



Sulfonation of blocky brominated PEEK to prepare hydrophilic-hydrophobic blocky copolymers for efficient proton conduction

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ABSTRACT

Hydrophilic-hydrophobic blocky copolymers of poly(ether ether ketone) (PEEK) were prepared using a two-step post-polymerization technique. First, PEEK was brominated in the semicrystalline gel state to create a blocky BrPEEK template, which was subsequently functionalized by sulfonating the remaining runs of unfunctionalized PEEK units. The resultant degree of sulfonation of the blocky brominated, sulfonated PEEK (BrSPEEK) copolymers was inversely related to the degree of bromination, and degrees of sulfonation ranging from 26 to 71 mol% were obtained for degrees of bromination between 27 and 144 mol%. Thermal analysis using DSC and DMA revealed distinct multi-phase behavior for blocky BrSPEEK copolymers at degrees of sulfonation up to 40 mol%, suggesting phase separation between the densely brominated blocks and the sulfonated blocks into hydrophobic and hydrophilic domains, respectively. This phase separation contributed to improved dimensional stability upon swelling and enhanced proton transport at lower water content for blocky BrSPEEK membranes compared to random SPEEK membranes. Finally, morphological analysis using SAXS demonstrated that ionic aggregate size remained relatively unchanged for blocky BrSPEEK at all degrees of sulfonation, and the ionic aggregates became more closely spaced with increasing degree of sulfonation. Overall, this work demonstrates a facile, post-polymerization technique to prepare hydrophilic, hydrophobic blocky copolymers with excellent dimensional swelling and transport properties that rival those of directly polymerized block copolymers.

1. Introduction

Aromatic hydrocarbon-based polymers have been widely explored as potential proton exchange (PEM) membranes due to their low cost, great mechanical properties, and high thermal and chemical stability [1,2]. Primarily, these membranes are prepared by post-polymerization sulfonation of high performance aromatic polymers such as poly(arylene ether ketones) [3–6], poly(sulfones) [7–9], and poly(ether sulfones) [10–12] or by direct polymerization using sulfonated monomers [1,13–15]. Membrane performance is dictated by the degree of sulfonation, and high proton conductivity is achieved at high ion exchange capacities (IEC) [16]. At high degrees of functionalization, however, excessive swelling in hydrated conditions is commonly observed in the randomly sulfonated membranes, leading to dilution of the charge carriers (i.e. a reduction in proton conductivity) and a loss of mechanical strength [17]. The incorporation of hydrophobic domains, such as halogenated repeat units, into these random copolymer systems has been found to enhance membrane mechanical properties, improve dimensional stability during swelling and deswelling, and provide suitable proton conductivity [18–21].

Further efforts to improve hydrocarbon membrane properties and to develop proton exchange membranes with controlled water uptake, mechanical stability, and excellent proton transport at high IEC have focused on the synthesis of multiblock copolymers comprised of hydrophobic blocks and hydrophilic blocks [19,22–27]. Most commonly, these block copolymers are prepared by step-growth polymerization from oligomers of each desired block, utilizing a densely sulfonated block to provide acidic sites for proton transport and a hydrophobic block to impart mechanical integrity. Enhanced phase-separation between the hydrophilic and hydrophobic domains results in continuous hydrophilic domains, leading to improved proton transport relative to random analogs. The water uptake, proton conductivity, and mechanical properties of multiblock copolymer membranes is readily tuned by varying the lengths of the hydrophilic and hydrophobic components [28]. The wide-spread application of these multiblock systems is limited, however, due to the generally arduous synthetic procedures, limited commercial availability of sulfonated monomers, and decreasing reactivity of the sulfonated oligomers at mild reaction conditions, which limits the resultant molecular weight of the copolymers [20,29].

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Our recent results show that it is now possible to synthesize blocky copolymers by functionalizing in the semicrystalline gel state [30–32]. During this gel-state process, the functionalization reagent is sterically excluded from the tightly-packed crystalline domains, and thus, functionalization is restricted to the solvent-swollen amorphous segments within the semicrystalline network. This results in a blocky copolymer with highly functionalized ‘blocks’ and unfunctionalized, crystallizable ‘blocks’. Blocky copolymers of sulfonated poly(ether ether ketone) (SPEEK) prepared in this manner exhibited enhanced crystallizability and more rapid crystallization kinetics than random copolymers at similar degrees of sulfonation, suggesting long ‘blocks’ of unfunctionalized PEEK remained due to the gel-state functionalization process. The blocky architecture also facilitated enhanced proton transport for blocky SPEEK compared to random SPEEK at similar degrees of sulfonation [31]. By establishing a blocky architecture during the gel-state functionalization process, it is now possible to perform secondary reactions in the homogeneous solution state while preserving the blocky architecture. For example, hydrophilic-hydrophobic block copolymers may be prepared by first brominating in the gel-state to establish the blocky architecture and then sulfonating the remaining unfunctionalized blocks. In this work, the secondary sulfonation of blocky BrPEEK prepared by gel-state bromination is examined. Blocky BrPEEK was chosen as the starting material because a high degree of functionalization is achievable (over 150 mol%) [33] with high degrees of crystallinity (i.e., attributed to long runs of unfunctionalized repeat units), thereby providing densely brominated hydrophobic “blocks” and polar functional “blocks.” It is anticipated that the sulfonation of blocky BrPEEK will yield copolymers capable of undergoing hydrophilic-hydrophobic phase separation [34], and the effect of this phase behavior will be investigated with respect to membrane properties such as water uptake, dimensional stability upon swelling, and proton conductivity.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) pellets (Vitrex 150G) were acquired from Vitrex. Dichloroacetic acid (DCA) was purchased from Sigma-Aldrich and was dried using magnesium sulfate (Fisher Scientific) then filtered through a 0.45 μm PTFE syringe filter prior to use. *N*-bromosuccinimide (NBS) was purchased from Sigma-Aldrich and was purified by recrystallization from water. Concentrated sulfuric acid (98%), sodium chloride, and cesium chloride were purchased from Fisher Scientific and used as received. Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich and used as received.

2.2. Synthesis of blocky brominated, sulfonated PEEK

Blocky BrPEEK was first prepared by brominating PEEK in the semicrystalline gel state. PEEK gels were prepared by dissolving PEEK (5 g) in dichloroacetic acid (DCA) to a final concentration of 20 w/v% at 185 °C. Once dissolved, the PEEK solution was removed from heat and left at room temperature for at least 24 h, during which PEEK crystallizes from solution to form a thermoreversible gel network (with a degree of crystallinity of about 40–50%, based on the mass of PEEK) [35,36]. The gel was then broken up into small pieces and dispersed in DCA to a final concentration of 10 w/v%. The gel suspension was equilibrated at 80 °C under argon for 1 h, and then a solution of *N*-bromosuccinimide (NBS) in DCA (20 mL) was added dropwise. Degrees of bromination of 25, 50, 75, 100, and 150 mol% were targeted by varying the molar ratio of NBS to PEEK repeat units used. The reaction proceeded at 80 °C for 24 h and was terminated by precipitation into DI H₂O. The product was filtered, washed with H₂O, and then washed by Soxhlet extraction over methanol for 24 h. The resulting blocky BrPEEK polymer was dried at 100 °C for 12 h to produce a white product that

was used for subsequent sulfonation. The degree of bromination was determined using ¹H NMR [33].

For the secondary sulfonation, blocky BrPEEK (5.0 g) was dissolved in dichloroacetic acid (DCA) at 150 °C to a final concentration of 10 w/v%. Once fully dissolved, the solution temperature was lowered to 80 °C and 140 mL of concentrated sulfuric acid (excess) was added to the reaction flask. The reaction was allowed to stir at 80 °C under argon for 24 h, and then the reaction was terminated by precipitation into cold DI H₂O. The product was filtered, washed with DI H₂O, and then washed by Soxhlet extraction over water for 24 h. The resulting polymer was dried at 100 °C for 12 h.

