Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 2349–2356 **2349**
DOI: 10.1021/ma902430y

Anion Exchange Membranes by Bromination of Benzylmethyl-Containing Poly(sulfone)s

Jingling Yan and Michael A. Hickner*

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Received November 2, 2009; Revised Manuscript Received January 22, 2010

ABSTRACT: This report details the properties of anion-conducting membranes synthesized by halomethylation and quaternization of benzylmethyl-containing poly(sulfone)s. The benzylmethyl moieties, which serve as precursors to cationic sites, are introduced during polymer synthesis, thereby circumventing postmodification of the polymer by chloromethylation. By directing the distribution of ionic groups, the anion conductivity and water uptake of the membranes could be tuned over a wide range. For homogeneously distributed cationic groups, the water uptake and anionic conductivity were high relative to the material's ion exchange capacity. When an unfunctionalizable comonomer was added, the water uptake decreased for a given ion content. A strong correlation between the water uptake and anion conductivity was observed for all materials. Interestingly, as the cation concentration in the membrane decreased due to an increase in water uptake, the anion conductivity increased. This unexpected relationship between the volumetric density of fixed charged sites and the anion conductivity underscores the importance of water uptake in these materials to promote fast anion transport.

Introduction

By employing a solid-polymer electrolyte, anion exchange membrane fuel cells (AMFC) circumvent the problems with electrolyte leakage and alleviate potassium or sodium carbonate precipitation encountered in liquid electrolyte alkaline fuel cells employing potassium or sodium hydroxide aqueous electrolytes. AMFCs are the high pH counterpart to the more familiar proton exchange membrane fuel cells (PEMFCs), which operate at low internal pH due to their sulfonic acid-based proton conductors. One of the defining differences between these two types of polymer membrane fuel cells is that anion exchange membrane fuel cells, by virtue of their high internal pH, enable oxygen reduction without platinum catalysts and provide facile oxidation of longer chain alcohol fuels. Additionally, the catalytic materials available for use in basic pH environments that do not corrode, especially nonprecious metals, are more plentiful than corrosion-resistant metals and alloys available for use at acidic pH. While PEMFCs have seen rapid gains in performance over the past 10 years due to a ready supply of appropriate materials, namely Nafion or other poly(perfluorosulfonic acid) membranes, ionomer dispersions for catalyst layer preparation, and nanostructured platinum and alloy electrocatalysts, there is no commercially available benchmark membrane material or electrode ionomer for AMFCs, which has slowed device development. Therefore, it is important to investigate a wide range of routes to highly conductive, robust anion exchange membranes and to develop the key structure−property relationships for these types of ion-conducting membranes that can foster increased fundamental understanding in this field. The insights gained from the materials investigations can then be used to design next-generation membranes for specific electrochemical or ion transport applications.

A renewed interest in AMFCs has prompted a variety of studies on new polymer architectures and synthetic approaches to anion exchange membranes (AEM).[1] In commercial anion exchange polymers, chloromethylated poly(styrene) or poly(vinylbenzyl chloride) is cross-linked with divinylbenzene and/or blended with other nonionic polymers or fabric materials to produce a robust, but thick, membrane. The conductivity of these blended or filled commercial membranes, targeted toward electrodialysis applications, is too low (ca. 5−10 mS cm^{-1} or less) for use in a high-performance solid-state fuel cell, and their thicknesses on the order of 200−400 μm are much too great to achieve low cell resistance in a fuel cell. Newer vinylbenzyl chloride-based anion exchange membranes produced by radiation grafting have shown very good performance, and the substrate-grafted approach allows for mechanically stable, yet thin, membranes.[2]

Poly(sulfone)s have high glass transition temperatures as well as excellent chemical and thermal stability, and have been widely used as a basis for novel proton exchange membranes. Indeed, many advances in the understanding of proton exchange membranes have been made using poly(sulfone) as an alternative polymer platform to the commercial fluoropolymer standard. Consequently, using poly(sulfone)s as a basis for exploring the structure−property relationships of AEMs is a reasonable approach to foster developments in this new area. By chloromethylation and subsequent amination, quaternary ammonium groups have been introduced onto poly(sulfone) backbones, and several examples of AEMs have been developed. Zschochke and Qullmalz described the synthesis of AEM from the chloromethylation of Udel (bisphenol A-based poly(sulfone)) and investigated the stability of these membranes and their application in eletrodialysis.[3] The effect of the quaternizing amine on the stability of AEMs was reported by Sata et al., and AEMs from trimethylamine were found to be more stable than *N*-methylpyridinium cations.[4] Furthermore, a variety of diamines have been used for quaternization, and better stability was observed.[5,6]

---

*Corresponding author: ph 814-867-1847, fax 814-865-2917, e-mail hickner@matse.psu.edu.

