



## Influence of processing history on water and salt transport properties of disulfonated polysulfone random copolymers

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### ABSTRACT

Disulfonated poly(arylene ether sulfone)s are high glass transition temperature polymers, and their water and salt transport properties depend sensitively on thermal processing history. In this study, films of a 32 mol% disulfonated poly(arylene ether sulfone) random copolymer (BPS-32), polymerized in the potassium counter-ion form, were acidified using solid state and solution routes. The resulting acid counter-ion form materials were then converted to sodium, potassium, and calcium counter-ion forms via ion exchange. Additionally, several films were subjected to various thermal treatments in the solid state. Water uptake as well as water and NaCl permeability of these BPS-32 films were measured. Acidification via immersion of BPS-32 films in boiling sulfuric acid solution increased water uptake, and water and salt permeability increased. Exposure of samples to elevated temperature also influenced transport properties. For example, immersing BPS-32 films in boiling water for 4 h increased water sorption by 50%, water permeability by 2.3 times, and NaCl permeability by 8 times. The counter-ion form of the sulfonated polymer influenced the polymer's transport properties, but these effects were weaker than the effect of thermal treatment. Generally, the BPS-32 samples prepared with different processing histories followed a trade-off between water/salt permeability selectivity and water permeability. These results suggest that, like many other glassy polymers, thermal processing history influences small molecule transport in these materials.

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### 1. Introduction

Disulfonated poly(arylene ether sulfone) random copolymers (BPS), synthesized by direct polymerization of sulfonated monomers, have been studied as potential desalination membrane materials [1–4]. These materials exhibit good tolerance to aqueous chlorine [2,5], and the polymer's water and salt transport properties can be tuned by varying the degree of sulfonation and counterion form. Such materials may also be of interest for other applications where control of water and ion transport properties is important, such as forward or pressure retarded osmosis [6–12], membrane-assisted capacitive deionization [13–18], electro dialysis [19–25] and reverse electro dialysis [26–34].

Interestingly, different transport properties are observed for acid and salt counter-ion form BPS polymers, with acid form materials exhibiting higher water uptake and water permeability but lower water/salt selectivity than salt form materials [4]. For

example, the pure water permeability of a film cast from the potassium salt form of the polymer having 35 mol percent disulfonated monomer and then converted to the acid form (BPSH-35) was  $2.1 \text{ L } \mu\text{m}/(\text{m}^2 \text{ h bar})$ ; its water/NaCl permeability selectivity was about 8.5, and its equilibrium pure water partition (or sorption) coefficient was 0.40 [4]. In a film cast from the potassium salt form of the same polymer (BPS-35), the pure water permeability was  $0.39 \text{ L } \mu\text{m}/(\text{m}^2 \text{ h bar})$ , more than 5 times lower than that of the acid form film. The water/NaCl permeability selectivity of BPS-35 was approximately 90, and its equilibrium water partition coefficient was 0.26 [4]. Presumably acid form samples undergo ion exchange during crossflow filtration (this hypothesis is tested in this study), so even initially acid form samples are in the salt form during crossflow filtration experiments [35], yet the transport properties still depend on the initial ionic form of the polymer prior to evaluation of permeation properties.

Furthermore, water and NaCl transport properties of BPS films have been correlated with free volume using positron annihilation lifetime spectroscopy (PALS). The PALS results also show differences between acid and salt form materials that are consistent with the observed changes in water sorption and transport properties

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[36]. Such history dependence motivated this study to further explore such effects in BPS polymers via their water and salt transport properties.

Cation exchange membranes prepared from sulfonated materials have been widely studied as fuel cell membranes, and thermal processing history influences conductivity and water uptake [37–41]. However, few studies focus on the influence of processing history on water and salt transport [42–45]. Processing history is likely to have a significant effect on these materials because, even when hydrated, many of these polymers are glassy, so their transport properties could and should depend upon thermal processing history [46–48].

Berezina et al. [43] reported the influence of processing history on water uptake and electro-transport properties of perfluorinated sulfonated polymer membranes (Nafion®). For example, heating membranes in aqueous salt or acid solutions increased water uptake and water permeability, and the duration of the thermal treatment further influenced membrane transport properties [43]. Characterization of sulfonated polymers prepared in different alkali counter-ion forms shows the influence of counter-ion form on water uptake and transport properties [43,49,50]. This observation was attributed to differences in cation-sulfonate binding affinity [42,51]. The influence of thermal processing history on water uptake and hydraulic permeability was also reported for Nafion films [44,45]. Thermal treatment of Nafion in water, salt solutions, or basic solutions increased water uptake and permeability; these effects were ascribed to morphological rearrangement [44].

This study investigates the influence of processing history on water and salt transport properties of BPS-32, which, unlike the perfluorinated polymers discussed above, is an aromatic polysulfone-based polymer. The polymer was conditioned via acid treatment, thermal treatment, and ion exchange, and the effect of solution and solid state acidification on film properties was investigated. We explore thermal treatments because previous film samples were converted from the potassium salt to acid form by boiling the potassium salt form films in aqueous 0.5 M sulfuric acid for 2 h followed by boiling for 2 h in deionized water to eliminate excess acid, and we wished to separate the influence of exposure to acid and exposure to elevated temperature on transport properties [2,4,52,53]. Free volume theory was used to help rationalize the results. One objective of these studies is to understand more completely the range over which salt and water transport properties may be manipulated by processing protocols as opposed to varying the chemical structure of the polymer, so the results of the current studies are placed in perspective by comparing with the influence of changing chemical structure, at fixed thermal processing history, on water and ion transport properties.

## 2. Experimental

### 2.1. Materials and chemicals

A 32 mol% disulfonated poly(arylene ether sulfone) random copolymer (BPS-32, Fig. 1) was prepared in the potassium counter-

ion form by direct aromatic nucleophilic substitution step polymerization, as reported previously [52,54]. The following chemicals were purchased from Fisher Scientific (Hampton, NH) and used as received unless otherwise noted: sodium chloride (NaCl, cat. #S78449), potassium chloride (KCl, cat. #P217-500), calcium chloride (CaCl<sub>2</sub>, cat. #C79-500), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 96%, cat. #A300-212), 0.1 M sodium hydroxide solution (NaOH, cat. # 1310-73-2), and 0.1 M hydrochloric acid solutions (HCl, cat. #7647-01-0). Solvents N,N-dimethylacetamide (DMAc, ≥99%, cat. #D5511) and dimethyl sulfoxide (DMSO, ≥99.5%, cat. #D4540) were purchased from Sigma–Aldrich (St. Louis, MO) and used as received. De-ionized (DI) water was generated using a Milli-Q Advantage A10 water purification system (Millipore, Billerica, MA).

### 2.2. Film preparation and conditioning

A 10 wt.% solution of BPS-32 in DMAc was filtered through an 0.45 μm PTFE syringe filter (cat. #Z260339, Sigma–Aldrich, St. Louis, MO). The solution was degassed under vacuum at room temperature for 24 h before being poured onto a glass plate and placed under an IR lamp (60–70 °C) for at least 8 h to begin the solvent removal process. Next, the film was placed in an oven under vacuum at 150 °C for 6 h to further remove solvent. Finally, a BPS-32 dense film was obtained by peeling the polymer off the glass plate while submerged in DI water. All films were stored in DI water until use to fully hydrate the films and extract residual solvent. Typical wet films were 40–70 μm thick. Films prepared in this manner are labeled “K” in Fig. 2 and represent films cast from polymer initially in the potassium salt form, which is the ionic form resulting from the synthesis process [55].

Fig. 2 presents a summary of the sample nomenclature and history. Some BPS-32 films were acidified in the solid state by boiling them in 0.5 M sulfuric acid for 2 h followed by boiling in DI water for 2 h (Sample K-HB in Fig. 2); this treatment was used previously to convert films of potassium form polymer to the acid form [2,4,52,53].

Alternatively, BPS-32 was acidified in solution by dissolving the polymer in DMSO and adding 0.5 M sulfuric acid at a ratio of 64 mols of H<sub>2</sub>SO<sub>4</sub> per equivalent of sulfonated polymer. Upon adding acid to the polymer solution, the polymer precipitated and formed a gel. After 4 h of mixing this gel suspension at ambient conditions, the suspension was filtered, and the recovered polymer was boiled in DI water for 2 h; this boiling procedure was repeated two more times before the polymer was filtered, dried, and dissolved in DMAc to form a 10 wt.% solution. This solution was cast into acid form films using the casting, drying and hydration/extraction procedures described above; films prepared in this manner are labeled “H”.

The potassium and acid form films were cut into 4 cm diameter circular coupons. The water uptake and transport properties of these coupons (samples K and H in Fig. 2) were measured. Other samples were subjected to the various histories outlined in Fig. 2, and then their water uptake and transport properties were measured.

Acid (nomenclature: H) or salt (nomenclature: K, Na, and Ca) solution treatment involved immersing coupons in 200 mL of

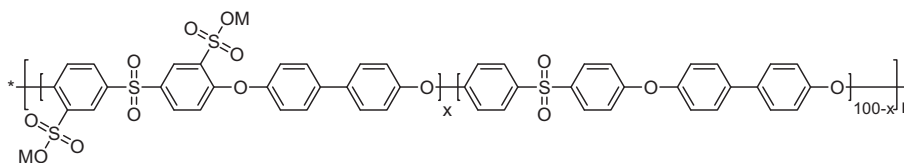
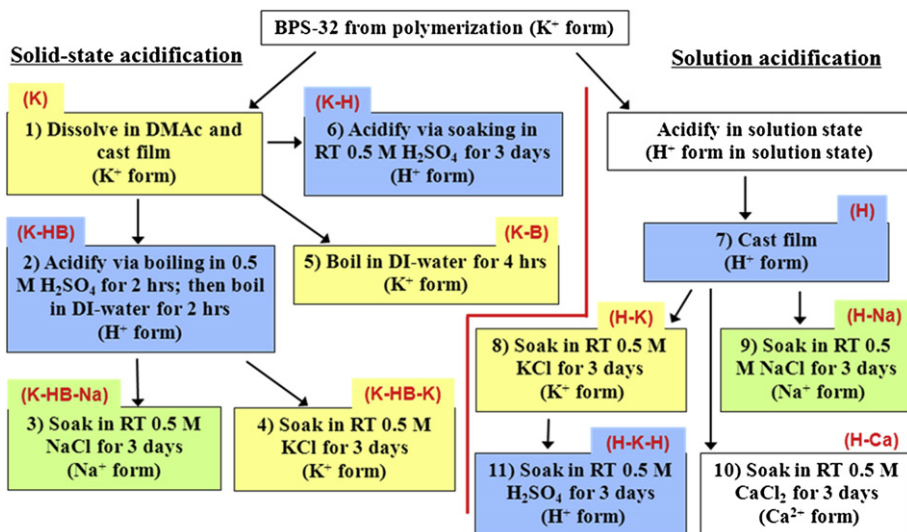


Fig. 1. Chemical structure of disulfonated poly(arylene ether sulfone) random copolymer BPS-32, M = H<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, or Ca<sup>+2</sup>. “x” represents the molar percentage of the sulfonated monomer, as a fraction of all sulfone-containing monomers, in the polymer structure. For the polymer used in this study, x = 32.



