivity. After additional AFM studies, it turned out that all the copolymers with target IEC values of 1.4 meq g^{-1} possessed similarly isolated hydrophilic segments. This unexpected morphology can be explained as follows. Although the multiblock copolymers have adequate sulfonic acid moieties to achieve high proton conductivity, their hydrophilic segment volume fractions were not sufficient to form well-connected channels. This observation suggests one critical consideration for designing hydrophilic–hydrophobic multiblock copolymers. In developing high proton conductive PEMs from hydrophilic–hydrophobic multiblock copolymers, the volume frac-
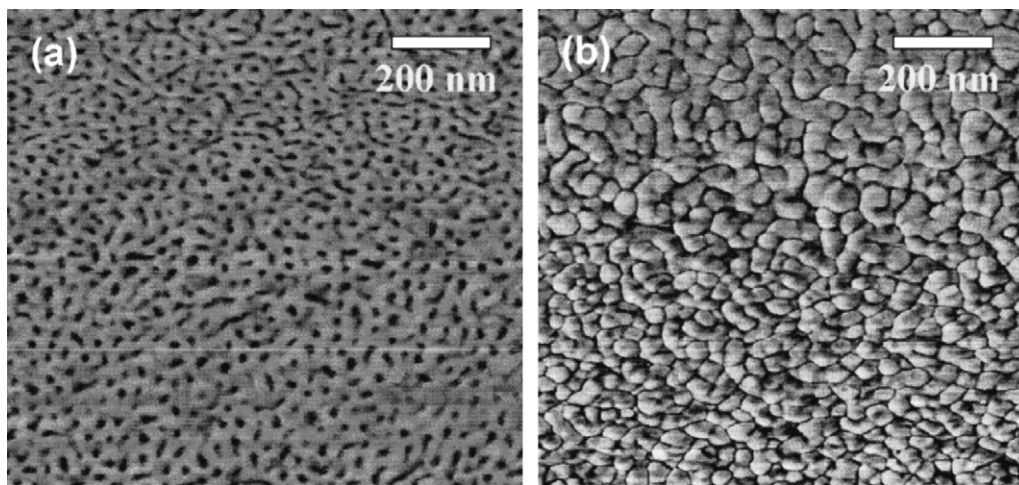
Fig. 11. AFM phase images of HQSH–BPS multiblock copolymers. (a) HQSH12-BPS20, and (b) HQSH10-BPS10.

tion of the hydrophilic segments should be considered as well as IEC values.

For this reason, in order to increase proton conductivity, we increased the hydrophilic fraction to induce the formation of well-connected hydrophilic regions. Thus, the third group of multiblock copolymers was designed with higher hydrophilic volume fractions by coupling equal block length hydrophilic and hydrophobic oligomers. The resulting multiblock copolymers showed significantly enhanced proton conductivities ranging from 0.13 to 0.21 S cm^{-1} as well as good mechanical properties. A uniaxial tensile test of HQSH10-BPS10 film samples showed around 25 MPa and 30% as yield stress and elongation at break, respectively. Water uptake values also significantly increased up to 183% with the HQSH5–BPS5 system. This significant improvement can be ascribed to the formation of well-connected hydrophilic regions, which was confirmed by AFM (Fig. 11(b)). As evidenced in this image, the HQSH10–BPS10 displays high connectivity in the hydrophilic segment of the membrane. Thus, by utilizing the well-connected hydrophilic regime for proton conduction, enhanced proton conductivity was realized.

4. Conclusions

Segmented sulfonated multiblock copolymers with varying block lengths were synthesized via a coupling reaction between phenoxide-terminated hydrophilic oligomers (HQS100) and HFB end-capped hydrophobic oligomers (BPS0). The coupling reaction was conducted under mild reaction conditions (<110 °C) to prevent an ether–ether exchange reaction, which could result in randomized hydrophilic–hydrophobic sequences. The coupling reactions were solvent sensitive due to the low reactivity of the phenoxide groups on hydroquinone moieties. All the copolymers produced tough, ductile membranes when cast from NMP or DMF.

Several fundamental membrane parameters were investigated, including water uptake and proton conductivity. Characterization studies revealed that the volume fraction of the hydrophilic segments was critical for forming continuous hydrophilic channels, as well as improving IEC values. Using HQSH–BPS multiblock copolymers with high IEC values, we were able to achieve high proton conductivity up to 0.21 S cm^{-1} at 30 °C in liquid water via the formation of a nano-phase separated morphology. The results confirm that the multiblock copolymers described herein are potential candidates for use as PEM materials.

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