2.3. Membrane preparation

BrSPEEK samples (H⁺-form) were dissolved in dimethylacetamide (DMAc) at 100 °C to a final concentration of 12 w/v%. Once dissolved, the casting solution was cooled to room temperature and was filtered through a 0.45 μm PTFE syringe filter. The solutions were cast onto glass at 80 °C using a doctor blade set to 7.5 mils. The films were left at 80 °C for 30 min to dry, resulting in a membrane thickness of 25 μm . Membranes were removed from the glass by swelling in water and were subsequently dried at 100 °C for 12 h. To convert BrSPEEK membranes to the sodium form (Na⁺-form), membranes were stirred in 2 M NaCl (aq) for 24 h. To convert to the cesium form (Cs⁺-form), BrSPEEK membranes were stirred in 1 M CsCl (aq) for 24 h. Following ion exchange, samples were removed from the salt solution, washed with DI H₂O to remove residual salt, and dried at 100 °C for 12 h.

2.4. Spectroscopic methods

¹H NMR spectra of the blocky BrPEEK were measured using a Bruker Avance III 600 MHz. BrPEEK samples were dissolved in DCA/CDCl₃ solvent mixture and a solvent suppression method was utilized to resolve the spectra, as described previously [31]. ¹H NMR spectra of blocky BrSPEEK were measured using an Agilent U4-DD2 400 MHz NMR. BrSPEEK samples were dissolved in DMSO-*d*₆ for analysis. FTIR was performed using a Varian 670-IR spectrometer with a deuterated triglycine sulfate (DTGS) detector using the Pike Technologies GladiATR™ attachment (diamond crystal). Spectra were collected as the average of 32 scans at 4 cm^{−1} resolution. FTIR spectra were ATR corrected, baseline corrected, and normalized to the peak at 1590 cm^{−1} (C=C skeletal ring vibration) [37] prior to analysis.

2.5. Thermal analysis

A TA Instruments Q2000 DSC was used to determine the thermal properties of blocky BrPEEK and BrSPEEK. BrSPEEK was ion-exchanged to Na⁺-form or Cs⁺-form prior to DSC measurements to ensure thermal stability [31,38,39]. Samples were pre-dried at 150 °C for 5 min before several heating and cooling cycles. Dried samples (~5–8 mg) were heated from room temperature to 380 °C at 20 °C/min, quench cooled to 0 °C, and then heated to 380 °C at a rate of 20 °C/min. A TA Instruments Q800 DMA in oscillatory tension mode was used to determine the thermo-mechanical properties of quenched BrPEEK samples as a function of temperature. Samples were ramped at 2 °C/min to 400 °C at a frequency of 1 Hz, an oscillatory amplitude of 10 μm , and a static force of 0.01 N. DMA was performed on Na⁺-form samples.

2.6. SAXS analysis

Small angle x-ray scattering (SAXS) data were collected at Argonne National Laboratory beamline 9ID-C using a photon energy of 24 keV [40]. Scattering profiles are plotted as absolute intensity vs. q , where $q = \left(\frac{4\pi}{\lambda}\right) \sin(\theta)$, θ is one half of the scattering angle, and λ is the X-ray wavelength (0.5895 Å). SAXS measurements utilized the Pilatus 100k

camera, and data reduction was performed using the Irena [41] and Nika [42] software packages provided by Argonne.

2.7. Water uptake and dimensional swelling

The water uptake and swelling ratios of the BrSPEEK (H⁺-form) membranes were determined by first drying membranes in a vacuum oven at 120 °C for 3 h. The mass (W_{dry}) and dimensions ($L_{x, \text{dry}} \times L_{y, \text{dry}}$) of the dry membranes were recorded. Then, the samples were equilibrated in room temperature deionized water for 12 h. Membranes were blotted to remove excess surface water and the mass (W_{wet}) and dimensions ($L_{x, \text{wet}} \times L_{y, \text{wet}}$) of the wet membranes were recorded. The water uptake and areal swelling ratio were calculated as:

$$\text{Water uptake} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100\% \quad (1)$$

$$\text{Areal Swelling ratio} = \frac{(L_{x, \text{wet}} \times L_{y, \text{wet}}) - (L_{x, \text{dry}} \times L_{y, \text{dry}})}{(L_{x, \text{dry}} \times L_{y, \text{dry}})} \times 100\% \quad (2)$$

The reported values are the average of four samples.

2.8. Proton conductivity

Prior to analysis, BrSPEEK membranes were equilibrated in DI H₂O at room temperature for at least 12 h. In-plane proton conductivity was conducted using a 4-point conductivity cell from Bekktech, which was immersed in DI H₂O at room temperature. Measurements were taken from 1 Hz to 1.5 MHz at a voltage amplitude of 50 mV using a 1255 HF frequency analyzer coupled to a 1286 electrochemical interface, both from Solartron Analytical. Data analysis was performed using the Zplot® and Zview® software from Scribner and Associates, Inc. The proton conductivity was calculated as:

$$\sigma = \frac{1}{\rho} = \frac{l}{R \times A} \quad (3)$$

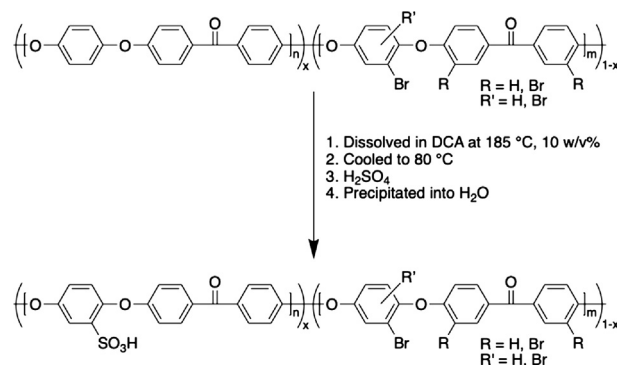
where σ (Scm⁻¹) is the conductivity, ρ (Ω cm) is the resistivity, l (cm) is the distance between the contacting electrodes, R (Ω) is the resistance determined from the real value of the complex impedance plot that corresponds to the minimum imaginary response, and A is the cross-sectional area of the membrane calculated from the width and thickness of the membrane. Measurements were performed on three separate membranes for each sample to ensure the reproducibility of results.

3. Results and discussion

3.1. Synthesis of blocky BrSPEEK

To synthesize blocky brominated-sulfonated PEEK (BrSPEEK), blocky BrPEEK was first prepared by brominating PEEK in the semi-crystalline gel state using *N*-bromosuccinimide (NBS) in dichloroacetic acid (DCA). Blocky BrPEEK was chosen as a template for further sulfonation due to the high stability of the semicrystalline gel-state during bromination, which yields blocky copolymers with a wide range of functionality, a high degree of crystallizability, and thereby a large content of unfunctionalized chain segments of sufficient length of crystallize. The unfunctionalized, crystallizable ‘blocks’ are readily sulfonated using conventional procedures, and thus blocky BrPEEK provides a suitable template for hydrophobic-hydrophilic blocky copolymers consisting of densely brominated and sulfonated segments along a given chain. It is also important to note that the initial gel-state reactions generate the blocky template, and this allows for secondary reactions in a homogeneous solution state while preserving the blocky architecture. Overall, this process allows for the development of hydrophilic-hydrophobic blocky copolymers using a simple post-polymerization functionalization procedure.

Blocky BrPEEK was prepared with target degrees of bromination at



Scheme 1. Reaction scheme for the sulfonation of blocky BrPEEK to prepare blocky BrSPEEK.

25, 50, 75, 100, and 150 mol%, and the resultant degree of bromination for each sample was found to be 27, 56, 78, 101, and 144 mol%. Thus, near quantitative bromination was achieved due to the highly electrophilic character of NBS in strong acid, consistent with literature precedence for small molecules and for PEEK brominated in methane-sulfonic acid [33,43,44]. It is important to note that these high degrees of bromination (> 100 mol%) are achievable because multiple sites on a single PEEK repeat unit are capable of being functionalized. A complete analysis of the spectroscopic, thermal, and morphological characteristics of blocky BrPEEK compared to random BrPEEK will be described in a subsequent publication.

Following the gel-state bromination, secondary sulfonation of the blocky BrPEEK was performed by dissolving the BrPEEK in DCA and then adding concentrated sulfuric acid (H₂SO₄), as shown in Scheme 1. Sulfonation using H₂SO₄ proceeds via an electrophilic aromatic substitution reaction and occurs exclusively within the hydroquinone ring of the PEEK repeat unit due to the increased electron density from the electron-donating ether linkages [6]. The previously brominated rings are deactivated towards sulfonation due to the electron-withdrawing effect of the halogen. Likewise, only one sulfonation event per repeat unit is expected due to the electron-withdrawing effect of the sulfonic acid group. Thus, sulfonation occurs exclusively on the unfunctionalized repeat units of the blocky BrPEEK copolymers, and although this procedure is identical to that typically used to prepare random SPEEK from PEEK, the previously established blocky brominated architecture templates the sulfonation into distinct ‘blocks.’