**Fig. 2.** Schematic diagram of processing history of BPS-32 samples. The first letter represents the ionic form of the original polymer (K: potassium form; H: acid form); the following letters represent the subsequent processing steps in the order that they were performed (K: soaked in ambient 0.5 M KCl solution; Na: soaked in ambient 0.5 M NaCl solution; Ca: soaked in ambient 0.5 M CaCl<sub>2</sub> solution; H: soaked in ambient 0.5 M H<sub>2</sub>SO<sub>4</sub> solution; B: boiled in water; HB: boiled in sulfuric acid and later in water). For example, the sample designation K-HB-Na means that a BPS-32 film originally in the potassium form (K) was boiled in 0.5 M sulfuric acid for 2 h and subsequently in water for 2 h (HB) and finally soaked in 0.5 M NaCl solution at room temperature (RT) for 3 days (Na). The final ionic form of the polymer, following the process history steps, is shown in parentheses (e.g., “K<sup>+</sup> form” represents a sample in the potassium salt form following the processing history shown in this figure).

0.5 M sulfuric acid or 0.5 M salt (NaCl, KCl, or CaCl<sub>2</sub>) solutions at room temperature for 3 days. The soaking solution was replaced with fresh solution one time per day. For example, sample K-H was originally a potassium salt form film that was acidified by soaking in ambient 0.5 M H<sub>2</sub>SO<sub>4</sub> for 3 days, and sample H-K is a solution acidified film that had been soaked in ambient 0.5 M KCl for 3 days.

Thermal treatment involved immersing polymer films in 800 mL of heated DI water at various temperatures (50 °C, 75 °C or 100 °C (i.e., boiling DI water)) for 4 h. Samples boiled in DI water are labeled “B”; for example, a potassium form sample boiled for 4 h in DI water is labeled “K-B”. Samples soaked in DI water at lower temperature are labeled with the soaking temperature; for example, K-50C represents a potassium salt form film that had been soaked in DI water at 50 °C for 4 h; these samples are not shown explicitly in Fig. 2 to simplify the figure, but they were prepared in the same manner as sample K-B except that the DI water soaking solution was 50 or 75 °C rather than boiling.

A combination of acid and thermal treatment (e.g., sample K-HB in Fig. 2) involved boiling polymer films in 800 mL of 0.5 M sulfuric acid for 2 h followed by boiling in 800 mL of DI water for 2 h.

### 2.3. Counter-ion form analysis

The polymer’s counter-ion form was determined using an ash analysis technique [50]. This procedure, which oxidizes the organic part of the sample, permits direct quantification of inorganic material, such as metal counter-ions, present in the polymer matrix [50,56–58]. Polymer samples, prepared as shown in Fig. 2, were soaked and equilibrated in a large volume of DI water prior to the counter-ion form measurement process to allow sorbed salt to desorb from the polymer, leaving only cations in the polymer matrix which were strongly bound to the sulfonate groups on the polymer backbone. Following this step, the volume of hydrated polymer was determined by measuring the diameter and thickness of the circular polymer discs; a typical hydrated sample was 4–5 cm in diameter and 40–70 μm thick depending on the treatment process. Samples were then dried under vacuum at 80 °C for

at least 48 h, and the sample’s dry mass was measured. Immediately following the dry mass measurement, the samples were placed in porcelain crucibles, and the crucibles were placed in a programmable forced-draft muffle furnace (Fisher Scientific Iso-temp<sup>®</sup> 750-58, Dubuque, IA) conforming to ASTM D3174 (determining inorganic residue in coal ash) [56]. The furnace temperature was ramped from room temperature to 700 °C at 10 °C/min and held at 700 °C for 3 h. Upon cooling to room temperature, the crucibles were removed from the furnace. A white polymer ash remained in the crucible. This ash was dissolved in 2% nitric acid (prepared from Fluka TraceSelect<sup>®</sup> grade nitric acid) by pouring a known amount of nitric acid into the crucible and pipette mixing the solution. Next, the solution was diluted, using 2% nitric acid, and analyzed for potassium and sodium concentration using a flame atomic absorption spectrophotometer (Varian AA240, Clayton South, Victoria, Australia) [59,60].

### 2.4. Polymer characterization

<sup>1</sup>H NMR spectra were collected using a Varian Unity 400 NMR spectrometer (Varian Analytical Instruments, Walnut Creek, CA) at a resonance frequency of 400 MHz. All spectra were obtained from a 10% solution (w/v) of polymer in DMSO-*d*<sub>6</sub> at room temperature. The <sup>1</sup>H NMR results were used to calculate the degree of sulfonation (or, equivalently, the ion exchange capacity (IEC)) of the as-synthesized polymer as described by Li et al. [55].

Differential scanning calorimetry (DSC), TA Instruments Q100 (New Castle, DE), was used to measure the polymer’s glass transition temperature, *T*<sub>g</sub>. Samples were placed in aluminum pans, and DSC scans were performed over a temperature range from –80 to 400 °C. Prior to loading in the pan, each sample was dried at 110 °C for one day under vacuum. During the scan, film samples were heated to 400 °C at 20 °C/min, held for 5 min, and then cooled to –80 °C at 10 °C/min. This cycle was repeated, and the second run was used to determine *T*<sub>g</sub>. The data were analyzed using TA Instruments Universal Analysis 2000 software. The glass transition temperature was taken as the midpoint of the heat capacity step change.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the chemical structure of BPS-32. The experiments were performed using a Thermo Nicolet Nexus 470 FTIR with an Avatar Smart Miracle ATR accessory and a ZnSe crystal (Thermo Fisher Scientific, Waltham, MA). Spectra were collected in air, in the mid-infrared region (600–4000  $\text{cm}^{-1}$ ), using 128 scans at resolution 4 (1.928  $\text{cm}^{-1}$  spacing) for each sample. After each measurement, a background spectrum was obtained and subtracted from the sample spectrum to eliminate atmospheric interference.

## 2.5. Transport property characterization

Water uptake was measured by equilibrating BPS-32 films in DI water at ambient conditions for 3 days. The water was changed one time per day to extract any residual solvent in the films. The film samples used for water uptake measurements were 150–250  $\mu\text{m}$  thick. The swollen polymer mass was periodically measured until a constant wet mass ( $m_h$ ) was obtained. Lint-free tissue paper was used to wipe the film surface to remove water droplets from the film's surfaces before weighing. Then, the hydrated film samples were dried under vacuum at 110  $^\circ\text{C}$  for at least 48 h. Samples were periodically weighed until a constant dry mass ( $m_d$ ) was obtained. While this procedure would perhaps not remove the small amount of water tightly bound to the sulfonate groups, it did remove the vast majority of water from the films [61–63]. The equilibrium volume fraction of water in the hydrated film,  $\phi_w$ , was estimated, assuming ideal mixing behavior, as follows [64]:

$$\phi_w = \frac{(m_h - m_d)/\rho_w}{(m_h - m_d)/\rho_w + m_d/\rho_p} \quad (1)$$

where  $\rho_p$  is the density of dry polymer and  $\rho_w$  is the density of water, 1.0  $\text{g}/\text{cm}^3$ . The density of dry BPS-32 was 1.351  $\text{g}/\text{cm}^3$  and was determined using the procedure described in Xie et al. [4].

Hydraulic water permeability,  $P_w^H$ , was measured using a high-pressure dead-end filtration system (Sterlitech TM HP4750 cell, Sterlitech Co., Kent, WA) with room temperature DI water used as feed. The active film area,  $A$ , in the test cell was 14.6  $\text{cm}^2$ . The transmembrane pressure difference,  $\Delta p$ , was 400 psi (27.6 bar), and the permeate pressure was atmospheric. Upon reaching steady state,  $P_w^H$  was calculated from the volume of permeate water,  $\Delta V$ , collected during time period  $\Delta t$ :

$$P_w^H = \frac{\Delta V \cdot L}{A \cdot \Delta t \cdot \Delta p} \quad (2)$$

where  $L$  is the average thickness of the hydrated film coupon.

For some samples, hydraulic water permeability was also measured using a crossflow filtration system as described previously [65]. The feed was an aqueous solution containing 2000 ppm (0.034 M) NaCl. Feed pH was adjusted to neutral using 0.1 M NaOH or HCl solutions. Feed flow rate was 1 gallon per minute (gpm) (3.8 L/min), giving an average crossflow velocity of 56  $\text{cm}/\text{s}$  and a Reynolds number of 3100. The applied pressure difference across the membrane was 400 psi (2.76 MPa or 27.6 bar), and the permeate pressure was atmospheric. Feed temperature was maintained at 25  $^\circ\text{C}$  using a refrigerated Neslab RTE 17 water bath (Thermo Fisher Scientific Inc., Waltham, MA). A carbon filter (KX CTO/2 carbon block carbon/5  $\mu\text{m}$  particle filter, Big Brand Water Filter, Chatsworth, CA) connected to the feed loop of the system continuously removed any contaminants (e.g., dust) that might inadvertently enter the system. Crossflow filtration was continued until the permeate flux had reached steady state, i.e., until the

volume of collected permeate increased linearly with time.  $P_w^H$  was calculated as follows:

$$P_w^H = \frac{\Delta V \cdot L}{A \cdot \Delta t \cdot (\Delta p - \Delta \pi)} \quad (3)$$

where  $\Delta \pi$  is osmotic pressure difference between the bulk feed and permeate solutions. The osmotic pressure,  $\pi$ , is related to NaCl concentration as follows [66]:

$$\pi = c_{\text{ion}}RT \quad (4)$$

where  $c_{\text{ion}}$  is the ion concentration in the feed or permeate solution.