Hwang et al. reported AEMs from chloromethylated, multiblock polysulfone and demonstrated that these AEMs showed improved electrochemical properties.[7,8] Recently, Hibbs et al. reported a series of AEMs from chloromethylated polysulfone and compared their transport properties with proton exchange membranes, such as Nafion and sulfonated poly(phenylene).[9]

In the majority of reports, poly(sulfone)-based AEMs are prepared via chloromethylation and quaternization of the benzylchloromethyl groups. However, there are some disadvantages of the chloromethylation reaction, which has limited its use in producing novel AEMs. Chloromethylation by chloromethyl methyl ether is rapid, but the reagent is acutely toxic and is a known human carcinogen. Chloromethyl octyl ether is a safer alternative to chloromethyl methyl ether for halomethylating polymers but still caries some toxic and carcinogenic risks. In-situ generation of chloromethyl methyl ether[10] is an alternative to direct use of the toxic reagents, however, this type of procedure requires excess reagents and long reaction times (several days) to obtain highly functionalized polymers, and maintaining polymer solubility in the reaction medium requires a large excess of solvent, which is undesirable. The long times and low-yield reactions reduce the quantitative repeatability of chloromethylation to target specific degrees of functionality, and there is high risk of cross-linking by keeping the chloromethyl form of the polymer in solution for an extended period during reaction. Furthermore, only randomly functionalized polymers can generally be obtained without major manipulations to the polymer backbone composition due to the nonspecific nature of the chloromethylation reaction. Thus, to further research in this area, it is important to develop a more quantitative, rapid, and selective method for production of anion exchange membranes.

Bromination of benzylmethyl groups is a promising method for preparing AEMs as the bromination reaction is rapid and allows for nearly quantitative conversion of the precursor benzylmethyl groups to quaternary ammonium moieties. AEMs based on brominated poly(2,6-dimethyl-1,4-phenylene oxide) were synthesized and characterized by Xu et al.[11,12] Hibbs et al. have also reported methyl-containing poly(sulfone) and poly(phenylene) AEMs using this type of procedure.[13] In this paper, we report poly(sulfone)-based anion exchange membranes from the bromination of benzylmethyl-containing polymers containing tetramethylbisphenol A monomer residues. Compared to chloromethylation, bromination of benzylmethyl-containing polymers has a faster reaction rate (several hours versus several days), high efficiency (80−95% according to the amount of bromination reagent added), and specificity where bromine and thus quaternary ammonium groups can be introduced to particular locations on the polymer chain based on where the benzylmethyl groups reside. Both homopolymers containing methyl groups in every polymer repeat unit and copolymers with clustered methyl groups were synthesized to vary the properties of the AEMs over a wide range. The structure−property relationships for this series of materials is eluciated in this work, and some insights are provided on how the chain microstructure influences the properties of poly(sulfone)-based AEMs.

Experimental Section

All reagents were purchased from Sigma-Aldrich Corp. (St. Louis, MO) and used without further purification unless specified. 4-Fluorophenyl sulfone and 4,4′-biphenol were recrystallized from ethanol and dried at 60 °C under vacuum. Tetramethyl bisphenol A was recrystallized from benzene and dried at 60 °C under vacuum.