The ¹H NMR spectra of blocky BrPEEK and the resultant blocky BrSPEEK is shown in Fig. 1. Prior to sulfonation, blocky BrPEEK shows distinct doublets at 7.85 ppm and 7.10 ppm and a singlet at 7.15 ppm that are attributed to unfunctionalized PEEK repeat units within the blocky copolymers [31], and peaks at 8.10 ppm, 7.75 ppm, 7.45 ppm, 7.03 ppm, and 6.75 ppm are attributed to the brominated repeat units [33]. Due to the large number of unfunctionalized repeat units, blocky BrPEEK is highly crystallizable and its solubility is limited to known solvents for PEEK, such as DCA. Upon sulfonation, the blocky BrSPEEK copolymers are no longer crystallizable and become readily soluble in polar aprotic solvents such as dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP). The ¹H NMR spectra of blocky BrSPEEK in DMSO-*d*₆ reveals new peaks that arise at 7.47 ppm, 7.23 ppm, and 7.07 ppm. These peak positions are in close agreement with those of sulfonated PEEK (SPEEK) and arise due to shifts in the protons of the hydroquinone ring upon sulfonation, as assigned in Fig. 1 [4,6,45]. With decreasing degree of bromination, the peaks at 7.47 ppm, 7.23 ppm, and 7.07 ppm increase in intensity, consistent with an increase in the degree of sulfonation. The actual degree of sulfonation was quantified by integration of the peak at 7.47 ppm (a₃*), and the results are displayed in Table 1.

Integration of the BrSPEEK ¹H NMR spectra revealed degrees of sulfonation ranging between 26 mol% and 71 mol%, for BrPEEK

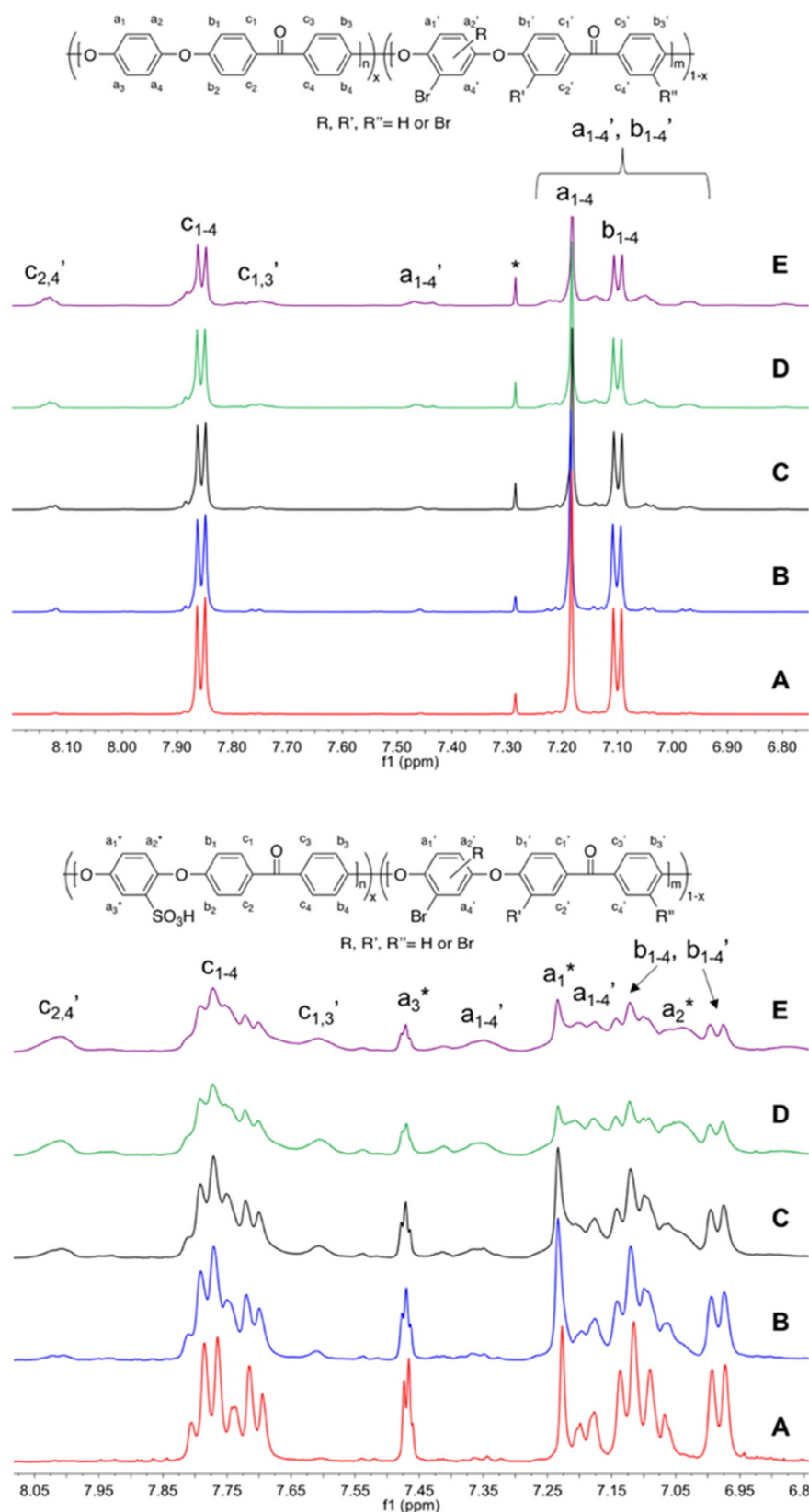


Fig. 1. ¹H NMR spectra of blocky BrPEEK (top) at 25 (A), 50 (B), 75 (C), 100 (D), and 150 (E) mol% bromination and the ¹H NMR spectra of the resultant blocky BrSPEEK (bottom) following sulfonation. Blocky BrPEEK samples were analyzed using solvent suppression ¹H NMR using DCA/CDCl₃ mixed solvent. CDCl₃ is represented by an asterisk. BrSPEEK samples were run in DMSO-*d*₆.

Table 1
Degree of bromination and degree of sulfonation determined by ^1H NMR.

Sample	Degree of bromination (mol%)	Degree of sulfonation (mol%)
BrSPEEK27-71	27	71
BrSPEEK56-52	56	52
BrSPEEK78-40	78	40
BrSPEEK101-30	101	30
BrSPEEK144-26	144	26

templates containing degrees of bromination ranging from 144 mol% to 27 mol%, respectively. The degree of sulfonation was clearly limited by the degree of bromination, and as expected, the resultant degree of sulfonation decreased with increasing degree of bromination due to deactivation of brominated hydroquinone rings towards sulfonation. Because these reactions were run for long periods of time, it is likely that the BrSPEEK products are sulfonated to near their maximum extent, and this further confirms that the previously established brominated architecture not only templates the distribution of repeat units available for sulfonation, but also dictates the quantity of reactive units. Henceforth, the blocky BrSPEEK samples will be named as BrSPEEK x - y where x is the degree of bromination and y is the degree of sulfonation. It should be noted that $x + y \neq 100$ because it is possible to brominate multiple sites on a single PEEK repeat unit.

