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Synthesis and characterization of multiblock semi-crystalline hydrophobic poly(ether ether ketone)—hydrophilic disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes

Yu Chen, Chang Hyun Lee, Jarrett R. Rowlett, James E. McGrath*

Macromolecular Science and Engineering Program, Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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ABSTRACT

Multiblock copolymers based on alternating segments of telechelic phenoxide terminated hydrophilic fully disulfonated poly(arylene ether sulfone) (BPS100) and decafluorobiphenyl (DFBP) terminated hydrophobic poly(arylene ether ketimine) (PEEKt), were synthesized from the hydrophilic and ketimine-protected amorphous hydrophobic telechelic oligomers by nucleophilic coupling reactions. After film formation from DMSO, the copolymer was acidified, which converted the ketimine to semi-crystalline ketone segments and the sulfonate salts to disulfonic acids. A semi-crystalline phase with a T_m of 325 °C was confirmed. The semi-crystalline multiblock copolymer membranes were tough, ductile and solvent resistant. Fundamental properties as proton exchange membranes (PEMs) showed enhanced conductivities under fully hydrated and reduced humidity conditions. These multiblock copolymers exhibited low in-plane anisotropic swelling behavior, in contrast to the random copolymers.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been extensively studied as potential alternative power sources for electric vehicles, portable, and residential power sources because of their high power density, excellent energy conversion efficiency, quiet operation and zero pollution emission. Proton exchange membranes (PEMs), the key component of PEMFCs, are responsible for transporting the protons from anode to cathode [1,2]. There are several critical requirements for a successful PEM material such as; high proton conductivity, good mechanical strength, high oxidative and hydrolytic stability, low fuel and oxidant permeability, ease of fabrication, and excellent water management under low relative humidity (RH) cycling [3,4]. Currently, perfluorinated sulfonic acid containing ionomers (PFSAs), such as Nafion[®], are widely used as PEM materials due to their good chemical stability, excellent mechanical properties, and high proton conductivity [5]. However, there are several major drawbacks of these materials, such as, high cost, high methanol permeability, and low ceiling operation temperature (<80 °C) [6].

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A number of sulfonated aromatic statistical copolymers such as; disulfonated poly(arylene ether sulfone)s (BPSHs), poly(ether ether ketone)s (SPEEKs), poly(arylene ether nitrile)s (SPAEBs), polyimides (SPIs), and polybenzimidazoles have been developed as potential alternatives to Nafion[®] [7–14]. Although some of the sulfonated statistical copolymers achieved reasonable proton conductivity under fully hydrated states [15], only limited performance was observed under partially humidified conditions. Further improvement of membrane properties for hydrogen/air fuel cells, especially the conductivity performance under partially hydrated states and reduced dimensional changes under hydrated conditions, remains a primary goal. For portable power, reduced permeability to fuels such as methanol is also important.

The disulfonated multiblock copolymer membranes have been demonstrated to exhibit hydrophilic/hydrophobic nanophase separated morphologies in the presence, or absence of water [16–18]. This nanophase separation permits the formation of lamellar or co-continuous hydrophilic domains and significantly enhances proton transport under partially hydrated conditions [19–22]. Wholly aromatic hydrophilic–hydrophobic multiblock copolymers based on fully disulfonated poly(arylene ether sulfone) (BPS100) hydrophilic blocks and various hydrophobic blocks have been introduced as new PEM materials by our group [16,23–30].



 ^{*} Corresponding author.
 E-mail address: jmcgrath@vt.edu (J.E. McGrath).

This paper reports the first synthesis and characterization of semi-crystalline hydrophobic poly(ether ether ketone)-hydrophilic disulfonated poly(arylene ether sulfone) (PEEK-BPSH100) multiblock copolymers. Semi-crystalline PEEK polymers exhibit excellent thermal and mechanical stability and solvent resistance [31,32], which could enhance the performance of PEMs. However, the semi-crystalline morphology of the PEEK blocks causes insolubility in most organic solvents at relative lower reaction temperature. This prevents the direct coupling reaction between the PEEK and BPS100 telechelic oligomers. The strategy to afford synthesis and processing employed the generation of labile bulky ketimine groups to synthesize amorphous PEEKt pre-oligomers [33–35]. The procedure first involved synthesis of hydrophobic poly(ether ether ketimine)-hydrophilic sulfonated poly(arylene ether sulfone) (PEEKt-BPS100) multiblock pre-copolymers via coupling reactions between phenoxide terminated hydrophilic BPS100 and decafluorobiphenyl (DFBP) end-capped hydrophobic PEEKt blocks. The highly reactive perfluorinated end groups of the PEEKt blocks allowed for a low temperature coupling reaction, which minimized the possibility of ether-ether interchange reactions, and made it possible to achieve high yields and molecular weights of the multiblock copolymers. Amorphous PEEKt-BPS100 copolymers were then cast into films and simultaneously hydrolyzed and acidified to produce semi-crystalline PEEK-BPSH100. The proton conductivity, water uptake and other characteristics of the acidified semicrystalline PEEK-BPSH100 membranes were evaluated.