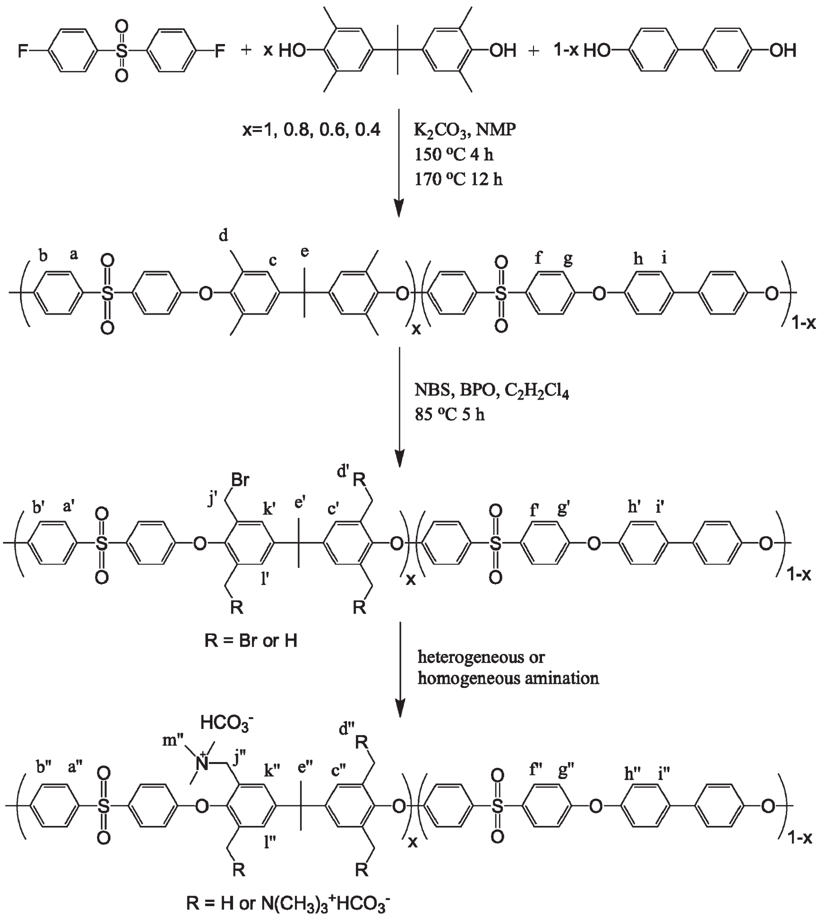
Synthesis of Tetramethyl bisphenol A-Based Poly(sulfone). The homo- and copolymers from 4-fluorophenyl sulfone, tetramethyl bisphenol A, and 4,4′-biphenol were adapted from literature procedures on preparation of poly(arylene ether sulfone)s based on the weak base route.[14] A typical procedure follows. 4-Fluorophenyl sulfone (2.5425 g, 0.010 mol), tetramethyl bisphenol A (2.8440 g, 0.010 mol), anhydrous potassium carbonate (4.1463 g, 0.030 mol), 1-methyl-2-pyrrolidinone (30 mL), and toluene (20 mL) were placed into a 100 mL, three-necked, round-bottomed flask equipped with Dean−Stark trap and condenser, magnetic stirrer, and gas inlet and outlet. The mixture was heated to 150 °C under an argon atmosphere. The toluene and residual water from the reaction solvent were removed from the system as an azeotrope by distillation. The temperature was then raised to 170 °C, and the reaction proceeded until the viscosity of the solution did not increase further. After cooling to room temperature, the mixture was poured into 200 mL of 0.5 M HCl. The fiberlike solid polymer was collected by filtration, Soxhlet extracted with water for 24 h, and dried in vacuum to afford a white solid (4.83 g, 97% yield). The polymers are named by the molar ratio of tetramethylbisphenol A versus 4,4′-biphenol, e.g., sample 60-X contains 0.6 mol of tetramethylbisphenol A and 0.4 mol of 4,4′-biphenol per 1.0 mol of 4-fluorophenyl sulfone.