The blocky BrSPEEK copolymers were also analyzed using FTIR spectroscopy, as shown in Fig. 2. Prior to sulfonation, blocky BrPEEK copolymers exhibited several defining peaks. Peaks at 1490 cm^{-1} and 1470 cm^{-1} were assigned to the skeletal ring vibrations of 1,4-disubstituted aromatic rings and 1,2,4-trisubstituted aromatic rings, respectively [46]. The peak at 1470 cm^{-1} was larger for blocky BrPEEK150 than blocky BrPEEK25 due to the increased functionality of BrPEEK150 yielding an increased number of trisubstituted aromatic rings. Furthermore, a peak is present at 1040 cm^{-1} that is attributed to aryl C–Br stretching [47,48]. Upon sulfonation of both BrPEEK27 and BrPEEK150, the peak at 1490 cm^{-1} drastically decreases in intensity and the peak at 1470 cm^{-1} increases in intensity, signifying the sulfonation of previously unfunctionalized hydroquinone rings of blocky BrPEEK copolymer. Little difference is observed between the normalized intensities of the BrSPEEK27-71 and BrSPEEK144-26 at 1490 cm^{-1} and 1470 cm^{-1} , suggesting that nearly all available reactive sites (on the hydroquinone ring) have been brominated or sulfonated in the resultant blocky BrSPEEK copolymers. Furthermore, new peaks arise at 705 cm^{-1} (S–O stretching), 1020 cm^{-1} (S=O stretching), 1075 cm^{-1} (O=S=O symmetric stretching), and 1250 cm^{-1} (O=S=O asymmetric stretching) due to introduction of the sulfonic acid sites to the polymer

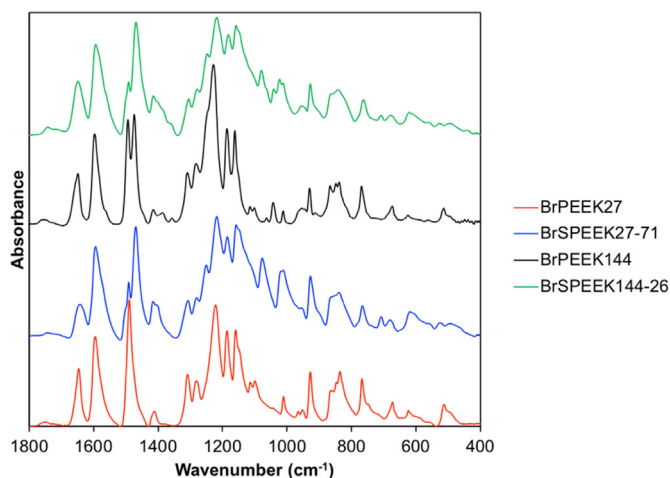


Fig. 2. FTIR spectra of BrPEEK27, BrSPEEK27-71, BrPEEK144, and BrSPEEK144-26.

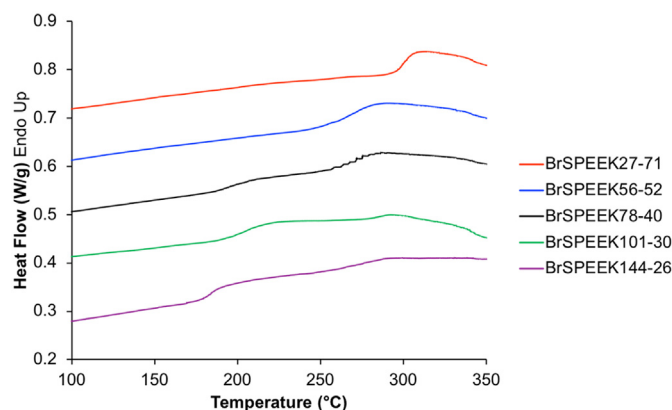


Fig. 3. DSC thermograms of BrSPEEK membranes in Cs^+ -form. The heat following a quench cool from the melt is shown.

backbone [47]. These peaks are more intense for BrSPEEK27-71 than BrSPEEK144-26 because of its higher degree of sulfonation [49].

3.2. Thermal properties of blocky BrSPEEK membranes

Due to the high solubility of BrSPEEK in polar aprotic solvents, BrSPEEK solutions were readily cast from DMAc to form tough, creaseable membranes. The thermal properties of the resultant membranes were analyzed using DSC, as shown in Fig. 3. All blocky BrSPEEK membranes are completely amorphous, indicating that all (or most) of the crystalline domains within the initial blocky BrPEEK have been functionalized. At high degrees of bromination, the BrSPEEK78-40, BrSPEEK101-30, and BrSPEEK144-26 samples all show two distinct glass transitions in the DSC thermograms. This dual T_g behavior, commonly observed in conventional block copolymers, is clear evidence that the gel-state functionalization process creates a well-defined blocky microstructure such that bromine-dense “blocks” phase separate from the ion-dense “blocks”, resulting in a low T_g and a high T_g for the brominated and sulfonated “blocks,” respectively. The T_g 's determined from the DSC thermograms are shown in Table 2. As the degree of bromination decreases (and degree of sulfonation increases), the low temperature glass transition decreases in magnitude and the high temperature glass transition increases in magnitude, consistent with the change in functionalization. At high degrees of sulfonation (i.e. BrSPEEK56-52, BrSPEEK27-71), only one glass transition temperature is observed at high temperatures, associated with the T_g of the sulfonated blocks. It is likely that at these lower degrees of bromination, the electrostatic network dominates the mobility of the polymer chains, and thus it is difficult to observe a T_g from the brominated blocks [50]. Overall, the DSC results suggest that the blocky BrSPEEK copolymers are forming phase-separated microstructures, attributed to a distinct blocky character, that results in multiple glass transitions.

To further elucidate the multi-phase behavior of the blocky BrSPEEK copolymers, dynamic mechanical analysis (DMA) was performed. Fig. 4 compares the $\tan\delta$ profiles of blocky BrSPEEK27-71, BrSPEEK78-40, and BrSPEEK144-26. Similar to the DSC results, two transitions are observed for BrSPEEK78-40 and BrSPEEK144-26, and

Table 2
Glass transition temperature(s) of blocky BrSPEEK samples.

Sample	T_{g1} (°C)	T_{g2} (°C)
BrSPEEK27-71	–	302
BrSPEEK56-52	–	272
BrSPEEK78-40	198	280
BrSPEEK101-30	201	293
BrSPEEK144-26	184	275

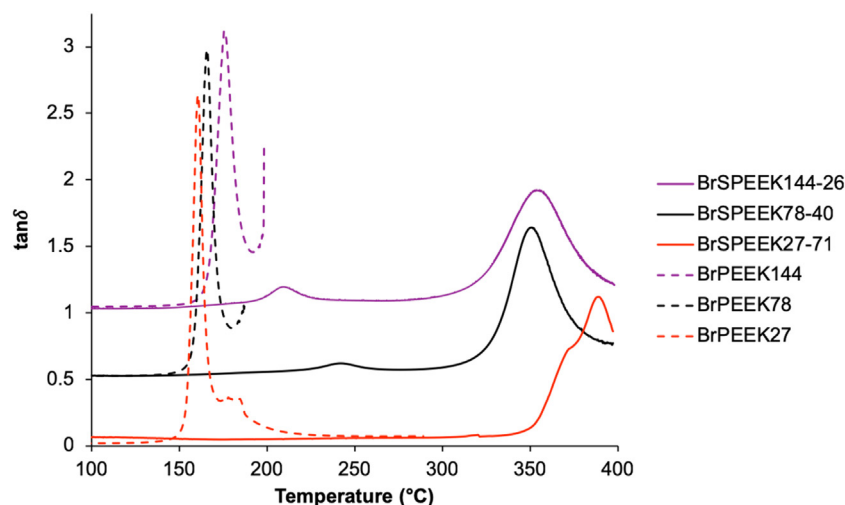


Fig. 4. $\tan\delta$ of blocky BrSPEEK27-71, BrSPEEK78-40, and BrSPEEK144-26 and blocky BrPEEK27, BrPEEK78, and BrPEEK144 starting material. All BrSPEEK samples are in Na^+ -form.

one transition is observed for BrSPEEK27-71. Again, the lower temperature transition is attributed to the glass transition of the brominated blocks while the upper temperature is attributed to the SPEEK blocks and is due to the onset of long-range mobility upon destabilization of the electrostatic network [51]. Comparison of the T_g 's from $\tan\delta$ to the starting blocky BrPEEK copolymers demonstrates that the T_g associated with the brominated blocks is higher for the BrSPEEK copolymers. This difference in T_g is likely due to restriction of mobility in the brominated blocks by the electrostatic network or by a small degree of phase-mixing between the brominated and sulfonated blocks. Because the length of the blocks is controlled by the semicrystalline microstructure of the PEEK gel (during bromination), it is likely that the blocks in these copolymers are relatively short compared to conventionally synthesized multiblock copolymers [32]. Thus, brominated blocks will likely be in close proximity to the ionic aggregates, thereby restricting their mobility and leading to a higher T_g than in the unsulfonated blocky BrPEEK copolymers. It is also of interest to note that the magnitude of $\tan\delta$ peak for the sulfonated blocks is much higher than the magnitude of the $\tan\delta$ peak for the brominated blocks. This is due to a much greater change in the loss modulus as the ionic phase transitions into a dynamic network. Thus, in agreement with our DSC results, it is clear that the electrostatic network is dominating the mobility of the polymer chains.