2. Experimental

2.1. Materials

4,4'-Difluorobenzophenone (DFK), was purchased from TCI America, and purified by recrystallization from ethanol. Decafluorobiphenyl (DFBP) was purchased from Aldrich and used as received. Hydroquinone was provide by Eastman Chemical Company, and recrystallized from ethanol. 4, 4'-hexafluoroisopropylidenediphenol (6F-BPA), received from Ciba, was sublimated and then recrystallized twice from toluene. Monomer grade 4,4'-dichlorodiphenylsulfone (DCDPS) and 4,4'-biphenol (BP) were provided by Solvay Advanced Polymers and dried under vacuum at 120 °C prior to use. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized from DCDPS and purified according to a procedure developed by us and reported elsewhere [36,37]. Aniline was purchased from Aldrich and purified by vacuum distillation from calcium hydride. N-Methyl-2pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), cyclohexane, and toluene were purchased from Aldrich and distilled from calcium hydride before use. The 3 Å molecular sieves and potassium carbonate (K₂CO₃) were purchased from Aldrich and dried under vacuum at 180 °C prior to use. Dimethyl sulfoxide (DMSO), chloroform, acetone, methanol and 2-propanol (IPA) were purchased from Fisher Scientific and used without further purification.

2.2. Synthesis of N-phenyl(4,4'-difluorodiphenyl) ketimine (DFKt)

DFK (60 g, 0.275 mol) and aniline (40 mL, 0.44 mol) were added to a two-necked round-bottom flask equipped with a nitrogen inlet, Dean–Stark trap and a condenser. Toluene (250 mL), along with 150 g of 3 Å molecular sieves were added into the flask. The reaction bath was heated to 140 °C to let toluene reflux over 24 h until 100% conversion to ketimine had occurred as confirmed by ¹H NMR. Toluene and excess aniline were then removed by rotary evaporation. The ketimine product was recrystallized twice from toluene to produce 40.0 g (50% yield) of a yellow crystalline solid with a melting point of 113–115 $^{\circ}$ C.

2.3. Synthesis of amorphous phenoxide terminated poly(ether ether ketimine) oligomer (PEEKt)

Amorphous phenoxide terminated poly(ether ether ketimine) oligomers (PEEKt) were synthesized with different molecular weights by offsetting the stoichiometry according to the Carothers equation. A sample synthesis of 9000 g/mol PEEKt oligomer was as follows; a 100-mL three-necked round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, a condenser and a Dean–Stark trap was charged with 5.6421 g (0.0192 mol) of DFKt, 2.2064 g (0.0200 mol) of hydroquinone and 40 mL of NMP. The mixture was stirred until dissolved, and then 3.33 g (0.0241 mol) of powdered and dried K₂CO₃, and 20 mL of toluene were added. The reaction bath was heated to 145 °C for 4 h in order to azeotropically remove water from the system. The bath temperature was slowly raised to 170 °C by the controlled removal of toluene and allowed to proceed at 170 °C for 24 h. The mixture was cooled to room temperature and filtered to remove the salt byproduct, then coagulated in 1 L of methanol. The precipitated oligomer was stirred in methanol for 24 h and then dried under vacuum at 140 °C for 48 h. The yield was 90%.