Bromination of Tetramethylbisphenol A-Based Poly(sulfone). The bromination of the benzylmethyl-bearing poly(sulfone)s were carried out in tetrachloroethane, using *N*-bromosuccinimide (NBS) as the bromination agent and benzoyl peroxide (BPO) to initiate the radial reaction. A typical procedure was 1.0 g of polymer and 20 mL of 1,1,2,2-tetrachloroethane were introduced into a 100 mL, three-necked, round-bottomed flask equipped with condenser, magnetic stirrer, and gas inlet and outlet. The mixture was heated to 85 °C in an argon atmosphere. After the polymer completely dissolved, NBS (0.5339 g, 0.003 mol) and BPO (0.036 33 g, 0.15 mmol) were added. The reaction was held at 85 °C for 5 h. Upon cooling to room temperature, the mixture was poured into 100 mL of methanol, collected by filtration, Soxhlet extracted with acetone for 24 h, and dried in vacuum to afford yellow solid (1.19 g, 92% yield). The polymers are classified by the molar ratio of tetramethylbisphenol A to 4,4′-biphenol as mentioned previously and the millimoles of NBS per 1.0 g of polymer added during bromination, e.g., 80-3, contains 0.8 mol of tetramethylbisphenol A and 0.2 mol of 4,4′-biphenol per 1.0 mol of 4-fluorophenyl sulfone and was brominated with 0.003 mol of NBS per gram of polymer.

Membrane Formation and Characterization. The anion exchange membranes were formed by two methods. The first method of membrane conversion entailed filtering a solution of brominated polymer in chloroform onto a flat glass substrate and letting the chloroform evaporate in a chemical fume hood at room temperature for 12 h. The membrane was then dried at 70 °C in a convection oven for 5 h. The completely dry membrane was removed from the substrate by immersion in water. The membrane was then immersed in 45% (w/w) trimethylamine in water in a sealed container for 48 h at room temperature to convert the bromomethylbenzyl groups in the membrane to quaternary ammonium moieties. The membrane was then soaked in 1 M KOH for 48 h and then was washed completely with deionized water multiple times and stored in water before characterization. This type of membrane-based conversion, from brominated form polymer to quaternary ammonium form polymer, is termed heterogeneous conversion in the present work.

The second conversion method, termed homogeneous amination, was achieved by adding 45% (w/w) trimethylamine in water (300% molar excess compared to the number of bromobenzyl groups on the polymer) to an 8% (w/v) *N*,*N*-dimethylacetamide solution of brominated poly(sulfone). The container was sealed and kept at room temperature for 48 h to affect conversion of the bromomethylbenzyl groups to quaternary ammonium groups while the polymer remained in solution. The aminated polymer was filtered onto a glass substrate and placed in an oven at 50 °C for 24 h. The membrane was then dried under vacuum at 50 °C for 12 h. The membrane was

Scheme 1. Synthesis of Quaternary Ammonium-Containing Polymers from Bromination of Tetramethyl bisphenol A-Based Poly(sulfone)s



removed from the glass by immersion in water, soaked in 1 M KOH for 48 h, and washed completely with deionized water before use. During washing after KOH exposure, the water was replaced every 30 min until the pH value of the water remained about 6−7, indicating that all KOH was extracted from the membrane.

Gel permeation chromatography (GPC) was performed in a *N*,*N*-dimethylformamide mobile phase with a Waters isocratic pump and autosampler. The average molecular weights were measured by calibration with poly(styrene) standards. ^{1}H NMR spectra were obtained on a Bruker-400 spectrometer using 5 mm tubes. The solvent for neutral polymers was $CDCl_3$-d_1, and DMSO-d_6 was used for quaternary ammonium-bearing polymers. Ionic conductivities of the membranes were measured by two-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 frequency response analyzer. EIS was performed on samples immersed in liquid water at 30, 50, and 70 °C, and the activation energies for ionic conduction using an Arrhenius relationship were determined as described in the literature.[15] The pH value of the water used for conductivity measurement was measured before and after each measurement, and it did not change. After each measurement, the deionized water was replaced. Methanol permeability was measured using a membrane-separated concentration cell equipped with a refractive index detector for monitoring the change in methanol concentration with time in the pure water compartment versus an initial concentration of 1 M CH_3OH in the solute compartment.[15] The membrane-separated cell was placed in a thermostated water bath to control the temperature. Measurements of methanol permeability were made between 30 and 70 °C in order to compute the activation energy of methanol permeability.