A hydrostatic pressure difference across a film generates a water concentration gradient, and this concentration gradient drives diffusion of water molecules [67,68]. If the Flory–Huggins model [69,70] adequately describes the influence of water activity on water uptake, which should be a reasonable first approximation over the narrow range of water activities explored in these studies, the so-called diffusive water permeability,  $P_w$ , is related to the hydraulic water permeability as follows [67,71,72]:

$$P_w = K_w \cdot D_w = P_w^H \cdot \frac{RT}{V_w} \left[ (1 - K_w)^2 (1 - 2\chi K_w) \right] \quad (5)$$

where  $R$  is the ideal gas constant,  $\chi$  is the Flory–Huggins interaction parameter,  $T$  is absolute temperature,  $D_w$  is the concentration-averaged effective water diffusion coefficient, and  $V_w$  is the partial molar volume of water, which was taken to be 18  $\text{cm}^3/\text{mol}$  [73]. The term in brackets in Equation (5) accounts for the effect of convection on the transport of water through the polymer film [72]. The water partition or water solubility coefficient,  $K_w$ , is often equal to the volume fraction of water in the polymer [59]. The approximation,  $K_w \approx \phi_w$ , was used in this study [4,64]. Flory–Huggins theory was used to relate the activity of water,  $a_w$ , surrounding a hydrated polymer to the volume fraction of water in the polymer [69,70]:

$$\ln a_w = \ln K_w + (1 - K_w) + \chi(1 - K_w)^2 \quad (6)$$

An effective Flory–Huggins interaction parameter was estimated from measured pure water sorption, i.e.,  $a_w = 1$ , using Equation (6). The diffusive water permeability,  $P_w$ , was estimated using this effective Flory–Huggins parameter and Equation (5).

Salt permeability,  $P_s$ , was measured at 25  $^\circ\text{C}$  using a dual chamber direct permeation cell (Side-Bi-Side Cells, PermeGear, Hellertown, PA). Film coupons were clamped between the two chambers to prevent leakage. The volume,  $V$ , of solution added to each chamber was 35 mL. The active area available for mass transport, defined by the circular openings in the direct permeation cells, was 1.77  $\text{cm}^2$ . The donor chamber was initially filled with 0.1 M NaCl aqueous solution, and the other chamber, the receiver chamber, was initially filled with DI water. A magnetic stir-bar was used in each chamber to ensure that the solutions were well mixed. The conductivity of the receiver chamber solution was monitored as a function of time using a conductivity meter (InoLab Cond 730, WTW, Germany) equipped with a conductivity probe (LR 325/01, WTW, Germany). Conductivity was converted to salt concentration using a calibration curve. At pseudo-steady state, salt permeability,  $P_s$ , was calculated as follows [74]:

$$\ln \left[ 1 - 2 \frac{c_R(t)}{c_D(0)} \right] \left[ -\frac{VL}{2A} \right] = P_s t \quad (7)$$

where  $c_R(t)$  is the receiver chamber salt concentration at time  $t$ , and  $c_D(0)$  is the initial donor chamber salt concentration.

### 3. Results and discussion

#### 3.1. Ion exchange in BPS-32 films

The concentration of counter-ions in the films was measured to ensure that the treatment protocols in Fig. 2 did, in fact, convert the polymers to the ionic form shown in Fig. 2. The results, recorded in Table 1, illustrate the effectiveness of the protocols in Fig. 2. For example, the H sample, acidified in solution, contained no appreciable potassium or sodium, as expected for an acidified film. Samples H-K and K-HB-K are predominantly in the potassium salt form, and samples H-Na and K-HB-Na are predominantly in the sodium salt form. Additionally, no sodium or potassium was detected in acid form samples H, H-K-H, and K-H. In summary, the observations of negligible concentrations of sodium and potassium in acid form polymers, as well as no sodium in films expected to be in the potassium form, and no potassium in films expected to be in the sodium form further suggests that the conditioning protocols, outlined in Fig. 2, largely produced films in the intended counter-ion form.

The measured counter-ion concentrations are consistent with the expected ion exchange capacity (IEC) of BPS-32. The IEC of sodium form BPS-32 (sample K-HB-Na) was calculated from solution-state  $^1\text{H}$  NMR spectra as described previously [55] and is 1.30 meq/g (dry polymer), and the IEC measured by solution-state potentiometric titration and solid state film titration is reported as 1.2 meq/g (dry polymer) [57]. In Table 1, the ion concentrations are also reported in meq/cm<sup>3</sup> (hydrated polymer) to provide an estimate of the volumetric charge density in the samples, which would influence salt sorption according to Donnan theory [35]. However, it was difficult to measure the hydrated sample volume precisely, so the values in Table 1 on a volumetric basis of hydrated polymer have more uncertainty than the values on a dry basis.

The counter-ion concentration in meq/g (dry polymer), was 4–6% higher in boiled samples (K-HB-Na and K-HB-K) than in samples not exposed to elevated temperature (H-Na and H-K). Previous reports suggest that acidifying BPS films by boiling in sulfuric acid does not measurably increase the IEC or the degree of sulfonation [52,53]. However, the increase in degree of sulfonation implied by the changes observed in Table 1 (i.e., an increase of 1–2% in degree of sulfonation) could be difficult to detect using  $^1\text{H}$  NMR or FTIR [52,53]. The counter-ion concentration in potassium form polymers (H-K and K-HB-K) was somewhat higher than in the sodium form polymers (H-Na and K-HB-Na). This observation is consistent with the tendency of potassium to bind more strongly to sulfonate groups than sodium [42,49], which may explain why the ion concentration as probed by potassium sorption is closer to the  $^1\text{H}$  NMR reported IEC than that probed by sodium sorption. Additionally, these samples were prepared with the protocol described in the Experimental section, using a fixed length of exposure time

**Table 1**  
Counter-ion concentration in BPS-32.

Sample	Ion concentration [meq/g (dry polymer)]		Ion concentration [meq/cm <sup>3</sup> (hydrated polymer)]	
	Sodium	Potassium	Sodium	Potassium
H	<0.01	<0.01	<0.01	<0.01
H-K	<0.01	1.26 ± 0.011	<0.01	1.30 ± 0.050
H-Na	1.09 ± 0.015	<0.01	1.10 ± 0.008	<0.01
H-K-H	<0.01	<0.01	<0.01	<0.01
K-H	<0.01	<0.01	<0.01	<0.01
K-HB-K	<0.01	1.31 ± 0.005	<0.01	1.40 ± 0.064
K-HB-Na	1.16 ± 0.003	<0.01	1.36 ± 0.178	<0.01

Note: The uncertainties were estimated as the standard deviation of ion concentration measurements made on 3 separate samples.

to salt solution to promote ion exchange, and it might be of interest to extend the NaCl soaking protocol to more than 3 days and/or more than 3 soaking solution changes to see if the sodium ion exchange would approach that of potassium. Ultimately, the counter-ion form measurement procedure verified the counter-ion form of the polymers considered, and the fundamental origins of the subtle differences mentioned above are not completely understood at this time.

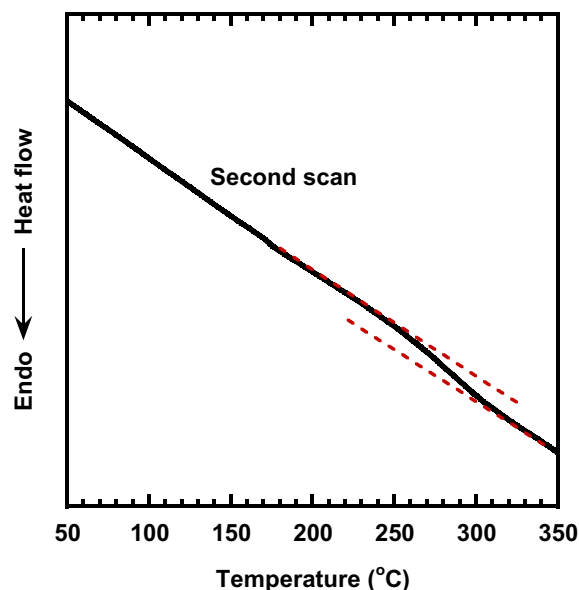
#### 3.2. Estimation of glass transition temperature of hydrated samples

If polymer samples were below their glass transition temperature,  $T_g$ , when they were subjected to various thermal processing steps (e.g., thermal treatment, ion exchange, etc.), their properties (e.g., water uptake and permeability) could be sensitive to these processing steps since the materials would be in an inherently nonequilibrium state (i.e., below their  $T_g$ ) [42–45]. The glass transition temperature of a dry BPS-32 potassium form sample (i.e., sample K) was measured to be 278 °C using DSC (see Fig. 3). This  $T_g$  is somewhat higher than the value reported for sodium form BPS-40 (271 °C) [52], which is unexpected since  $T_g$  typically increases as extent of sulfonation increases. In the present measurement, a solvent extraction process, i.e., storing films in DI water for at least 3 days and vacuum drying at 110 °C for 1 day, was used; no solvent extraction process was used in the previously reported  $T_g$  measurement, so residual solvent may have depressed the previously reported BPS-40  $T_g$ .