2.4. End-capping of phenoxide terminated PEEKt hydrophobic oligomer with DFBP

Phenoxide terminated PEEKt oligomers were end-capped with DFBP via a nuclephilic aromatic substitution mechanism. A sample end-capping reaction of 7000 g/mol PEEKt oligomer is as follows; a 100-mL three-necked round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, a Dean-Stark trap, and a condenser was charged with 7.000 g (1 mmol) of phenoxide terminated DFKt oligomer, 0.5528 g (4 mmol) of K₂CO₃ and 70 mL DMAc. The mixture was stirred until dissolved and 25 mL of toluene were added. The reaction bath was heated to 145 °C in order to azeotropically remove water from the system. After 4 h, toluene was removed and the reaction temperature was set at 105 °C, then 2.0067 g (6 mmol) DFBP was added into the flask. The reaction was allowed to proceed at 105 °C for 24 h, cooled to room temperature, filtered to remove the salt byproduct, and then coagulated in 1 L of methanol. The precipitated oligomer was stirred in methanol for 24 h and then dried under vacuum at 140 °C for 48 h. The yield was over 90%.

2.5. Synthesis of phenoxide terminated fully disulfonated hydrophilic oligomer (BPS100)

Phenoxide terminated fully disulfonated hydrophilic oligomers (BPS100) were synthesized with different molecular weights by offsetting the stoichiometry according to the Carothers equation. A sample synthesis of 7000 g/mol BPS100follows; a 100-mL three-necked round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser was charged with 4.0230 g (0.0216 mol) of BP, 9.8020 g (0.0200 mol) of SDCDPS, and 70 mL DMAc. The mixture was stirred until dissolved, then 3.50 g (0.0254 mol) of K₂CO₃ and 35 mL toluene were added. The reaction bath was heated to 145 °C for 4 h in order to azeotropically remove water from the system. The bath temperature was slowly raised to 180 °C by the controlled removal of toluene and allowed to proceed at 180 °C for 72 h. The mixture was cooled to room temperature, filtered to remove most of the salt, and then coagulated in 2 L of acetone. The precipitated oligomer was stirred in



Fig. 1. Synthesis of amorphous phenoxide terminated poly(ether ether ketimine) oligomer (PEEKt).

acetone for 24 h and dried under vacuum at 140 $^\circ C$ for 48 h. The yield was 90%.

2.6. Synthesis of amorphous hydrophobic—hydrophilic multiblock copolymers (PEEKt-BPS100)

A typical multiblock copolymerization coupling reaction of a 9k-7k PEEkt-BPS100 multiblock copolymer was conducted as follows: 5.00 g (0.714 mmol) of 7 kg/mol BPS100, 0.25 g (1.81 mmol) of K₂CO₃, 50 mL of NMP and 15 mL of cyclohexane were added to a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap and a condenser. The reaction bath was heated to 125 °C for 6 h to dehydrate the system. After removing cyclohexane, the reaction temperature was lowered to 105 °C, and 6.50 g (0.722 mmol) of 9 kg/mol DFBP end-capped PEEKt oligomer was added. The coupling reaction was allowed to proceed for 24 h. The reaction mixture was filtered and precipitated into 1 L of IPA. The copolymer was purified in a Soxhlet extractor with methanol for 24 h, then with chloroform for 24 h. The copolymer was dried under vacuum at 140 °C for 24 h. The yield was 85%.

2.7. Film casting, hydrolysis and acidification

The PEEKt-BPS100 copolymers in the potassium salt form were dissolved in DMSO (7% w/v) and filtered through 0.45 mm PTFE syringe filters. The solutions were then cast onto clean glass substrates and dried for 24 h with an infrared lamp at 45–55 °C. The residual solvent was largely removed by drying in a vacuum oven at 190 °C for 24 h. The amorphous PEEKt-BPS100 membranes were then converted into the semi-crystalline acid form PEEK-BPSH100 in 0.5 M hydrochloric acid (HCl) solution at 80 °C for 24 h, followed by boiling in 0.5 M sulfuric acid (H₂SO₄) solution for 2 h and in deionized water for 2 h. The initial use of HCl facilitated the removal of the aniline salt.

2.8. Characterization

¹H NMR and ¹⁹F NMR analyses were conducted on a Varian INOVA spectrometer operating at 400 MHz. The spectra of BPS100 oligomers and 6FK-BPS100 multiblock copolymers were obtained from a 10% solution (w/v) in a DMSO-d₆ at room temperature. The spectra of DFBP end-capped PEEKt hydrophobic oligomers were obtained from a solution in CDCl₃. ¹³C NMR analyses were conducted on a Varian Unity spectrometer, operating at 100.58 mHz with DMSO-d₆ as the solvent.