The location of the glass transition temperatures observed in $\tan\delta$ is dependent on the sulfonate counterion, as shown in Fig. 5. Blocky BrSPEEK144-26 shows similar $\tan\delta$ peaks in Na^+ -form and Cs^+ -form, however the peak locations are at higher temperatures for Na^+ -form

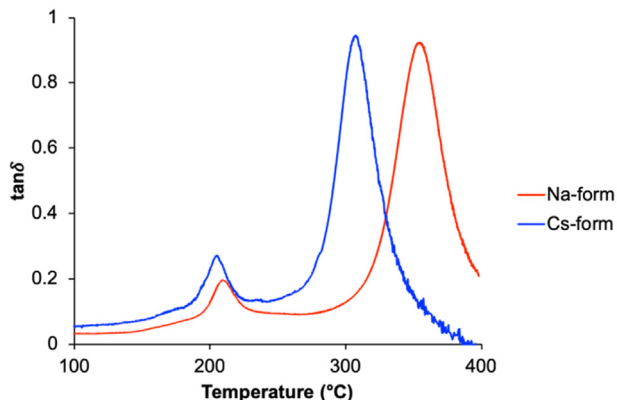


Fig. 5. $\tan\delta$ of blocky BrSPEEK144-26 in Na^+ -form and Cs^+ -form.

than Cs^+ -form. As the size of the counterion increases, the charge becomes more delocalized and the electrostatic attractive forces are weaker between ion pairs within the ionic aggregate [52,53]. Thus, changing the counterion from Na^+ to Cs^+ weakens the electrostatic network and decreases the T_g of the sulfonated blocks significantly. It is also important to note that the peak attributed to the BrPEEK blocks shifts to lower temperatures when changing from Na^+ to Cs^+ counterions, further confirming that the brominated blocks are influenced by the strength of the electrostatic network due to their close proximity to sulfonated blocks.

To confirm that the multiple transitions observed for the blocky BrSPEEK copolymers using DSC and DMA are accurately attributed to phase-separation of the brominated and sulfonated blocks, a simple blend of sulfonated PEEK and brominated PEEK was prepared. Random SPEEK52 and random BrPEEK150 were dissolved at a 1:1 (w:w) ratio in DMAc and were cast onto glass at 80 °C. Blend membranes were converted into Na^+ -form and were analyzed using DSC and DMA. As shown in Fig. 6, the blend of SPEEK and BrPEEK shows two distinct glass transitions that are readily attributed to the glass transitions of the two components. The T_g 's do not change upon blending, and there is no evidence of miscibility and phase mixing between the SPEEK and BrPEEK. The multi-phase behavior of the SPEEK/BrPEEK blend closely resembles that of the blocky BrSPEEK copolymers, suggesting that the blocky BrSPEEK undergoes phase separation between the brominated and sulfonated blocks.

3.3. Blocky BrSPEEK membrane properties

Water uptake is an important parameter dictating not only the proton conductivity but also the mechanical stability of proton exchange membranes [54]. The gravimetric water uptake, λ , and areal swelling of the as-cast blocky BrSPEEK membranes (H^+ -form) is shown in Fig. 7. The results are compared to random SPEEK prepared by sulfonation in DCA. As expected, water uptake and areal swelling increases with increasing degree of sulfonation for all samples due to the introduction of more hydrophilic acid sites. Overall, on a per mol% sulfonation basis, blocky BrSPEEK membranes exhibit considerably less water uptake and areal swelling than random SPEEK membranes. This effect is magnified at high degrees of sulfonation (i.e. > 40 mol%), where random SPEEK membranes tend to over-swell in water as noted by the sharp climb in water uptake, λ , and areal swelling with increasing degree of sulfonation. In contrast, blocky BrSPEEK membranes exhibit a more gradual rise in water uptake and dimensional swelling with increasing degree of sulfonation. It is evident that the hydrophobic

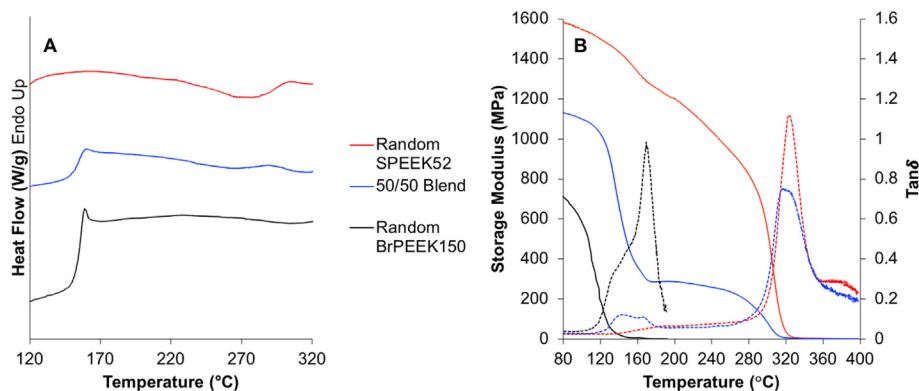


Fig. 6. DSC (A) and DMA (B) thermograms of random SPEEK52, random BrPEEK150, and a 50/50 blend of the two.

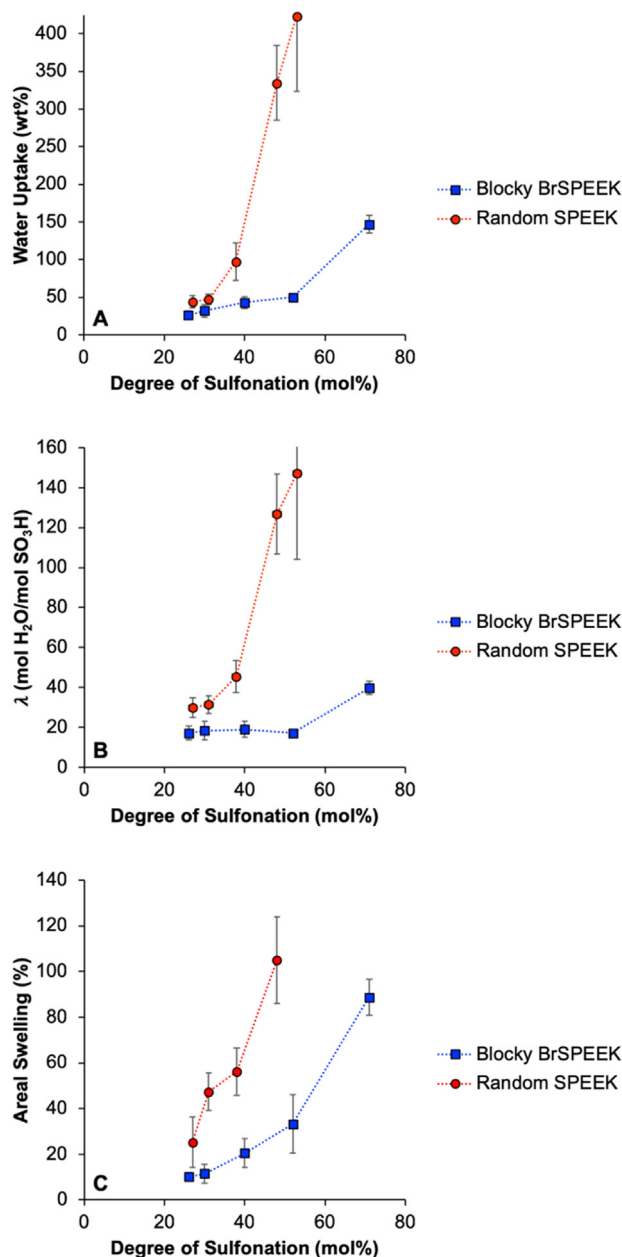


Fig. 7. Gravimetric water uptake (A), λ (B), and areal swelling (C) as a function of degree of sulfonation for blocky BrSPEEK and random SPEEK.

bromine blocks limit the total water uptake and enable control over swelling, especially at high degrees of sulfonation.