Since many of the processing steps considered in this study were conducted on hydrated samples, it was of interest to estimate the extent to which the presence of water in BPS-32 lowered its  $T_g$ .  $T_g$  depression due to small molecule plasticization is widely known for polymer-diluent systems [62,75–78]. In BPS polymers, Kim et al. [62] estimated the  $T_g$  of water swollen films using the Kelley-Bueche equation [79]:

$$T_g = \frac{R\phi_1 T_{g1} + \phi_2 T_{g2}}{R\phi_1 + \phi_2} \quad (8)$$

where  $\phi_1$  and  $\phi_2$  are the volume fractions of component 1 (water) and component 2 (polymer) in hydrated BPS films,  $T_{g1}$  and  $T_{g2}$  are



**Fig. 3.** DSC thermogram for potassium form BPS-32.

the glass transition temperatures of water ( $-137\text{ }^{\circ}\text{C}$ ) [80] and dry BPS polymer, respectively, and  $R \equiv \alpha_1/\alpha_2$ , with  $\alpha_i$  being the difference in thermal expansivity between liquid and glass for component  $i$ . These coefficients were reported to be  $\alpha_1 = 10^{-3}$  and  $\alpha_2 = 4.8 \times 10^{-4}$ , so  $R = 2.1$  [62,81,82]. For BPS-32, the dry  $T_g$  was set to  $278\text{ }^{\circ}\text{C}$  based on the DSC thermogram in Fig. 3.

The influence of water content on the  $T_g$  of hydrated potassium form BPS-32 was estimated using Equation (8) and is shown in Fig. 4. The volume fraction of water in fully hydrated potassium form BPS-32 was 0.20 (as discussed in more detail below), so the  $T_g$  of this hydrated polymer is predicted to be approximately  $135\text{ }^{\circ}\text{C}$ . Based on this calculation, BPS-32 films undergoing ion exchange or other processes at ambient conditions were often far below the  $T_g$  of the hydrated polymer, so long-lived, history dependent, changes in water uptake and transport properties might be expected. Water contents of samples considered in this study ranged from 20 to 36 vol. %, so if the results shown in Fig. 4 apply, even the most hydrated samples were below  $T_g$  at ambient conditions.

### 3.3. Infrared characterization of samples before and after thermal processing steps

ATR-FTIR spectroscopy was used to characterize the chemical structure of BPS-32 films. The IR spectra of selected films, including those prepared via solid state acidification (K, K-H, K-HB, and K-HB-Na) and solution acidification (H, H-K, and H-Ca), are presented in Fig. 5. No significant differences in IR spectra exist between films prepared via different acidification routes. However, some subtle differences appear when comparing salt and acid form films. The strong characteristic peaks at  $1030$  and  $1098\text{ cm}^{-1}$  were assigned to symmetric and asymmetric stretching of the sulfonate groups in BPS-32, and the peak at  $1006\text{ cm}^{-1}$  corresponds to the diphenyl ether band which is taken as a reference peak [52]. The acid form films in Fig. 5 (H, K-H, and K-HB) exhibit weaker peaks at both  $1030$  and  $1098\text{ cm}^{-1}$  than the salt form films (K, K-HB-Na, H-K, and H-Ca), probably due to extensive hydrogen bonding in the acid form polymer matrix, which inhibits both symmetric and asymmetric stretching of the sulfonate groups on the polymer backbone [83].

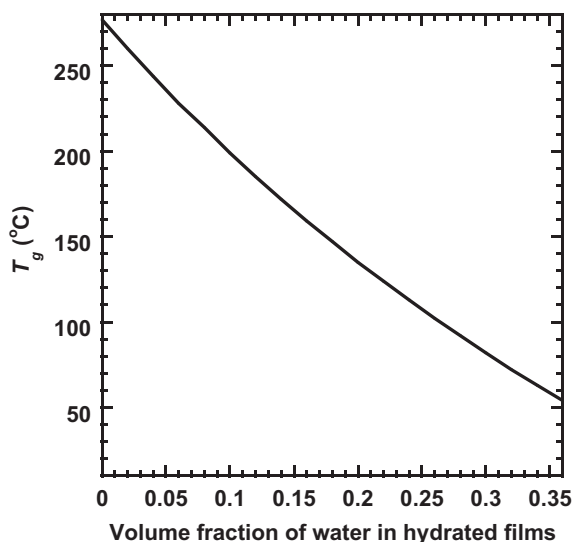


Fig. 4. Estimated glass transition temperature ( $T_g$ ) of hydrated  $\text{K}^+$  form BPS-32 film as a function of volume fraction of water in the hydrated film.  $T_g$  was estimated from the Kelley-Bueche equation, which is Equation (8) [79].

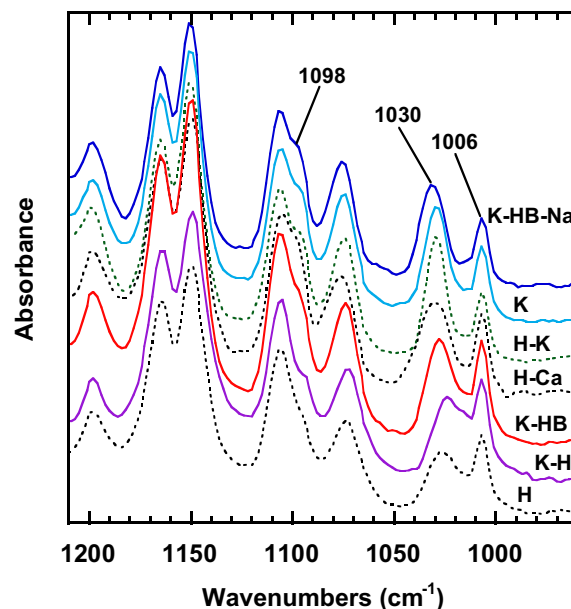


Fig. 5. ATR-FTIR spectra of BPS-32 films. The spectra of samples acidified in the solid state (K-HB-Na, K, K-HB and K-H) are shown as solid lines, and the spectra of samples acidified in solution (H-K, H-Ca and H) are shown as dashed lines. The spectra have been displaced vertically for easier viewing.

### 3.4. Effect of thermal conditioning on transport properties

In previous studies, BPS polymers were acidified in the solid state by boiling salt form films in  $0.5\text{ M H}_2\text{SO}_4$  for 2 h followed by boiling in DI water for 2 h [4,36,52,53]. However, the thermal treatment associated with boiling may also influence the properties of sulfonated polymer films [43,44]. For example, boiling acid form Nafion 117 films in DI water for 1 h doubles water permeability [44]. Therefore, to separate the influence of thermal treatment from those associated solely with ion exchange due to contact with acid, solution-state acidification was performed before casting films into the solid state.

The water uptake, water and NaCl permeability, and water/salt permeability selectivity of BPS-32 films, initially in the acid form, are recorded in Table 2. For solid state acidified films, K-H samples were obtained by soaking K films in  $0.5\text{ M}$  sulfuric acid at room temperature for 3 days, while K-HB samples were obtained by soaking K films in boiling  $0.5\text{ M}$  sulfuric acid for 2 h and then in boiling DI water for 2 h, similar to the protocol reported in previous studies [2,4,52,53]. Focusing first on samples K-H and K-HB in Table 2, which are both acid form samples, acidification via boiling

Table 2

Effect of acidification method on water uptake, water permeability, NaCl permeability, and water/NaCl permeability selectivity of  $\text{H}^+$  form BPS-32 films.

Sample	$K_w$	$P_w^H$ (L $\mu\text{m}/(\text{m}^2\text{ h bar})$ )	$P_w \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$P_s \times 10^9$ ( $\text{cm}^2/\text{s}$ )	$P_w/P_s$
Solid state acidification					
K <sup>a</sup>	$0.20 \pm 0.01$	$0.25 \pm 0.05$	$3.0 \pm 0.6$	$0.59 \pm 0.05$	510
K-H	$0.24 \pm 0.01$	$0.65 \pm 0.03$	$6.4 \pm 0.3$	$1.4 \pm 0.1$	460
K-HB	$0.36 \pm 0.01$	$2.75 \pm 0.19$	$14.6 \pm 1.0$	$30 \pm 2$	49
Solution acidification					
H	$0.27 \pm 0.01$	$0.36 \pm 0.03$	$3.0 \pm 0.2$	$0.70 \pm 0.12$	430
H-K	$0.26 \pm 0.01$	$0.38 \pm 0.03$	$3.4 \pm 0.3$	$0.76 \pm 0.04$	450
H-K-H	$0.29 \pm 0.01$	$0.48 \pm 0.03$	$3.7 \pm 0.2$	$0.91 \pm 0.20$	410

<sup>a</sup> Sample K, prepared by casting a potassium salt form film from solution, is included in this table for comparison with acid form materials.

in acid and then boiling in water (K-HB) changes the water uptake and transport properties relative to that of the sample converted to acid form at ambient temperature (K-H). The water uptake of the boiled sample (i.e., K-HB) was 50% higher than that of the un-boiled sample (K-H); water diffusive permeability and NaCl permeability of the boiled sample were 2.3 and 21 times higher than those of the un-boiled sample, respectively. The water/NaCl permeability selectivity decreased by nearly an order of magnitude, from 460 in sample K-H to 49 in sample K-HB.

Consistent with previous literature reports [2,4,38,43,51], both solid state acid form samples have higher water uptake and higher permeability than their parent potassium salt form material (i.e., sample K) as reported in Table 2. This behavior may be related to stronger potassium to sulfonate group binding compared to proton to sulfonate group binding as has been reported for other sulfonated polymers [38,43,51]. The potassium-sulfonate group bond may be less polar (i.e., less hydrophilic) than the proton-sulfonate group bond, so that films initially cast from the potassium salt form (i.e., sample K) yield samples that sorb less water than the corresponding acid form films.

Qualitatively, as water content increases, increases in diffusive water permeability and salt permeability and decreases in water/salt permeability selectivity is consistent with expectations from free volume theory [84]; any change to a material that increases water uptake (and, therefore, free volume, which has been shown to be proportional to water content in these materials [36]) should increase permeability. Moreover, the permeability of hydrated ions (which are larger than water molecules [85]) should increase more than the diffusive permeability of water as water uptake increases, which would lead to decreased water/salt permeability selectivity [36,64]. Thus, the change in transport properties reported earlier [4] for solid state acidified samples is qualitatively coherent with free volume theory and depends at least on the thermal history as well as the ionic form.