The degree of functionalization of the brominated polymers was determined by the ratio of the integrals in the ^{1}H NMR spectra for the protons in the bromobenzylmethyl group (j′ in Scheme 1) to the protons adjacent to the sulfone residue (a′ + f′ in Scheme 1). Ion exchange capacities (IEC) were calculated from the ratio of the ^{1}H NMR peaks from the methylene group adjacent to the quaternary ammonium (j″ in Scheme 1) or the methyl protons in the quaternary ammonium moiety (m″ in Scheme 1) and the sum of the signals from the aromatic protons adjacent to the sulfone group, a″ and f″. IECs of the membranes in chloride form were also determined by Mohr titration. About 0.15 g of membrane was ion exchanged in 0.5 M HCl for 24 h (solution changed three times) and then washed with DI water completely. The membrane in chloride form was immersed in 50 mL of 0.2 M $NaNO_3$ for 8 h three times. All the $NaNO_3$ solution was collected and titrated with 0.1000 M $AgNO_3$, using K_2CrO_4 as a colorimetric indicator. After titration the membrane was dried at 50 °C in vacuum for 24 h and weighed. The IEC was calculated from the membrane dry mass and the amount of $AgNO_3$ consumed in the titration.

The water uptake and average number of water molecules per quaternary ammonium group (λ) were obtained according to literature methods.[16] The fully hydrated anion exchange membranes were taken out of water, blotted quickly to remove surface liquid, and weighed immediately. The measurement was repeated after sufficient soaking time (5−10 min) to rehydrate the membranes in order to get a repeatable average value for the hydrated mass of the membrane. The membranes were then dried at 50 °C in vacuum for 24 h and weighed again. Water uptake (%) was calculated from

$$\mathrm{wu} = \frac{m_{\mathrm{hyd}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \times 100\%$$

where m_{hyd} is the hydrated mass of the membranes and m_{dry} is the dry mass. The average number of water molecules per