The conductivity of fully-hydrated BrSPEEK membranes in water at room temperature is shown in Fig. 8A. Conductivity increases with increasing degree of sulfonation, and little difference is observed between the conductivity of BrSPEEK and random SPEEK at similar degrees of sulfonation. When compared to SPEEK prepared by conventional means [55–57] (i.e. sulfonation in H_2SO_4), however, BrSPEEK membranes exhibit profoundly improved proton conductivity, likely due to the more controlled sulfonation microstructure. It is also important to note that at high degrees of sulfonation BrSPEEK27-71 approaches the conductivity of Nafion® (77 mS/cm). Surprisingly, the random SPEEK also produces comparably high conductivity on a per mol% sulfonate group basis, relative to the conventional SPEEK. This is also likely a result of an improved distribution of functional groups along the chains attributed to our “dissolution first, then sulfonate” process using the non-sulfonating solvent DCA. In contrast, the conventional sulfonation process, using concentrated H_2SO_4 , involves simultaneous dissolution and sulfonation, which likely leads to a very heterogeneous degree of sulfonation from chain to chain (i.e., the first chains to dissolve are in contact with the sulfonating reagent for a much longer time, leading to higher degrees of sulfonation), compared to the lightly sulfonated chains that were last to dissolve. Thus, the polar domains in the conventional SPEEK are presumably less ordered with more heterogeneous percolation pathways for the transport of protons and water – leading to lower conductivity.

Despite the similar proton conductivities for as-cast BrSPEEK and random SPEEK as a function of degree of sulfonation, it is important to consider the differences in water uptake among these samples. The conductivity as a function of λ is shown in Fig. 8B. Clearly, the blocky BrSPEEK membranes exhibit improved proton transport at much lower λ than random SPEEK. The blocky BrSPEEK membranes are capable of undergoing hydrophilic-hydrophobic phase separation, as shown by the multi-phase behavior in DSC and DMA. This phase separation creates continuous hydrophilic domains that enable efficient proton transport at lower water contents compared to the random system. In contrast, the sulfonic acid groups on the random SPEEK likely form discrete polar aggregates that are not well inter-connected. Thus, to successfully connect the polar domains and achieve adequate proton transport, high water contents are necessary for random SPEEK.

The conductivity of as-cast BrSPEEK78-40 as a function of humidity at 80 °C is shown in Fig. 9, as compared to the benchmark Nafion®, random SPEEK42, and blocky SPEEK41. The blocky SPEEK41 sample was prepared by gel-state sulfonation in 1,2-dichloroethane, as described in our previous work [31]. Blocky BrSPEEK78-40 exhibited improved proton transport compared to random SPEEK42 at all humidity values examined. Furthermore, the conductivity of blocky BrSPEEK78-40 approaches that of blocky SPEEK41 and Nafion® at high humidity. These results further reiterate the improved hydrophilic-

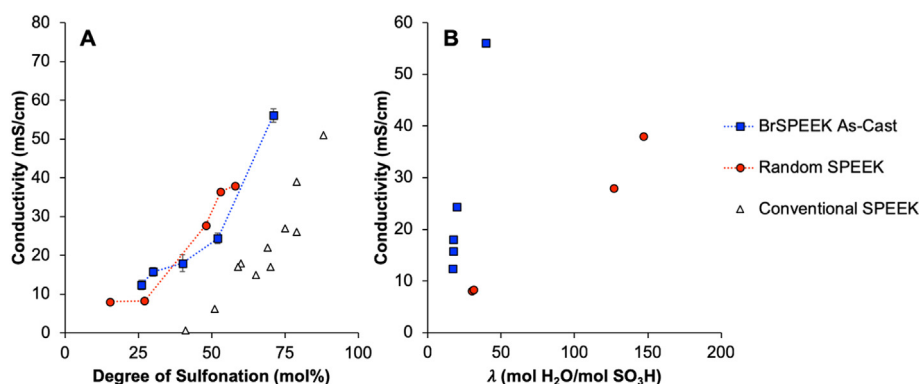


Fig. 8. Conductivity of as-cast blocky BrSPEEK, random SPEEK, and conventional SPEEK from literature [56–58] in water at room temperature as a function of degree of sulfonation (A) and λ (B).

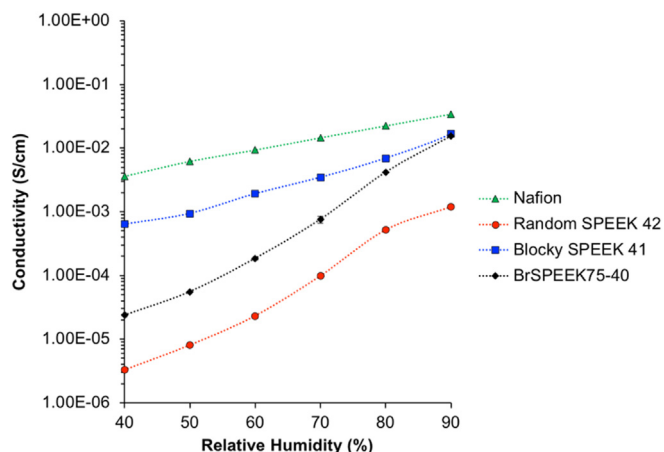


Fig. 9. Conductivity of Nafion®, random SPEEK at 42 mol% sulfonation, blocky SPEEK at 41 mol% sulfonation, and blocky BrSPEEK75-40 as a function of relative humidity. Measurements were conducted at 80 °C.

hydrophobic phase separation of blocky BrSPEEK copolymers compared to random SPEEK copolymers. Continuous hydrophilic domains are created even at low water contents (i.e. low humidity), creating less tortuous paths for proton transport. The difference in proton conductivity between blocky BrSPEEK78-40 and blocky SPEEK41 at low humidity likely stems from semicrystalline nature of blocky SPEEK41, which helps drive ionic aggregation into small, closely-spaced domains [31]. Regardless, it is evident that the blocky architecture of the BrSPEEK copolymers contributes significantly to improved proton transport and more controlled water uptake due to hydrophilic-hydrophobic phase separation. Future efforts will focus on annealing studies to further improve the conductivity of the blocky BrSPEEK membranes in hopes of surpassing the performance of the benchmark Nafion®. Likewise, the influence of gel concentration and morphology on block length and membrane performance will be investigated as a means to improve conductivity.

3.4. Ionomer morphology

The ionic aggregate morphology of the BrSPEEK membranes was investigated using small-angle x-ray scattering (SAXS) at Argonne National Laboratory. The SAXS scattering profiles of the as-cast blocky BrSPEEK membranes in Cs⁺-form are shown in Fig. 10A. A clear ionomer peak at approximately $q = 0.25 \text{ \AA}^{-1}$ is observed, and this peak increases in intensity with increasing degree of sulfonation [58]. Furthermore, the ionomer peak shifts slightly to higher q with increasing degree of sulfonation, suggesting a decrease in the inter-aggregate distance. The center-to-center distance between ionic aggregates was

quantified by determining the Bragg spacing of the ionomer peak ($d_{\text{Bragg}} = 2\pi/q$) [59] (see Supplementary material Table S1), and the Bragg spacing decreased nominally from 26 Å to 22 Å with increasing degree of sulfonation.

For comparison, the SAXS profiles of random SPEEK with degrees of sulfonation from 20 to 53 mol% are shown in Fig. 10B. A pronounced ionomer peak is present that shifts from $q \approx 0.1 \text{ \AA}^{-1}$ to $q \approx 0.3 \text{ \AA}^{-1}$ as the degree of sulfonation increases from 20 to 53 mol%. Thus, the distance between ionic aggregates decreases from 45 Å to 27 Å with increasing degree of sulfonation. Based on these results, it is apparent that the ionomer morphology and inter-aggregate distance is much more dependent on the degree of sulfonation for random SPEEK than for blocky BrSPEEK. Furthermore, blocky BrSPEEK membranes exhibit smaller inter-aggregate spacings than random SPEEK at similar degrees of sulfonation; which, in correlation with the improved proton conductivity, suggests a more closely-packed, interconnected ionomer morphology due to the hydrophobic-hydrophilic phase separation of blocky BrSPEEK.