To further isolate the influence of thermal treatment temperature *per se* on transport properties, potassium form BPS-32 films were soaked in DI water at different temperatures, and the transport properties were subsequently measured. The results of this study are reported in Table 3. As soaking temperature increased, water uptake as well as permeability coefficients increased, but water/NaCl permeability selectivity decreased. For example, diffusive water permeability in a sample boiled in DI water (sample K-B) was 3.3 times higher than that of a sample not exposed to boiling water (Sample K), and NaCl permeability was almost an order of magnitude higher in the sample exposed to boiling water. As mentioned previously, the greater increase in NaCl permeability compared to water permeability is likely due to an increase in free volume in the sample soaked at higher temperature, which is reflected in the increased water uptake of the sample exposed to higher temperature.

### 3.5. Transport properties in solution acidified samples

To further isolate the influence of history on transport properties, solution acidified films were prepared and studied. These

samples were in the acid form prior to film casting. These acid form films (sample H in Fig. 2) were converted to the potassium salt form by soaking sample H in 0.5 M KCl at ambient conditions to produce sample H-K in Fig. 2. This sample (i.e., H-K) was soaked in 0.5 M H<sub>2</sub>SO<sub>4</sub> at ambient conditions to convert it back to the acid form (sample H-K-H in Fig. 2). Based on the ion exchange results in Table 1, sample H-K was fully converted to the potassium salt form, and sample H-K-H contained negligible potassium, indicating its conversion back to the acid form. The water uptake and transport properties of these samples are reported in Table 2, and they are rather similar. Sample H-K-H may have slightly higher water permeability than that of the other samples, but the difference is not far from the uncertainty in the measurements, and the molecular basis for such a difference, if it exists, is not currently well understood. Therefore, in samples initially cast from acid form material, there is little change in water uptake or transport properties when the ion exchange is performed at ambient conditions. This result is in contrast to that obtained when initially potassium form polymer (i.e., sample K) is acidified at ambient conditions to form sample K-H. In this case, water uptake and transport properties increase significantly upon acidification. The molecular basis for these differences in behavior of acid and salt form materials upon ion exchange in the solid state at ambient conditions is not well understood at this time.

The sample converted to acid form in the solid state (sample K-H) had higher water and salt permeability coefficients than that of a sample cast directly from acid form polymer (sample H), even though sample K-H had perhaps slightly lower water content than sample H. This departure from the observation that samples with higher water content generally exhibit higher permeabilities illustrates that while water content is important in governing transport properties, it is not an infallible predictor of permeability, suggesting that other, more subtle effects, such as the influence of thermal history on free volume distribution, may also influence the results.

The films prepared in this study had different water/NaCl permeability selectivity than previously reported analogs [4] because the upstream NaCl concentration in the salt permeability measurements was different from that used in previous studies (0.1 M in this study versus 1 M previously [4]), and the NaCl permeability of sulfonated polymers increases as feed NaCl concentration increases [4,35,43,63]. Moreover, the current film preparation conditions were not exactly identical to those of previous studies [4], which could also influence the water and salt transport properties of the resulting films. For example, there are differences in the pore size of the filter used to filter the polymer solution (0.45 μm in this study versus 2 μm previously [4]), and film drying temperature (vacuum drying at 150 °C in this study versus 110 °C previously [4]). A complete study of the effect of these variables on sample properties has not yet been performed.

### 3.6. Transport properties of samples ion exchanged at ambient conditions

It was possible to begin with acid form films, prepared either via solution or solid state acidification, and ion exchange them at ambient conditions, in the absence of thermal treatment, to explore the effect of ion exchange *per se* on water uptake and transport properties. The properties of these films are recorded in Table 4. A striking difference in Table 4 is the higher water uptake and permeation properties of sodium and potassium form samples prepared from solid state acidified samples (i.e., K-HB-Na and K-HB-K) relative to analogous samples prepared from solution acidified samples (i.e., H, H-Na, H-K, and H-Ca), which likely reflects differences in the sample processing history (specifically, the

**Table 3**  
Effect of thermal treatment temperature on water uptake, water permeability, NaCl permeability, and water/NaCl permeability selectivity of K<sup>+</sup> form BPS-32 films.

Sample	$K_w$	$P_w^H$ (L μm/ (m <sup>2</sup> h bar))	$P_w \times 10^7$ (cm <sup>2</sup> /s)	$P_s \times 10^9$ (cm <sup>2</sup> /s)	$P_w/P_s$
K	0.20 ± 0.01	0.25 ± 0.05	3.0 ± 0.6	0.59 ± 0.05	510
K-50C	0.22 ± 0.01	0.31 ± 0.05	3.3 ± 0.5	0.88 ± 0.12	380
K-75C	0.26 ± 0.01	0.71 ± 0.19	6.3 ± 1.6	2.5 ± 0.1	250
K-B	0.30 ± 0.01	1.33 ± 0.14	9.8 ± 1.0	5.4 ± 0.2	180

**Table 4**

Effect of ion form and thermal processing history on water uptake, water permeability, NaCl permeability, and water/NaCl permeability selectivity.

Sample	$K_W$	$P_{W_s}^H$ (L $\mu\text{m}/(\text{m}^2 \text{h bar})$ )	$P_W \times 10^7$ ( $\text{cm}^2/\text{s}$ )	$P_S \times 10^9$ ( $\text{cm}^2/\text{s}$ )	$P_W/P_S$
Solid state acidification					
K-HB-Na	$0.33 \pm 0.02$	$1.99 \pm 0.10$	$11.9 \pm 0.6$	$31 \pm 2$	38
K-HB-K	$0.33 \pm 0.02$	$2.85 \pm 0.17$	$17.3 \pm 1$	$28 \pm 2$	62
Solution acidification					
H <sup>a</sup>	$0.27 \pm 0.01$	$0.36 \pm 0.03$	$3.0 \pm 0.2$	$0.70 \pm 0.12$	430
H-Na	$0.26 \pm 0.01$	$0.34 \pm 0.02$	$3.0 \pm 0.2$	$0.98 \pm 0.06$	310
H-K <sup>a</sup>	$0.26 \pm 0.01$	$0.38 \pm 0.03$	$3.4 \pm 0.3$	$0.76 \pm 0.04$	450
H-Ca	$0.24 \pm 0.01$	$0.20 \pm 0.01$	$2.0 \pm 0.1$	$0.87 \pm 0.06$	230

<sup>a</sup> Data for samples H and H-K are included from Table 2 to permit easier comparisons among this sample set.

boiling protocol used to convert the solid state acidified samples to the acid state prior to ion exchanging them to the potassium (i.e., K-HB-K) or sodium (i.e., K-HB-Na) forms) prior to ion exchange at ambient conditions.

In solid state acidified samples, water uptake was identical in sodium (K-HB-Na) and potassium (K-HB-K) form samples. Salt permeability coefficients were also quite similar in these materials. The water permeability of K-HB-K appears to be somewhat higher than that of K-HB-Na for reasons that are not clear at this time. In solution acidified samples, the water uptake, water permeability, and salt permeability values are fairly similar among samples H, H-Na, and H-K. Consequently, conversion of films cast from acid form polymer to their sodium or potassium salt forms, caused little change in water uptake or water and salt permeability. Thus, the major effect of boiling samples in acid and water to convert them from salt to acid form, as reported in the literature [2,4,52,53], appears to be exposure of the samples to elevated temperature.

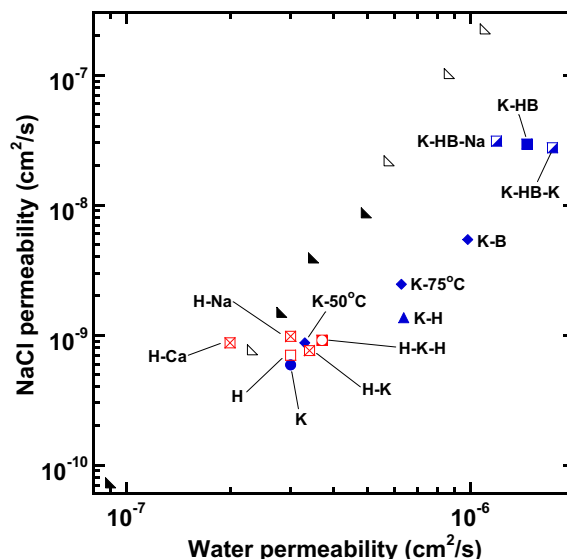
The water uptake and water permeability values reported thus far were measured using pure water as the solute, to avoid further ion exchange during the measurements. Of course, it is impossible to measure salt permeability without exposing the sample to salt, so the salt permeability measurements were conducted on samples exposed to salt during the measurements. Results from measurements of water permeability as the ion exchange process occurred will be presented later to provide an indication of the change in water permeability that can occur as a solution acidified sample converts to its salt form.

The properties of the calcium exchanged sample, H-Ca, is also shown in Table 4 for comparison with the monovalent alkali counter-ion form BPS-32 films (i.e., H, H-Na or H-K samples). The H-Ca sample appears to have slightly lower water content than the H, H-Na or H-K samples, though the differences were small; correspondingly, the water permeability of H-Ca appeared to be somewhat lower than that of H, H-Na or H-K samples. However, the NaCl permeability of the H-Ca sample was similar to that of the H, H-Na, and H-K samples, which resulted in the water/salt selectivity being lower in the H-Ca sample than in the H, H-Na, and H-K samples. This result is qualitatively consistent with the observation that divalent calcium cations interact strongly with sulfonate groups on polymer chains [86–88], which might have the effect of reducing water uptake and, in turn, water permeability [50]. Furthermore, in sulfonated polymers, divalent cations can reduce the Donnan exclusion of monovalent ions, resulting in lower rejection (i.e., higher permeability) of monovalent ions in the presence of divalent ions [35,88,89]. Typically, such effects are reported when mixtures of monovalent and divalent ions are copermeated through a polymer film. However, if calcium remains bound to the sulfonate groups in the H-Ca film during the NaCl permeation measurement and partially screens their ability to reduce the permeation of

negative chloride ions, then one would expect higher NaCl permeability. If so, then the increase in NaCl permeability due to Ca-induced screening of the negatively charged sulfonate groups is likely offset by the slightly lower water content in the H-Ca sample, resulting in a net NaCl permeability that is similar among all of these samples (i.e., H, H-Na, H-K, and H-Ca).