Absorbance mode FT-IR spectra of thin films were obtained using a Bruker Tensor 27 spectrophotometer in a wave number range from 600 cm^{-1} to 4000 cm^{-1} .

Intrinsic viscosity (IV) values for PEEKt, DFBP end-capped PEEKt, BPS100 oligomers and PEEKt-BPS100 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 refractiveindex detector, and a Viscotek 270 viscometric detector. NMP (containing 0.05 M LiBr) was used as the mobile phase [38].

Thermogravimetric analyses (TGA) of the PEEK-BPSH100 membranes were determined with the TA Instrument TGA Q500. Prior to TGA characterization, all the samples were vacuum-dried and kept in the TGA furnace at 150 °C for 30 min in order to remove residual solvent and moisture. The samples were then evaluated over the temperature range of 50–650 °C at a heating rate of 10 °C/min under an air atmosphere. Glass transition temperatures (T_{o} s) and melting exotherms were determined by



Fig. 2. End-capping of PEEKt oligomer with DFBP.



Fig. 3. ¹⁹F NMR of DFBP end-capped PEEKt with 6F-BPA as a reference.

 Table 1

 IV of PEEKt before and after DFBP end-capping.

Target M _n	Hydrophobic blocks				
(g/mol)	M _n ^a (g/mol) (measured from ¹⁹ F NMR)	IV ^b (dL/g) (before end-capping)	IV ^c (dL/g) (after end-capping)		
7k	7300	0.16	0.17		
9k	9200	0.20	0.24		
14k	14,500	0.27	0.29		
17k	17,400	0.31	0.38		
21k	20,800	0.36	0.42		

^a M_n were calculated from Eq. (3).

^b Measured by SEC with 0.05 M LiBr/NMP as mobile phase at 60 °C.

^c Measured by SEC with 0.05 M LiBr/NMP as mobile phase at 60 °C.

differential scanning calorimetry (DSC) with a TA Instruments DSC Q-1000 at a heating rate of 10 °C/min under a stream of nitrogen.

2.9. Determine of proton conductivity

The ohmic resistance (R, Ω) of the PEM membrane was measured using a test cell [39] via four-point probe alternating current (a.c.) impedance spectroscopy in the frequency range from

3 MHz to 10 Hz under two different conditions (liquid water at 30 °C and relative humidity (RH) from 30% to 95% at 80 °C). The resistance value of each membrane was obtained by averaging at least five measurements to guarantee the water equilibration of the membranes at certain temperature and humidity. The wiring system for measuring the ohmic resistance was shielded from the platinum electrodes to the potentiometer (a combined system of an electrochemical interface, Solartron 1287, and an impedance/gain-phase analyzer, Solartron 1252A) to avoid electromagnetic noise. The proton conductivity (σ , S cm⁻¹) was obtained from the following equation (Eq. (1)):

$$\sigma = \frac{L}{R \cdot S} \tag{1}$$

Where σ (S/cm) is proton conductivity, *L* (cm) is the distance between two electrodes, *R* (Ω) is the resistance of the membrane and *S* (cm²) is the surface area that protons transport though the membrane. For measurements of proton conductivity in liquid water, each membrane was fully hydrated by soaking in DI water at room temperature for 24 h. For determining proton conductivity under partially hydrated conditions, membranes were equilibrated



Fig. 4. Synthesis of phenoxide terminated fully disulfonated hydrophilic oligomer (BPS100).



Fig. 5. ¹H NMR of phenoxide terminated BPS100 oligomer.

in a humidity-temperature controlled oven (ESPEC, SH-240) at the desired relative humidity (RH) level and 80 $^\circ C$ for 45 min before each measurement.

was not possible to use the integrations of ¹H NMR spectra to calculate the number average molecular weight (M_n).

2.10. Determination of water uptake and dimensional swelling

The water uptake of all membranes were determined gravimetrically. The acidified PEEK-BPSH100 membranes (~25 microns) were equilibrated in DI water at room temperature for 2 days. Wet membranes were removed from the DI water, blotted dry to remove surface droplets, and quickly weighed. The membranes were then dried at 120 °C under vacuum for 24 h and weighed again. The water uptake of the membranes was calculated according to the following equation (Eq. (2)), where W_{dry} and W_{wet} refer to the mass of the dry and wet membrane, respectively.