The ionomer peaks of blocky BrSPEEK and random SPEEK were further analyzed using the Kinning-Thomas modified hard sphere model [60]. The core ionic radius (R), the radius of closest approach (R_{ca}), and the inter-particle radius (R_{ip}) determined using this method are shown in Table 3. Ionomer radii around 3–5 Å and R_{ca} around 8.5–10.5 Å were determined for as-cast BrSPEEK membranes using this analysis. No specific trend in R or R_{ca} is observed with increasing degree of sulfonation, suggesting that blocky BrSPEEK forms similar sized ionic aggregates independent of ion content. This result is consistent with the work of Weiss, who demonstrated that ionic aggregate size in a sulfonated poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) block copolymer was insensitive to the degree of sulfonation [61]. In contrast, the R of random SPEEK decreases systematically from 8.3 to 3.1 Å and R_{ca} decreases from 19.2 to 13.0 Å as the degree of sulfonation increases. Thus, by blocking up the ionic aggregates in BrSPEEK, more consistent ionic aggregate morphologies are obtained due facile hydrophobic-hydrophilic phase separation and the close proximity of sulfonate groups along the polymer chain within the sulfonated “blocks.” Moreover, for both blocky BrSPEEK and random SPEEK, R_{ip} decreases with increasing degree of sulfonation, suggesting more closely spaced ionic aggregates as was observed with the Bragg spacing analysis.

4. Conclusions

In this work, blocky BrSPEEK copolymers were prepared by sulfonation of blocky BrPEEK using H₂SO₄. The resultant degree of sulfonation depended on the initial blocky BrPEEK templating, and increasing degree of sulfonation was observed with decreasing bromine content in the initial blocky BrPEEK. Distinct multi-phase behavior was observed using DSC and DMA for blocky BrSPEEK membranes at degrees of sulfonation up to 40 mol%, suggesting phase-separation

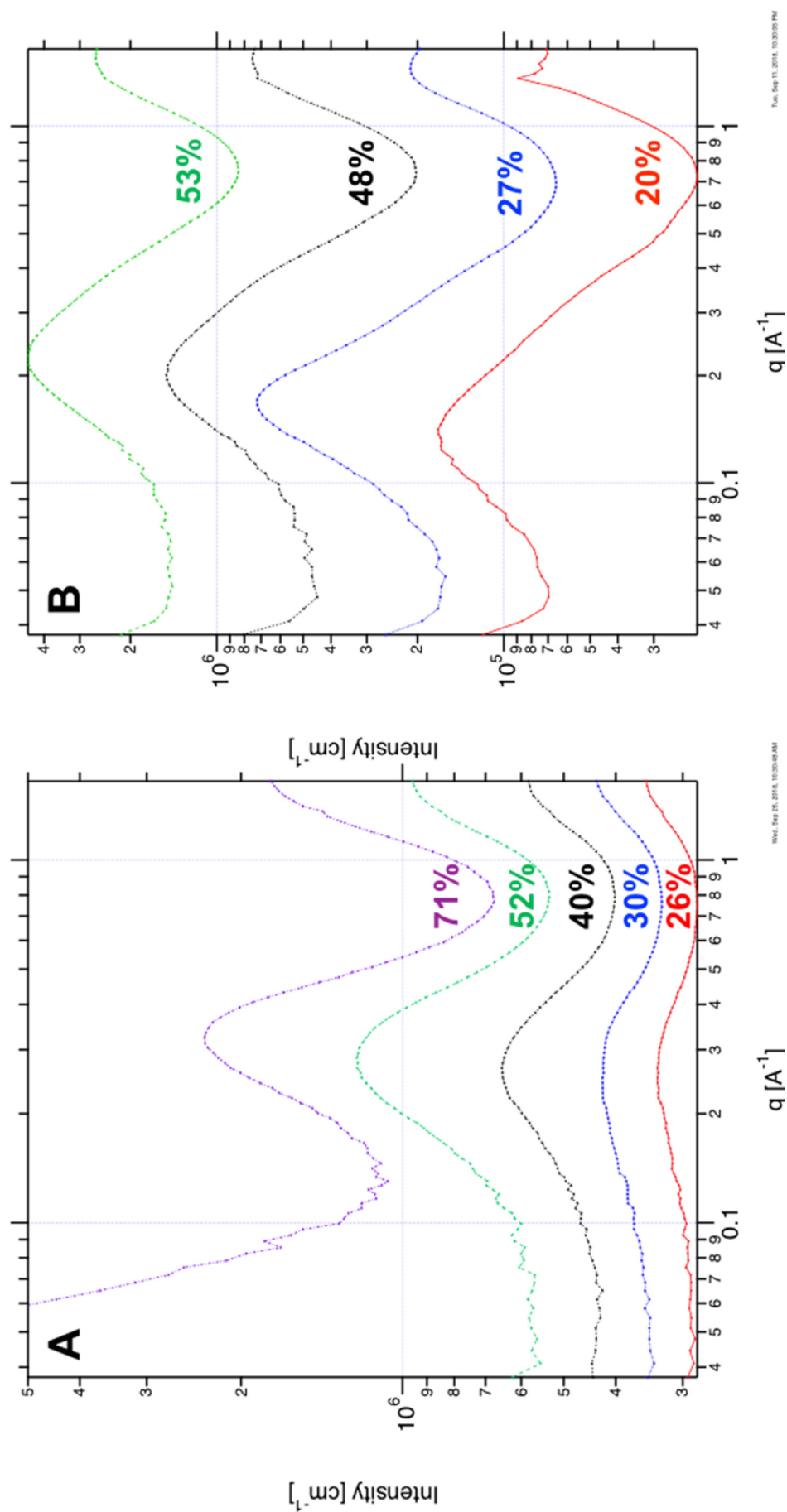


Fig. 10. SAXS profiles of as-cast blocky BrSPEEK (A) and as-cast random SPEEK (B) at various degrees of sulfonation. All samples are in Cs^+ -form.

Table 3

Ionomer radius (R), radius of closest approach (R_{ca}), and inter-particle radius (R_{ip}) of BrSPEEK membranes determined by fitting to the Kinning-Thomas model.

Sample	DS (mol%)	R (Å)	R_{ca} (Å)	R_{ip} (Å)
Blocky BrSPEEK27-71	71	3.0 ± 0.2	9.7 ± 0.1	17.8 ± 0.2
Blocky BrSPEEK56-52	52	5.0 ± 0.1	10.1 ± 0.1	19.8 ± 0.2
Blocky BrSPEEK78-40	40	4.4 ± 0.1	9.8 ± 0.1	22.8 ± 0.2
Blocky BrSPEEK101-30	30	3.9 ± 0.1	8.5 ± 0.2	29.6 ± 1.0
Blocky BrSPEEK144-26	26	3.7 ± 0.1	10.5 ± 0.2	36.8 ± 1.8
Random SPEEK53	53	3.1 ± 0.2	13.0 ± 0.1	23.2 ± 0.9
Random SPEEK48	48	4.9 ± 0.2	12.2 ± 0.1	22.8 ± 1.0
Random SPEEK27	27	7.6 ± 0.2	16.7 ± 0.1	28.9 ± 0.3
Random SPEEK20	20	8.3 ± 0.3	19.2 ± 0.3	37.2 ± 1.5

between the brominated blocks and sulfonated blocks into hydrophobic and hydrophilic domains, respectively. SAXS analysis revealed similar ionic-aggregate sizes for blocky BrSPEEK membranes at all degrees of functionality, and ionic aggregates became more closely spaced with increasing degree of sulfonation. Improved dimensional stability upon swelling and enhanced proton transport at lower water content were observed for blocky BrSPEEK membranes compared to random SPEEK ionomers due to the hydrophilic-hydrophobic phase separation and a closer packing of ionic aggregates, resulting in improved order within the blocky hydrophilic domains.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ssi.2019.03.006>.