The water and NaCl permeability of all BPS-32 films are presented in Fig. 6. By varying processing conditions, water and salt transport properties of BPS-32 films could be modified over a broad range. Generally speaking, thermal processing history that brought about higher water permeability typically increased salt permeability. For example, the potassium form BPS-32 sample K-HB-K had diffusive water permeability an order of magnitude higher and NaCl permeability almost two orders of magnitude higher than those of sample K. Among all BPS-32 samples, films boiled in acid (K-HB, K-HB-Na, and K-HB-K) had the highest permeability to both water and salt; the films that experienced elevated temperature treatment in DI water (K-B and K-75 °C) had higher permeability than samples that were not thermally treated. Films with no thermal treatment or treated at a low temperature (i.e., K-50 °C), typically had lower permeability coefficients.

Also shown in Fig. 6 are literature data from acid (unfilled triangles) and potassium salt (filled triangles) form BPS samples where variations in properties were brought about by varying the degree of sulfonation from 20 to 40 mol % [4]. The salt permeability coefficients of these polymers from the literature lie somewhat above those reported in this study, which is likely due to the higher concentration of salt used in the feed for the literature studies (1.0 M) than in the studies reported here (0.1 M), since salt permeability usually increases with increasing salt concentration in sulfonated polymers [4]. However, the data presented in Fig. 6 show that roughly comparable changes in water and salt permeability can be brought about by thermal processing steps or by changing the sulfonic acid concentration of the polymer over a wide range, illustrating the sensitivity of the properties of such materials to processing history.



**Fig. 6.** NaCl permeability versus diffusive water permeability of BPS-32 films. In this study, feed NaCl concentration for salt permeability measurement = 0.1 M. The triangles represent potassium (▲) and acid (△) form BPS data reported previously (feed NaCl concentration for salt permeability measurement = 1 M) [4]. Differences in the water and ion transport properties of these samples (i.e., those represented by the ▲ and △ symbols) were brought about by changing the concentration of sulfonated monomer in the polymer (from 20 to 40 mol %) at fixed film processing conditions.



### 3.7. Use of free volume to correlate transport properties

Correlation of water and salt transport properties with free volume, characterized either by water uptake or based on positron annihilation lifetime spectroscopy (PALS) measurements, has been reported for acid and potassium counter-ion form BPS samples synthesized with varying amounts of sulfonic acid comonomer [4,36]. In this study, the concentration of sulfonic acid comonomer was fixed at 32%, and thermal processing history was used to vary transport properties. The changes in thermal processing history changed both water uptake and water permeability as well as salt transport properties in some cases, and it was of interest to see if the water uptake and transport properties could be correlated.

As discussed previously [4], the water partition coefficient has been shown to be proportional to free volume, as measured by positron annihilation lifetime spectroscopy (PALS) studies, in hydrated BPS [36] and other families of hydrated polymers [64]. According to free volume theory, the connection between free volume and penetrant diffusivity,  $D$ , is [84]:

$$D = A_D \cdot \exp\left[-\frac{\gamma \cdot v^*}{v_f}\right] = A_D \cdot \exp\left[-\frac{\gamma \cdot v^*}{k \cdot K_W}\right] \quad (9)$$

where  $A_D$  and  $k$  are constants,  $\gamma$  is a parameter introduced to avoid double counting free volume elements,  $v^*$  is a characteristic minimum volume required to accommodate a small molecule diffusing through the polymer, and  $v_f$  is the average free volume in polymer. Previously, the free volume, as measured by PALS, was found to be proportional to the water partition coefficient,  $K_W$ , and the constant of proportionality in Equation (9) is  $k$  [36,64].

In the solution-diffusion model, the diffusive permeability ( $P$ ) depends on the product of the partition (or solubility) coefficient of a penetrant in a polymer ( $K$ ) and the concentration-averaged effective diffusion coefficient of that penetrant through the polymer ( $D$ ) [67,68,90]:

$$P = K \cdot D \quad (10)$$

As discussed previously [36], changes in water content tend to strongly influence diffusion coefficients and weakly influence partition coefficients, so  $K$  in Equation (10) could be regarded, roughly speaking, as a constant. Thus,

$$P \cong B \cdot \exp\left[-\frac{\gamma \cdot v^*}{k \cdot K_W}\right] \quad (11)$$

where  $B$  is the product of  $A_D$  and the partition coefficient  $K$ .

The measured water and NaCl permeability of various BPS-32 films are presented in Fig. 7(a) and Fig. 7(b), respectively. For films prepared via solid state acidification (samples K, K-50 °C, K-75 °C, K-B, K-H, K-HB, K-HB-Na, and K-HB-K), both water and NaCl permeability vary exponentially with reciprocal water partition coefficient, indicating reasonable qualitative agreement with Equation (11). The data points for the films prepared via solution acidification (H, H-Na, H-K, H-Ca, and H-K-H) also exhibit a trend following Equation (11) for water (mainly due to the lower water permeability and water uptake of the calcium exchanged sample, since the other samples have similar water uptake and water permeability values), though the trend lines are somewhat displaced from the data points of the films prepared via solid state acidification. The NaCl permeability in solution acidified samples was approximately independent of water uptake, though the inclusion of the calcium exchanged sample (H-Ca) in this data set might skew this result slightly since the presence of divalent calcium in the sample could have additional effects (mentioned

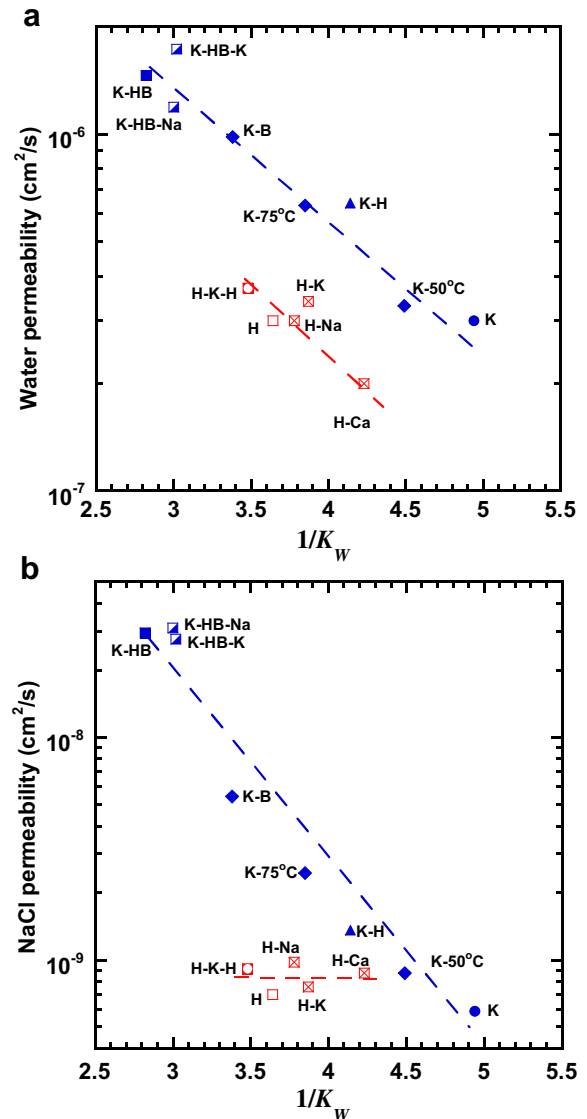
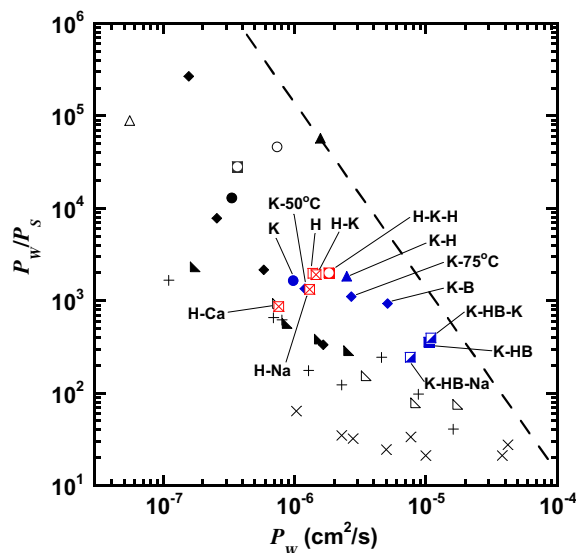


Fig. 7. Correlation between reciprocal water uptake and: a) diffusive water permeability, and b) NaCl permeability of BPS-32 films. The dashed lines are provided to guide the eye.

above) that monovalent ions do not show. However, like the water permeability data, at the same water uptake level, films prepared via solution acidification have lower water and salt permeability than those prepared via solid state acidification. The fundamental basis for this difference between solid state acidified and solution acidified samples is not yet clear and will be explored in future studies. This difference may reflect differences in free volume distribution between solution acidified and solid state acidified samples, but this notion is speculative at this point.