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

The volume swelling ratios of the membranes were determined from the dimensional changes from wet to dry state. Membranes were equilibrated in DI water, and dimensions in the wet state were measured. The dried dimensions were obtained after drying the wet membrane at 80 °C in a convection oven for 2 h.

3. Results and discussion

3.1. Synthesis of phenoxide terminated PEEKt oligomers

Phenoxide terminated amorphous PEEKt hydrophobic oligomers were synthesized by copolymerization of DFKt and excess hydroquinone monomers as shown in Fig. 1. The number average molecular weight and end group functionality of the oligomers were precisely controlled by offsetting the molar feed ratios of monomers according to the Carothers equation. In all cases, the molar feed ratios of HQ over DFKt were larger than 1 to afford phenoxide telechelic functionality and target number-average molecular weights from 4 kg/mol to 21 kg/mol. Unfortunately, due the overlap of the proton signals in the ¹H NMR spectrum, it

3.2. Synthesis and characterization of DFBP end-capped PEEKt oligomers

The PEEKt and BPS100 oligomers possessed the same phenoxide telechelic functionality and were necessary to modify one of the oligomers to the activated halide functionality produce the multiblock copolymers. Phenoxide terminated PEEKt oligomers were end-capped with DFPB to achieve highly reactive fluorine-terminated PEEKt, as shown in Fig. 2. A large molar excess (6 times the amount of PEEKt) of DFBP was added to minimize the inter-oligomer coupling reaction of PEEKt oligomers. Due to the high reactivity of DFBP, a mild reaction temperature (105 °C) and relatively short reaction time (\sim 12 h) were sufficient to afford the fluorine-terminated PEEKt.

The measurement of the M_n s of the PEEKt oligomers was very important for the synthesis of multiblock copolymers with proper block lengths (X_n) and IECs. Analysis of a ¹⁹F NMR spectrum was utilized to determine the M_n of the fluorine-terminated oligomer, with a small amount 6F-BPA added as a reference. By comparing the respective integrations of the fluorine groups of a quantitative amount of PEEKt oligomer and 6F-BPA, the M_n of the oligomer was determined. Fig. 3 shows a ¹⁹F NMR spectrum of precisely weighed DFBP end-capped PEEKt-9k oligomer and 6F-BPA. The peak at -64.2 ppm is attributed to the fluorine in the 6F-BPA. Five peaks at -137.3, -137.9, -149.9, -152.9 and -160.3 ppm are attributed to

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Characterization of hydrophilic (BPS100) oligomers.

Target M _n (g/mol)	Hydrophilic blocks		
	M_{n}^{a} (g/mol)	IV ^b (dL/g)	
5000	5200	0.13	
7000	7100	0.18	
9000	9100	0.20	
13,000	13,700	0.28	
15,000	14,600	0.32	

^a Measured by ¹H NMR.

 $^{\rm b}\,$ Measured by SEC with 0.05 M LiBr/NMP as mobile phase at 60 °C.



Fig. 6. ln η vs. ln $M_{\rm n}$ plot of BPS100 oligomers.

the fluorines on the end-capping DFBP. The M_n of the DFBP endcapped PEEKt can be calculated with the following equation (Eq. (3)), where W_{PEEKt} and $W_{\text{6F-BPA}}$ are the weights of PEEKt sample and 6F-BPA reference, MW of 6F-BPA is 336.23 g/mol. I_b , I_c and I_f are the integrations of corresponding fluorines in Fig. 3. The calculated M_n of PEEK includes the molecular weight of end-capping groups.

$$\frac{\frac{W_{\text{PEEKt}}}{\overline{M_n \text{ of PEEKt}}}}{\frac{W_{\text{GF}-\text{BPA}}}{\overline{MW \text{ of GF}-\text{BPA}} \times 6}} = \frac{\frac{I_b + I_c}{8}}{I_f}$$
(3)

The intrinsic viscosity (IV) of PEEKt before and after DFBP endcapping as well as the M_n calculated from ¹⁹F NMR are listed in Table 1. After end-capping with DFBP, the IV of PEEKt only increased slightly due to chain length extension by the end-capping reagent DFBP.

3.3. Synthesis and characterization of phenoxide terminated BPS100 oligomers

Phenoxide terminated fully disulfonated poly(arylene ether sulfone) hydrophilic oligomers (BPS100) were synthesized via a nucleophilic aromatic substitution reaction. Excess BP monomer was used to control the telechelic functionality and molecular weight, as shown in Fig. 4.