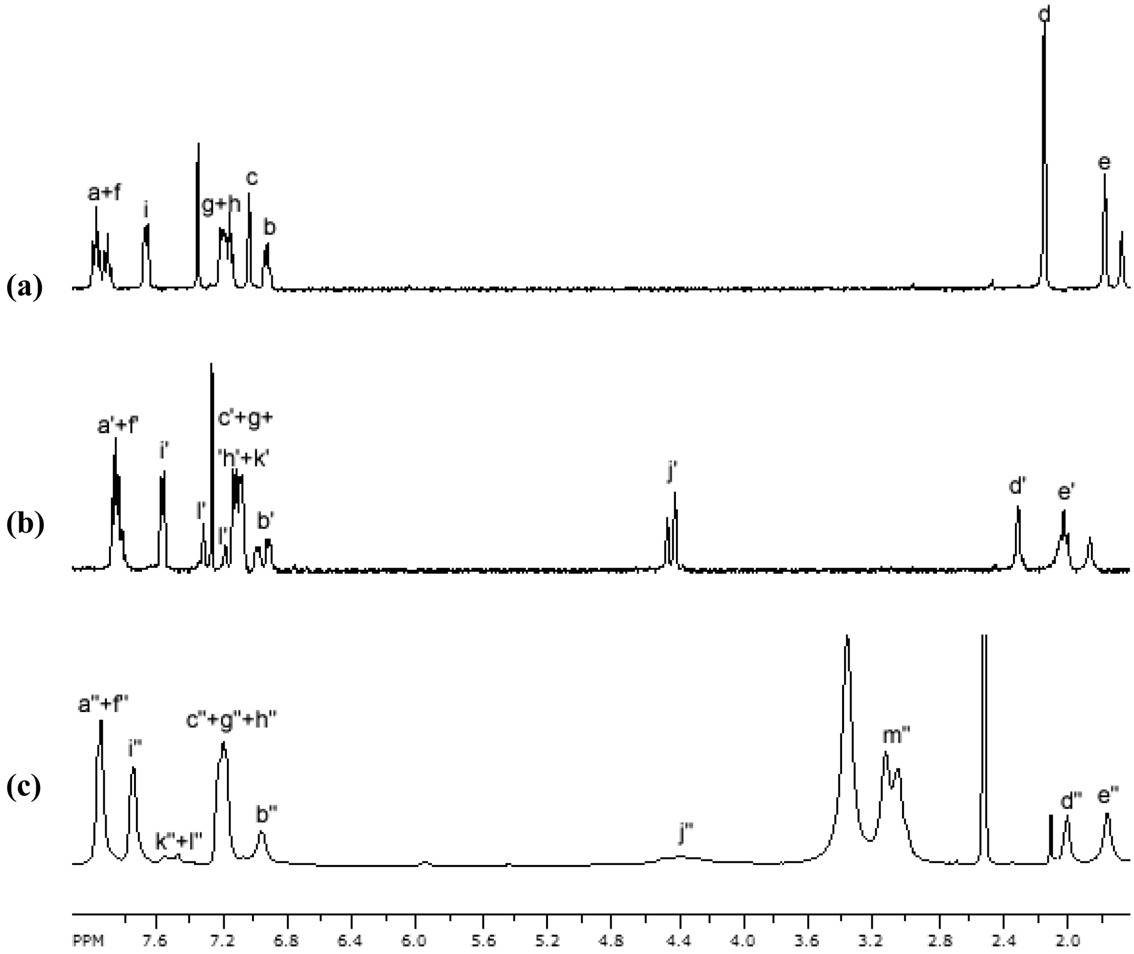


Figure 1. ^{1}H NMR spectra of (a) poly(sulfone) with 40 mol % tetramethyl bisphenol A, (b) brominated 40-3, and (c) 40-3 in quaternary ammonium chloride form. Difference in spectra baselines is due to CDCl$_3$-d_1 as a solvent in (a) and (b) and DMSO-d_6 as the solvent in (c).

quaternary ammonium group, λ, was calculated by

$$\lambda = \frac{\text{wu}}{\text{IEC} \times \text{MW}_{\text{H}_2\text{O}}}$$

The ion concentration in hydrated membranes was calculated using the methods of Kim et al.[17]

Results and Discussion

As shown in Scheme 1, benzylmethyl-containing poly(sulfone)s were prepared by condensing 4-fluorophenyl sulfone with varying molar ratios (1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6) of tetramethylbisphenol A and 4,4′-biphenol. The bromination of the methyl groups in the tetramethylbisphenol A poly(sulfone) was performed in tetrachloroethane at 85 °C. The ^{1}H NMR spectra of the poly(sulfone) with 40 mol % tetramethylbisphenol A, the brominated polymer, 40-3 (3 mequiv of brominating agent per g of polymer), and the quaternary ammonium chloride form of 40-3 are compared in Figure 1. Three new peaks, j′, k′, and l′, appeared in the brominated polymer, and d′ decreased in size, compared with the unbrominated form. The j′ peaks near 4.4 ppm were assigned to the protons in bromomethyl groups, and the degree of bromination was determined by the comparison of the integrals of peaks a′ + f′ and j′. The bromination yield was calculated from the molar amount of NBS introduced into the reaction and the amount of bromine detected in the brominated poly(sulfone) (Table 1). The bromination was nearly quantitative for polymers with a high methyl group content (100 mol % tetramethylbisphenol A) and decreased as the amount of methyl groups in the polymer decreased. Nevertheless, a 70% yield in the bromination reaction over 5 h is superior to the yields usually associated with chloromethylation using the precursor route where 20−50 equiv of reagents are needed and reaction times are on the order of 2−6 days are required. Additionally, the bromination reaction was repeatable for a targeted DF as demonstrated by the standard deviations given in the Table 1 derived from the data in Table S1 (see Supporting Information). While the repeatability of time-based reactions such as chloromethylation can be optimized, the quantitative radical bromination of methyl groups provides a more convenient method for controlling the IEC of AEMs. The amount of methyl groups converted for each of the polymer backbone repeat units increased as the methyl group content decreased in order to keep the DF (or IEC) at a reasonable level for conductivity (Table 1). Thus, polymers with a low mole fraction of tetramethylbisphenol A had more closely clustered ionic groups on the polymer chain than those with high mole fractions of tetramethylbisphenol A for a given IEC. The table shows that attachment of up to three ionic groups per tetramethyl bisphenol A residue was achieved.