The water/salt permeability selectivity of BPS-32 films is presented as a function of water permeability in Fig. 8, and data from this study are compared with data from the literature [2,4,64,90–92]. Roughly speaking, the various BPS-32 films exhibit a trade-off between permeability selectivity and water permeability, i.e., selectivity increases as water permeability decreases, and vice versa. Among the BPS-32 films, the H-Ca sample showed the poorest combinations of water and salt transport properties, not surprisingly given that the calcium neutralization appears to decrease water transport but not NaCl transport. The K-HB and



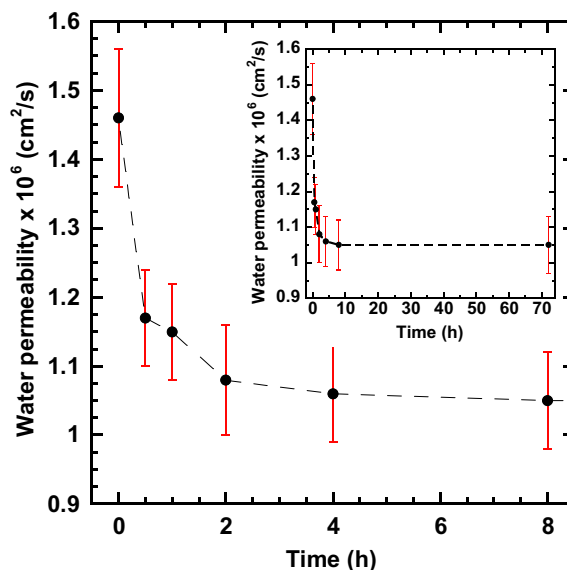
**Fig. 8.** Water/NaCl permeability selectivity as a function of diffusive water permeability in dense films: PI ( $\Delta$ ) = polyimide [91], PA1 ( $\bullet$ ) = aromatic polyamide [91], PBP ( $\blacktriangle$ ) = polybenzimidazopyrrolone [91], PAH ( $\square$ ) = polyamide-hydrazide [91], CA ( $\blacklozenge$ ) = cellulose acetate [90], PA2 ( $\circ$ ) = aromatic polyamide [92], PEG ( $\times$ ) = poly(ethylene glycol) [64], BPS ( $+$ ) [2,93],  $\blacktriangleleft$  and  $\blacktriangleright$  [4]) = disulfonated polysulfones reported previously (feed NaCl concentration for salt permeability measurement = 1 M). In this study, feed NaCl concentration for salt permeability measurement = 0.1 M. To be consistent with the literature data where the Flory–Huggins convection correction was not introduced,  $P_W$  for BPS-32 films in this figure were calculated using Equation (5) assuming  $(1 - K_W)^2(1 - 2\chi K_W) = 1$  (i.e., the water permeability coefficients in this figure were not corrected for the effect of convection on water transport). The dashed line is the upper bound from literature [93].

K-HB-K samples showed the best combinations of water and salt transport properties, based on distance to the upper bound line shown in Fig. 8. For the H-Ca sample, this result is consistent with the calcium ions being able to effectively ionically crosslink at least some of the sulfonate linkages [86–88], reducing their ability to prevent NaCl transport based on either Donnan exclusion [89] or slowing the diffusion of negatively charged chloride ions.

### 3.8. Change in water permeability during ion exchange

Because the counter-ion form of the polymer influences water uptake and, in turn, transport properties, the ion exchange process may be monitored by transport property measurements. In this regard, pure water permeability of an initially acid form BPS-32 film was measured as a function of NaCl solution contact time. During this procedure, the sample was converted from the acid to the sodium salt form. Several K-HB samples were loaded into dead-end filtration cells, and pure water permeability was measured. Next, the cells were emptied and refilled with 0.1 M NaCl solution, and the upstream surface of the BPS-32 film, mounted in each cell, was allowed to contact the NaCl solution for a specified period of time at ambient temperature and pressure. After the contact time, the cell was rinsed with DI water three times, and pure water permeability was measured again. This procedure was repeated for 3 days. The results of this experiment are presented in Fig. 9.

Water permeability decreased within the first 2 h of NaCl solution contact time. After 2 h, water permeability remained essentially constant. The final pure water permeability measured in this experiment was  $(1.05 \pm 0.08) \times 10^{-6}$  cm<sup>2</sup>/s. After the experiment, the counter-ion form of the samples was measured using the ash analysis technique, and the results showed a Na<sup>+</sup> concentration of  $1.26 \pm 0.02$  meg/g (dry polymer), which indicates practically



**Fig. 9.** Water permeability as a function of exposure time of initially acid form BPS-32 films (K-HB) to 0.1 M NaCl solution at ambient conditions.

complete exchange of protons for Na<sup>+</sup> ions during the experiment, since this value is very similar to the IEC from <sup>1</sup>H NMR measurements. The pure water permeability of K-HB-Na samples, obtained by soaking acid form K-HB samples in 0.5 M NaCl solution for 3 days, was  $(1.19 \pm 0.06) \times 10^{-6}$  cm<sup>2</sup>/s, and the Na<sup>+</sup> concentration in the K-HB-Na samples was  $1.16 \pm 0.003$  meg/g (dry polymer) (cf. Table 1). The somewhat higher water permeability in the K-HB-Na sample may reflect its somewhat less extensive conversion to the sodium salt form relative to the sample converted to the sodium form in the permeation cell. Also, in this technique, ion exchange from the BPS-32 acid to sodium counter-ion form occurs rather completely over a period of just a few hours in films that are 40–70  $\mu$ m thick.

### 3.9. Water permeability measured using deionized water or an aqueous solution containing 2000 ppm NaCl as feed

Water permeability discussed previously in this study was measured using DI water as the feed. However, in practical applications, desalination membranes are exposed to salt/water mixtures where ion exchange may occur during permeation and result in changes in transport properties of the membranes. One example was shown in Fig. 9. To further characterize the effect of ion exchange on transport properties of BPS films, hydraulic water permeability coefficients of potassium form and solid state acidified forms of BPS films of varying degrees of substitution were measured in a crossflow system using an aqueous solution containing 2000 ppm (0.034 M) NaCl as the feed, which is a typical synthetic salt solution used to represent brackish water. The water permeability values measured in this method were compared, in Table 5, with those reported previously using DI water as the feed [4]. For all potassium BPS films and BPSH films with lower degrees of sulfonation (BPSH-20 and BPSH-30), the water permeability coefficients were very similar whether measured using DI water or 2000 ppm NaCl solution as the feed solution, indicating a small effect of ion exchange on transport properties for these films, at least at the feed salt concentration considered. However, there was a somewhat larger difference between the water permeability measured using DI water rather than 2000 ppm NaCl solution for BPSH-40. This higher IEC acid form material appeared to be more

**Table 5**

Hydraulic water permeability measured using a feed of DI water or 2000 ppm NaCl aqueous solution.

Sample	$P_W^H$ (L $\mu\text{m}/(\text{m}^2 \text{ h bar})$ )	
	Feed = DI water [4]	Feed = 2000 ppm NaCl <sup>a</sup>
BPS-20	0.044 ± 0.003	0.041
BPS-30	0.22 ± 0.01	0.23
BPS-40	0.65 ± 0.02	0.63
BPSH-20	0.19 ± 0.01	0.16
BPSH-30	0.89 ± 0.03	0.85
BPSH-40	4.44 ± 0.27	3.71

NOTE: The sample nomenclature is that used by Xie et al. [4]; BPS-X refers to a potassium form sample with X mol percent disulfonated monomer, and BPSH-X refers to a solid state acidified sample with X mol percent disulfonated monomer.

<sup>a</sup> Calculated according to Equation (3).

sensitive to ion exchange effects than other BPS films with lower degrees of sulfonation or other salt form films (e.g., BPS-20, BPS-30, and BPS-40). This sample had the highest water uptake (48 volume %) among all of the samples considered [4], so any effects, such as osmotic deswelling, which tend to decrease water uptake, might have a stronger effect on this sample than the others, which may explain its higher sensitivity to salt concentration.

#### 4. Conclusions

The effect of thermal processing and ion exchange on water and ion transport properties of a glassy, sulfonated polysulfone was measured in this study. The alkali cation ( $\text{Na}^+$  and  $\text{K}^+$ ) concentration in BPS-32 films was measured to confirm the expected ion exchange. The effect of acid treatment, thermal treatment, and counter-ion form on transport properties was determined. Soaking BPS-32 films in 0.5 M sulfuric acid at room temperature increased water uptake and permeability. BPS-32 films treated in DI water at different temperatures showed a broad range of transport properties, indicating that thermal treatment in water can be used to tune BPS-32 transport properties. A combination of acid and thermal treatment, i.e., boiling BPS-32 films in sulfuric acid, showed the strongest effect on transport properties, resulting in substantial increases in water uptake as well as water and salt transport. Counter-ion form also affected properties, but this effect was secondary compared to the effects of thermal treatment. Water and salt transport properties of BPS-32 films prepared via solid state acidification correlated well with water uptake as expected according to free volume theory. In solution acidified samples, water permeability increased with increasing water content as expected from free volume theory; however, the salt permeability was essentially independent of water uptake. Generally, the BPS-32 films followed a trade-off between water/salt permeability selectivity and water permeability.