The M_n s of the hydrophilic oligomers were determined by ¹H NMR. Fig. 5 shows the ¹H NMR spectrum of BPS100; protons from the terminal BP moieties were assigned to four small peaks at 6.80, 7.05, 7.40, and 7.55 ppm, while the peaks at 7.10 and 7.65 were assigned to the protons of the BP moieties in the middle of BPS100 oligomer backbone. By comparing the integrations of the protons on the end-group BP to the protons on the SDCDPS moieties, the M_n of each BPS100 oligomer was determined.

The molecular weights (M_n) and IV obtained from size exclusion chromatography (SEC) are summarized in Table 2. An increase in IV was correlated with the M_n of BPS100. There is a linear relationship between the log M_n and logIV, which indicates that control of the molecular weights for the hydrophilic oligomers was successful, as shown in Fig. 6.

3.4. Synthesis and characterization of PEEKt-BPS100 multiblock copolymers

A series of amorphous hydrophobic—hydrophilic multiblock copolymers was synthesized via the coupling reaction between phenoxide terminated BPS100 and DFBP end-capped PEEKt oligomers (Fig. 7). The stoichiometry of the reactions was set as 1:1. The IV data confirmed that high molecular weight PEEKt-BPS100 multiblock copolymers were obtained.

Fig. 8 shows the ¹H NMR of a PEEKt-BPS100 multiblock copolymer. It is difficult to monitor the degree of the coupling reaction from the disappearance of the phenoxide end group peaks of BPS100 (peak **a** in Fig. 5) as described in the literature [25]. At this chemical shift position on ¹H NMR spectrum of PEEKt-BPS100, there are overlapping peaks from the protons of SDCDPS and DFKt moieties (peak **c** and peak **k**).

The very high reactivity of DFBP end groups allowed the copolymerization to be accomplished at a relatively low temperature and short reaction time. This minimizes the possible ether–ether interchange scrambling side reactions. Fig. 9 shows the ¹³C NMR of PEEKt-BPS100 9k-7k. In the chemical shift range of 150–170 ppm, the peaks can be properly assigned to the carbons on the backbone of the PEEKt-BPS100 polymer. The two peaks at 156.3 ppm and 158.8 ppm, which are assigned to the carbons on each end of the ether bond in BPS100 blocks (Fig. 9 peaks **b** and **a**),



Fig. 7. Synthesis of PEEKt-BPS100 multiblock copolymers.



Fig. 8. ¹H NMR of PEEKt-BPS100 9k-7k multiblock copolymer.

are still sharp and narrow. This phenomenon suggests that the multiblock copolymer maintains an ordered sequence and confirms the minimization of the ether—ether interchange side reactions.

3.5. Film casting, hydrolysis and acidification

The PEEKt-BPS100 multiblock copolymer membranes were cast from DMSO solutions. The membranes were then boiled in aqueous 0.5 M HCl then in 0.5 M H_2SO_4 solutions in order to hydrolyze the amorphous PEEKt blocks to the semi-crystalline PEEK blocks and to simultaneously acidify the salt form BPS100 blocks to the acid form BPSH100 blocks, as Fig. 10 shows. The reason for using 0.5 M HCl first was that the aniline chloride byproduct is easier to remove from the membrane. After acidification, the loss of the ketimine groups induced a change in the molecular weight of the hydrophobic blocks (e.g. PEEKt-BPS100 9k-7k becomes PEEK-BPSH 7k-7k). After this procedure, the semi-crystallinity of the PEEK blocks prevented the PEEK-BPSH100 multiblock copolymer from dissolution in any organic solvent, such as DMSO, DMAc or NMP. Resistance to organic solvents could be important in some applications.

Fourier transform infrared (FT-IR) spectroscopy was used to characterize the functional groups. The hydrolysis and acidification of the PEEKt-BPS100 to PEEK-BPSH100 membranes was determined by FT-IR. Fig. 11 shows the FT-IR spectra of a PEEKt-BPS100 17k-13k membrane before and after acidification. The absorption bands at 1247 cm⁻¹, 1095 cm⁻¹ and 1029 cm⁻¹ can be assigned to asymmetric and symmetric O—S—O stretching vibrations of the sulfonate groups [8,29]. The absorption band assigned to the S–O stretching of sulfonate group shifts from 696 cm⁻¹ to 686 cm⁻¹ after acidification. This absorption band shift confirms the acidification of the potassium sulfonate groups to the desired sulfonic acid groups.