References

- [1] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Lee, *Prog. Polym. Sci.* 36 (11) (2011) 1443.
- [2] S.J. Peighambari, S. Rowshanzamir, M. Amjadi, *Int. J. Hydrog. Energy* 35 (17) (2010) 9349.
- [3] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, *J. Membr. Sci.* 219 (1) (2003) 113.
- [4] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *J. Membr. Sci.* 229 (1–2) (2004) 95.
- [5] L. Li, J. Zhang, Y. Wang, *J. Membr. Sci.* 226 (1) (2003) 159.
- [6] R.Y.M. Huang, P. Shao, C.M. Burns, X. Feng, *J. Appl. Polym. Sci.* 82 (11) (2001) 2651.
- [7] Y.Z. Fu, A. Manthiram, *J. Power Sources* 157 (1) (2006) 222.
- [8] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, *Solid State Ionics* 145 (1) (2001) 47.
- [9] A. Noshay, L.M. Robeson, *J. Appl. Polym. Sci.* 20 (7) (1976) 1885.
- [10] R. Guan, H. Zou, D. Lu, C. Gong, Y. Liu, *Eur. Polym. J.* 41 (7) (2005) 1554.
- [11] R. Nolte, K. Ledjeff, M. Bauer, R. Mülhaupt, *J. Membr. Sci.* 83 (2) (1993) 211.
- [12] K. Matsumoto, T. Higashihara, M. Ueda, *Macromolecules* 42 (4) (2009) 1161.
- [13] F. Wang, M. Hickner, Q. Ji, W. Harrison, J. Mecham, T.A. Zawodzinski,

- J.E. McGrath, *Macromol. Symp.* 175 (1) (2001) 387.
- [14] M. Andrew, T. Mukundan, J.E. McGrath, *J. Bioact. Compat. Polym.* 19 (4) (2004) 315.
- [15] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (1) (2002) 231.
- [16] Y. Chang, Y.-B. Lee, C. Bae, *Polymers* 3 (1) (2011) 222.
- [17] K.D. Kreuer, *J. Membr. Sci.* 185 (1) (2001) 29.
- [18] Y.-G. Jeong, D.-W. Seo, Y.-D. Lim, H.-M. Jin, M.S. Islam Mollah, S.-C. Ur, S.-Y. Pyun, W.-G. Kim, *Electrochim. Acta* 55 (4) (2010) 1425.
- [19] H. Ghassemi, J.E. McGrath, T.A. Zawodzinski Jr., *Polymer* 47 (11) (2006) 4132.
- [20] X. Yu, A. Roy, S. Dunn, A.S. Badami, J. Yang, A.S. Good, J.E. McGrath, *J. Polym. Sci. A Polym. Chem.* 47 (4) (2009) 1038.
- [21] K.B. Wiles, C.M. de Diego, J. de Abajo, J.E. McGrath, *J. Membr. Sci.* 294 (1) (2007) 22.
- [22] R. Abhishek, H.M. A., Y. Xiang, L. Yanxiang, G.T. E., M.J. E., *J. Polym. Sci. B Polym. Phys.* 44 (16) (2006) 2226.
- [23] L. Assumma, C. Jojoiu, R. Mercier, S. Lyonard, H.D. Nguyen, E. Planes, *J. Polym. Sci. A Polym. Chem.* 53 (16) (2015) 1941.
- [24] B. Bae, K. Miyatake, M. Uchida, H. Uchida, Y. Sakiyama, T. Okanishi, M. Watanabe, *ACS Appl. Mater. Interfaces* 3 (7) (2011) 2786.
- [25] Y. Chen, R. Guo, C.H. Lee, M. Lee, J.E. McGrath, *Int. J. Hydrog. Energy* 37 (7) (2012) 6132.
- [26] Y.A. Elabd, M.A. Hickner, *Macromolecules* 44 (1) (2011) 1.
- [27] M.S. Jung, T.-H. Kim, Y.J. Yoon, C.G. Kang, D.M. Yu, J.Y. Lee, H.-J. Kim, Y.T. Hong, *J. Membr. Sci.* 459 (2014) 72.
- [28] A. Roy, M.A. Hickner, X. Yu, Y. Li, T.E. Glass, J.E. McGrath, *J. Polym. Sci. B Polym. Phys.* 44 (16) (2006) 2226.
- [29] *Membranes for Energy Conversion*
- [30] G.B. Fahs, S.D. Benson, R.B. Moore, *Macromolecules* 50 (6) (2017) 2387.
- [31] L.J. Anderson, X. Yuan, G.B. Fahs, R.B. Moore, *Macromolecules* 51 (16) (2018) 6226.
- [32] K.F. Noble, A.M. Noble, S.J. Talley, R.B. Moore, *Polym. Chem.* 9 (41) (2018) 5095.
- [33] T.R. Bock, *Catalytic Phosphonation of High Performance Polymers and POSS - Novel Components for Polymer Blend and Nanocomposite Fuel Cell Membranes*, Albert-Ludwig University, Freiburg, Germany, 2006.
- [34] W.H. Ferrell, D.I. Kushner, M.A. Hickner, *J. Polym. Sci. B Polym. Phys.* 55 (2017) 1365.
- [35] S.J. Talley, C.L. Anderson-Schoepe, C.J. Berger, K.A. Leary, S.A. Snyder, R.B. Moore, *Polymer* 126 (Supplement C) (2017) 437.
- [36] S.J. Talley, X. Yuan, R.B. Moore, *ACS Macro Lett.* 6 (3) (2017) 262.
- [37] Y. Xu, N. Ye, D. Zhang, J. Yang, R. He, *J. Colloid Interface Sci.* 497 (2017) 333.
- [38] P. Knauth, H. Hou, E. Bloch, E. Sgreccia, M.L. Di Vona, *J. Anal. Appl. Pyrolysis* 92 (2) (2011) 361.
- [39] B.T. Koziara, E.J. Kappert, W. Ogieglo, K. Nijmeijer, M.A. Hempenius, N.E. Benes, *Macromol. Mater. Eng.* 301 (1) (2016) 71.
- [40] J. Ilavsky, F. Zhang, A.J. Allen, L.E. Levine, P.R. Jemian, G.G. Long, *Metall. Mater. Trans. A* 44 (1) (2013) 68.
- [41] J. Ilavsky, P.R. Jemian, Irena: Tool Suite for Modeling and Analysis of Small Angle Scattering, (2009).
- [42] J. Ilavsky, *J. Appl. Crystallogr.* 45 (2) (2012) 324.
- [43] K. Rajesh, M. Somasundaram, R. Saiganesh, K.K. Balasubramanian, *J. Org. Chem.* 72 (15) (2007) 5867.
- [44] J.X. Duan, L.H. Zhang, W.R. Dolbier, A Convenient New Method for the Bromination of Deactivated Aromatic Compounds, (1999).
- [45] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *J. Membr. Sci.* 173 (1) (2000) 17.
- [46] A.G. Al Lafi, *J. Appl. Polym. Sci.* 132 (2) (2015) (n/a).
- [47] D. Shukla, Y.S. Negi, V. Kumar, *J. Appl. Chem.* (2013) (2013) 7.
- [48] C. Perrot, L. Gonon, C. Marestin, A. Morin, G. Gebel, *J. Power Sources* 195 (2) (2010) 493.
- [49] J. Devaux, D. Delimoy, D. Daoust, R. Legras, J.P. Mercier, C. Strazielle, E. Nield, *Polymer* 26 (13) (1985) 1994.
- [50] K.A. Page, K.M. Cable, R.B. Moore, *Macromolecules* 38 (15) (2005) 6472.
- [51] J.-M. Song, J. Shin, J.-Y. Sohn, Y.C. Nho, *Macromol. Res.* 20 (5) (2012) 477.
- [52] E.B. Orlor, B.H. Calhoun, R.B. Moore, *Macromolecules* 29 (18) (1996) 5965.
- [53] E.B. Orlor, R.B. Moore, *Macromolecules* 27 (17) (1994) 4774.
- [54] J. Alipour Moghaddam, M.J. Parnian, S. Rowshanzamir, *Energy* 161 (2018) 699.
- [55] R. Jiang, H.R. Kunz, J.M. Fenton, *J. Power Sources* 150 (2005) 120.
- [56] S. Kaliaguine, S. Mikhailenko, K. Wang, P. Xing, G. Robertson, M. Guiver, *Catal. Today* 82 (1) (2003) 213.
- [57] D.X. Luu, E.-B. Cho, O.H. Han, D. Kim, *J. Phys. Chem. B* 113 (30) (2009) 10072.
- [58] G. Gebel, *Macromolecules* 46 (15) (2013) 6057.
- [59] X. Li, G. Zhang, D. Xu, C. Zhao, H. Na, *J. Power Sources* 165 (2) (2007) 701.
- [60] D.J. Kinning, E.L. Thomas, *Macromolecules* 17 (9) (1984) 1712.
- [61] X. Lu, W.P. Steckle, R.A. Weiss, *Macromolecules* 26 (22) (1993) 5876.