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#### References

- Paul M, Park HB, Freeman BD, Roy A, McGrath JE, Riffle JS. *Polymer* 2008; 49(9):2243–52.
- Park HB, Freeman BD, Zhang ZB, Sankir M, McGrath JE. *Angewandte Chemie, International Edition* 2008;47(32):6019–24.
- Xie W, Park HB, Cook J, Lee CH, Byun G, Freeman BD, et al. *Water Science and Technology* 2010;61(3):619–24.
- Xie W, Cook J, Park HB, Freeman BD, Lee CH, McGrath JE. *Polymer* 2011;52(9):2032–43.
- McGrath JE, Park HB, Freeman BD. Chlorine resistant desalination membranes based on directly sulfonated poly(arylene ether sulfone) copolymers. US Patent 8,028,842 B2, 2011.
- Thorsen T, Holt T. *Journal of Membrane Science* 2009;335(1–2):103–10.
- Cath TY, Childress AE, Elimelech M. *Journal of Membrane Science* 2006; 281(1–2):70–87.
- McCutcheon JR, Elimelech M. *Journal of Membrane Science* 2006;284(1–2): 237–47.
- McCutcheon JR, McGinnis RL, Elimelech M. *Journal of Membrane Science* 2006;278(1–2):114–23.
- McCutcheon JR, Elimelech M. *AIChE Journal* 2007;53(7):1736–44.
- Achilli A, Cath TY, Childress AE. *Journal of Membrane Science* 2009;343(1–2): 42–52.
- Tan CH, Ng HY. *Journal of Membrane Science* 2008;324(1–2):209–19.
- Biesheuvel PM, van der Wal A. *Journal of Membrane Science* 2010;346(2): 256–62.
- Welgemoed TJ, Schutte CF. *Desalination* 2005;183(1–3):327–40.
- Lee JB, Park KK, Eum HM, Lee CW. *Desalination* 2006;196(1–3):125–34.
- Biesheuvel PM, van Limpt B, van der Wal A. *Journal of Physical Chemistry C* 2009;113(14):5636–40.
- Jung HH, Hwang SW, Hyun SH, Kang-Ho L, Kim GT. *Desalination* 2007; 216(1–3):377–85.
- Farmer JC, Fix DV, Mack GV, Pekala RW, Poco JF. *Journal of the Electrochemical Society* 1996;143(1):159–69.
- Grimm J, Bessarabov D, Sanderson R. *Desalination* 1998;115(3):285–94.
- Xu TW. *Journal of Membrane Science* 2005;263(1–2):1–29.
- Balster J, Stamatialis DF, Wessling M. *Journal of Membrane Science* 2009; 341(1–2):131–8.
- Balster J, Stamatialis DF, Wessling M. *Journal of Membrane Science* 2010; 360(1–2):185–9.
- Nagarale RK, Gohil GS, Shahi VK. *Advances in Colloid and Interface Science* 2006;119(2–3):97–130.
- Kalogirou SA. *Progress in Energy and Combustion Science* 2005;31(3): 242–81.
- Van der Bruggen B, Vandecasteele C. *Desalination* 2002;143(3):207–18.
- Turek M, Bandura B. *Desalination* 2007;205(1–3):67–74.
- Post JW, Hamelers HVM, Buisman CJN. *Journal of Membrane Science* 2009; 330(1–2):65–72.
- Veerman J, Saakes M, Metz SJ, Harmsen GJ. *Journal of Membrane Science* 2009;327(1–2):136–44.
- Brauns E. *Desalination* 2009;237(1–3):378–91.
- Weinstein JN, Leitz FB. *Science* 1976;191(4227):557–9.
- Lacey RE. *Ocean Engineering* 1980;7(1):1–47.
- O'Brien RN. *Chemistry in Britain* 1986;22(10):927–9.
- Veerman J, de Jong RM, Saakes M, Metz SJ, Harmsen GJ. *Journal of Membrane Science* 2009;343(1–2):7–15.
- Dlugolecki P, Gambier A, Nijmeijer K, Wessling M. *Environmental Science and Technology* 2009;43(17):6888–94.
- Geise GM, Lee H-S, Miller DJ, Freeman BD, McGrath JE, Paul DR. *Journal of Polymer Science Part B: Polymer Physics* 2010;48(15):1685–718.
- Xie W, Ju H, Geise GM, Freeman BD, Mardel JI, Hill AJ, et al. *Macromolecules* 2011;44(11):4428–38.
- Parrondo J, Ortueta M, Mijangos F. *Brazilian Journal of Chemical Engineering* 2007;24(3):411–9.
- Steck A, Yeager HL. *Analytical Chemistry* 1980;52(8):1215–8.
- Chaabane L, Bulvestre G, Larchet C, Nikonenko V, Deslouis C, Takenouti H. *Journal of Membrane Science* 2008;323(1):167–75.
- Zawodzinski TA, Springer TE, Davey J, Jestel R, Lopez C, Valerio J, et al. *Journal of the Electrochemical Society* 1993;140(7):1981–5.
- Yeager HL, Steck A. *Journal of the Electrochemical Society* 1981;128(9): 1880–4.
- Okada T, Satou H, Okuno M, Yuasa M. *Journal of Physical Chemistry B* 2002; 106(6):1267–73.
- Berezina NP, Timofeev SV, Kononenko NA. *Journal of Membrane Science* 2002;209(2):509–18.
- Evans CE, Noble RD, Nazeri-Thompson S, Nazeri B, Koval CA. *Journal of Membrane Science* 2006;279(1–2):521–8.
- Hensley JE, Way JD, Dec SF, Abney KD. *Journal of Membrane Science* 2007; 298(1–2):190–201.
- Struik LCE. *Physical aging in amorphous polymers and other materials*. Amsterdam: Elsevier; 1978.
- Rowe BW, Freeman BD, Paul DR. *Polymer* 2010;51(16):3784–92.
- Rowe BW, Pas SJ, Hill AJ, Suzuki R, Freeman BD, Paul DR. *Polymer* 2009; 50(25):6149–56.
- Bonner OD, Payne WH. *The Journal of Physical Chemistry* 1954;58(2):183–5.
- Geise GM, Willis CL, Doherty CM, Hill AJ, Bastow TJ, Winey KI, Choi J-H, Ford J, Freeman BD, Paul DR. *Industrial and Engineering Chemistry Research* 2012; (submitted).
- Bonner OD, Smith LL. *The Journal of Physical Chemistry* 1957;61(3):326–9.
- Wang F, Hickner M, Kim YS, Zawodzinski TA, McGrath JE. *Journal of Membrane Science* 2002;197(1–2):231–42.

- [53] Kim YS, Wang F, Hickner M, McCartney S, Hong YT, Harrison W, et al. *Journal of Polymer Science Part B: Polymer Physics* 2003;41(22):2816–28.
- [54] Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, et al. *Journal of Polymer Science Part A: Polymer Chemistry* 2003;41(14):2264–76.
- [55] Li YX, Wang F, Yang J, Liu D, Roy A, Case S, et al. *Polymer* 2006;47(11):4210–7.
- [56] ASTM Standard D3174. Standard test method for ash in the analysis sample of coal and coke from coal. West Conshohocken, PA: ASTM International; 2011. doi:10.1520/D3174-11.
- [57] Passaniti LK. Salt solubility measurements in partially disulfonated poly(arylene ether sulfone) for reverse osmosis water purification applications. M.S. thesis, Austin, TX: The University of Texas at Austin, 2010.
- [58] Chen SL, Bocarsly AB, Benziger J. *Journal of Power Sources* 2005;152(1):27–33.
- [59] Parsons ML. Atomic absorption and flame emission spectrometry. In: Ewing GW, editor. *Analytical instrumentation handbook*. New York: Marcel Dekker; 1997.
- [60] Crompton TR. Determination of metals in natural and treated waters. New York: Spon Press; 2002.
- [61] Ludvigsson M, Lindgren J, Tegenfeldt J. *Electrochimica Acta* 2000;45(14):2267–71.
- [62] Kim YS, Dong LM, Hickner MA, Glass TE, Webb V, McGrath JE. *Macromolecules* 2003;36(17):6281–5.
- [63] Geise GM, Freeman BD, Paul DR. *Polymer* 2010;51(24):5815–22.
- [64] Ju H, Sagle AC, Freeman BD, Mardel JJ, Hill AJ. *Journal of Membrane Science* 2010;358(1–2):131–41.
- [65] Van Wagner EM, Sagle AC, Sharma MM, Freeman BD. *Journal of Membrane Science* 2009;345(1–2):97–109.
- [66] Baker RW. *Membrane technology and applications*. 2nd ed. Chichester: J. Wiley; 2004.
- [67] Wijmans JG, Baker RW. *Journal of Membrane Science* 1995;107(1–2):1–21.
- [68] Paul DR. *Journal of Membrane Science* 2004;241(2):371–86.
- [69] Flory PJ. *Journal of Chemical Physics* 1941;9(8):660–1.
- [70] Huggins ML. *Journal of Chemical Physics* 1941;9(5):440.
- [71] Yasuda H, Lamaze CE, Peterlin A. *Journal of Polymer Science Part B: Polymer Physics* 1971;9(6):1117–31.
- [72] Paul DR. *Journal of Polymer Science Part B: Polymer Physics* 1973;11(2):289–96.
- [73] CRC handbook of chemistry and physics. Cleveland, OH: CRC Press; 1978.
- [74] Yasuda H, Lamaze CE, Ikenberry LD. *Die Makromolekulare Chemie* 1968;118:19–35.
- [75] Banerjee T, Lipscomb GC. *Journal of Applied Polymer Science* 1998;68(9):1441–9.
- [76] Kalachandra S, Turner DT. *Journal of Polymer Science Part B: Polymer Physics* 1987;25(9):1971–9.
- [77] Ellis TS, Karasz FE. *Polymer* 1984;25(5):664–9.
- [78] Tenbrinke G, Karasz FE, Ellis TS. *Macromolecules* 1983;16(2):244–9.
- [79] Kelley FN, Bueche F. *Journal of Polymer Science* 1961;50(154):549–56.
- [80] Velikov V, Borick S, Angell CA. *Science* 2001;294(5550):2335–8.
- [81] Sugisaki M, Suga H, Seki S. *Bulletin of the Chemical Society of Japan* 1968;41(11):2586–91.
- [82] Stanley HE. *Mrs Bulletin* 1999;24(5):22–30.
- [83] Harrison W. Synthesis and characterization of sulfonated poly(arylene ether sulfone) copolymers via direct copolymerization: Candidates for proton exchange membrane fuel cells. Ph.D. Dissertation, Blacksburg, VA: Virginia Polytechnic Institute and State University, 2002.
- [84] Cohen MH, Turnbull D. *Journal of Chemical Physics* 1959;31:1164–9.
- [85] Nightingale Jr ER. *Journal of Physical Chemistry* 1959;63:1381–7.
- [86] Plazinski W, Rudzinski W. *Journal of Colloid and Interface Science* 2010;344(1):165–70.
- [87] Russo R, Malinconico M, Santagata G. *Biomacromolecules* 2007;8(10):3193–7.
- [88] Geise GM, Freeman BD, Paul DR. Comparison of the permeation of MgCl<sub>2</sub> versus NaCl in highly charged sulfonated polymer membranes. In: Escobar IC, Bruggen Bvd, editors. *ACS symposium series - modern applications in membrane science and technology*, vol. 1078. Washington, D.C.: American Chemical Society; 2011. p. 239–45.
- [89] Donnan FG. *Journal of Membrane Science* 1995;100(1):45–55.
- [90] Lonsdale HK, Merten U, Riley RL. *Journal of Applied Polymer Science* 1965;9:1341–62.
- [91] Koros WJ, Fleming GK, Jordan SM, Kim TH, Hoehn HH. *Progress in Polymer Science* 1988;13(4):339–401.
- [92] Frommer MA, Murday JS, Messalem RM. *European Polymer Journal* 1973;9:367–73.
- [93] Geise GM, Park HB, Sagle AC, Freeman BD, McGrath JE. *Journal of Membrane Science* 2011;369:130–8.