Fig. 9. ¹³C NMR of PEEKt-BPS100 9k-7k multiblock copolymer.



Fig. 10. Hydrolysis and acidification to convert amorphous PEEKt-BPS100 to semi-crystalline PEEK-BPSH100.

A representative FT-IR spectrum of PEEKt-BPS100 17k-13k (Fig. 11, top) exhibits a large peak at 1590 cm⁻¹, which is a overlap of C=N stretching vibration and C-C vibration in aromatic rings [33,35]. The decease of the C=N stretching peak and the appearance of the C=O stretching peak at 1650 cm⁻¹ in the PEEK-BPSH100 13k-13k spectrum (Fig. 11, bottom) confirm the hydrolysis of PEEKt-BPS100 to PEEK-BPSH100.

3.6. Thermal characterization

Two thermal transitions at around 165 °C and a broad change at 245 °C were observed in the differential scanning calorimetry (DSC) thermogram of PEEKt-BPS100 17k-13k, as Fig. 12 shows. These can be assigned to the glass transition temperature of the hydrophobic PEEKt blocks and that of hydrophilic BPS100 blocks, respectively. No melting endotherm transition was observed since the soluble PEEKt-BPS100 series copolymers are amorphous.

The amorphous PEEKt-BPS100 17k-13k was hydrolyzed and acidified to semi-crystalline PEEK-BPSH100 13k-13k in dilute hydrochloric acid and then sulfuric acid solution. The DSC thermogram (2nd heating cycle) of PEEK-BPSH100 13k-13k is shown in Fig. 13. A very broad thermal transition from 150 °C to 230 °C was observed. This very broad thermal transition suggests the decreased T_g of BPSH100 blocks after acidification may partially overlaps with the T_g of PEEK blocks. However a melting endotherm at 325 °C was observed and attributed to the presence of semicrystalline domains in the PEEK-BPSH100 13k-13k membrane.

Thermal and oxidative stability of the PEEK-BPSH100 multiblock copolymers were investigated by TGA, as shown in Fig. 14. The TGA was conducted in an air atmosphere to assess the oxidative stability of the copolymers. Such copolymers displayed a two-step weight loss; the first was observed at 270 °C assigned to the desulfonation of BPSH100 blocks, the second degradation began at 450 °C, which was related to the decomposition of the copolymer backbones. The



Fig. 11. FT-IR spectra of PEEKt-BPS100 17k-13k (before hydrolysis) (top) and PEEK-BPSH100 13k-13k (after hydrolysis) (bottom).



Fig. 12. DSC thermogram of PEEKt-BPS100 17k-13k.

block length variation in the copolymers did not affect the thermal and oxidative stability. All the copolymers showed very similar weight loss behavior indicating the control of IEC (or degree of disulfonation) was successful.

3.7. Characterization of the membrane properties of PEEK-BPSH100

Tough, ductile, and transparent PEEKt-BPS100 membranes were cast from DMSO. Table 3 shows some properties of PEEKt-BPS100 and PEEK-BPSH100 multiblock copolymer membranes. After hydrolysis and acidification, the PEEK-BPSH100 multiblock copolymer membranes turned to light yellow and were insoluble in normal organic solvents such as NMP and DMSO, due to the high crystallinity of the PEEK blocks. The water uptake of PEEK-BPSH100 block copolymers increases with an increase in block length, which is consistent with other reported block copolymers [25].

The proton conductivity of the PEEK-BPSH100 multiblock copolymer membranes were measured in liquid water at 30 °C as shown in Table 3. A random sulfonated poly(arylene ether sulfone)



Fig. 13. DSC thermogram of PEEK-BPSH100 13k-13k.



Fig. 14. TGA traces of PEEK-BPSH100 multiblock copolymers.

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Characterization of PEEK-BPSH100 multiblock copolymers.	

PEEKt- BPS100	PEEK- BPSH100	IV (dL/g) ^a	IEC (meq/g) ^b	Water uptake (wt%)	Proton conductivity (S/cm) ^c
7k-5k	5k-5k	0.83	1.60	47	0.11
12k-9k	9k-9k	0.96	1.65	50	0.12
17k-13k	13k-13k	1.10	1.70	53	0.12
21k-17k	17k-17k	1.13	1.70	85	0.13
Nafion [®] 112		N/A	0.90	22	0.12
BPSH40		0.85	1.52	50	0.11

 $^{\rm a}$ Measured by SEC with 0.05 M LiBr/NMP as mobile phase at 60 $^\circ\text{C}\textsc{,}$ in PEEKt-BPS100 state.

^b Measured from ¹H NMR.

^c Measured in liquid water at 30 °C.

copolymer with 40% of SDCDPS (BPSH40) and a Nafion[®] 212 were also included as controls. The proton conductivity is relatively constant with the increase in block length for PEEK-BPSH100 block copolymer membranes. All the PEEK-BPSH100 membranes exhibited comparable or higher conductivity values than random copolymer BPSH40 and Nafion[®] 212 in liquid water at 30 °C.



Fig. 15. Proton conductivity vs. RH of PEEK-BPSH100 17k-17k multiblock copolymers with Nafion[®] and BPSH40 as references (measured at 80 °C).



Fig. 16. Comparison of dimensional swelling data for PEEK-BPSH100 multiblock, copolymers, BPSH35, 6FK-BPSH 17k-17k, and Nafion® 112.

Fig. 15 shows proton conductivity at 80 °C as a function of relative humidity (RH) for PEEK-BPSH 17k-17k, Nafion[®] 212 and BPSH40 membranes. The proton conductivity of the randomly copolymerized BPSH40 dropped significantly at lower RH levels as expected. Sufficient water molecules provide proton transport under fully hydrated states; however, the isolated hydrophilic domains in the random copolymer can't facilitate proton transport under partially hydrated conditions. In contrast, under partially hydrated states, proton species are better transported along the sulfonic acid groups and water molecules through the long, co-continuous channels in multiblock copolymers.

3.8. Swelling–deswelling behavior of PEEK-BPSH100 multiblock copolymer

The compatibility between the proton exchange membrane (PEM) and electrodes is always a major concern under real operation conditions for a membrane electrode assembly (MEA). When a proton exchange membrane shows a significant in-plane swelling, during the wet-dry cycles, considerable stress can be created at the interface between the membrane and electrodes. The high stress could lead to premature failure of the MEA.

The dimension swelling behavior of PEEK-BPSH100 multiblock copolymers with BPSH35, a amorphous partially fluorinated poly(arylene ether ketone sulfone) hydrophilic-hydrophobic multiblock copolymers (6FK-BPSH100 17k-17k) and Nafion[®] used as comparison is shown in Fig. 16. The BPSH35 and Nafion[®] 112 membranes show isotropic swelling behavior. In contrast, PEEK-BPSH100 multiblock copolymer membranes exhibit anisotropic swelling behavior. For PEEK-BPSH100 membranes, in-plane swelling (x- and y-directions) decreases, while through-plane (zdirection) swelling increases as the block length increases. This behavior indicates the development of enhanced ordered lamellar morphology as the block length increases. PEEK-BPSH100 17k-17k shows a significantly low in-plane swelling ratio compared to its corresponding 6FK-BPSH 17k-17k amorphous multiblock copolymer membrane, which may be induced by the enhanced semicrystalline hydrophobic domains in longer block length PEEK-

BPSH100 membranes. The lower in-plane swelling of PEEK-BPSH100 membranes may be important in fuel cell MEAs to keep the in-plane interface stress low, and to prevent the failure of the MEAs under dry—wet cycling conditions.

4. Conclusions

Multiblock semi-crystalline hydrophobic solvent resistance poly(ether ether ketone)-hydrophilic disulfonated poly(arylene ether sulfone) (PEEK-BPSH100) copolymers were synthesized and characterized. PEEK-BPSH100 multiblock copolymers were produced by hydrolysis of the amorphous multiblock PEEKt-BPS100 ketimine protected pre-copolymers. FT-IR spectra confirmed the hydrolysis of PEEKt-BPS100 to PEEK-BPSH100. DSC thermograms showed a sharp melting endotherm, confirming the presence of semi-crystalline domains in the PEEK-BPSH100. The proton conductivities of the multiblock semi-crystalline PEEK-BPSH100 copolymers were comparable or higher than that of Nafion212 and BPSH40 random copolymer. PEEK-BPSH100 17k-17k shows better conductivity performance under low RH, presumably due to its more distinct nanophase morphology separation between semi-crystalline hydrophobic domains and disulfonated hydrophilic domains.

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