Anion exchange membranes were fabricated by two different methods termed heterogeneous amination and homogeneous amination. Heterogeneous amination occurs when the membrane is cast in nonionic form and subsequently converted to ionic form in the solid state by introduction of the quaternizing amine to the already-cast and dried membrane. Homogeneous amination is the process by which the polymer is converted to ionic form in solution and then cast from organic solvent to form a membrane. The peaks near 3.1 ppm in the ^{1}H NMR spectrum of the

Table 1. Molecular Weight, Bromination Yield, Methyl Group Conversion, and Degree of Functionalization of Brominated Tetramethyl bisphenol A-Based Poly(sulfone)s[a]

sample[b]	M_n (kg mol^{-1})	M_w (kg mol^{-1})	bromination yield (%)[c]	methyl group conversion (%)	DF[d]	Br per TMBA monomer
100-2	71	131	92 ± 3	23 ± 1	0.9 ± 0.1	0.9 ± 0.1
100-3	59	118	94 ± 3	35 ± 1	1.4 ± 0.1	1.4 ± 0.1
80-3	53	85	94 ± 3	42 ± 1	1.4 ± 0.1	1.7 ± 0.1
80-4	39	76	83 ± 3	50 ± 3	1.6 ± 0.1	2.0 ± 0.1
60-3	76	118	83 ± 2	48 ± 1	1.1 ± 0.1	1.9 ± 0.1
60-4	48	76	85 ± 5	65 ± 4	1.6 ± 0.1	2.6 ± 0.2
40-3	92	178	82 ± 6	68 ± 5	1.1 ± 0.1	2.7 ± 0.2
40-4	86	127	70 ± 4	78 ± 4	1.2 ± 0.1	3.1 ± 0.2

[a] Errors were calculated from the standard deviations of at least three independent bromination reactions (see Table S1). [b] The first number stands for the mol % of tetramethyl bisphenol A versus biphenol. The second number stands for the molar equivalents of NBS used per gram poly(sulfone). [c] Calculated from the bromine added in NBS and resulting bromine on the poly(sulfone) by ^{1}H NMR. [d] Number of bromomethyl groups on average per repeat unit by ^{1}H NMR.

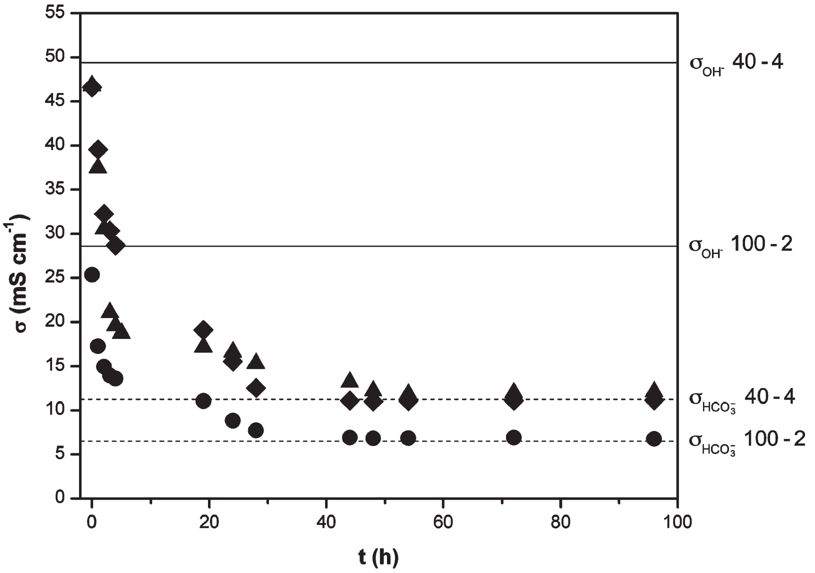


Figure 2. Anion conductivity of 100-2 (●), 40-4 (◆), and 80-3 (▲) as a function of time during conversion from OH^- to HCO_3^- form during exposure to ambient air containing CO_2. Individual points are measured conductivity with time during in-situ conversion of OH^- to HCO_3^-. Dashed lines for $\sigma_{HCO_3^-}$ represent the measured conductivity of the samples ion exchanged with sodium bicarbonate. Solid lines for σ_{OH^-} were projected from the dilute solution mobility of the anionic species.

quaternary ammonium chloride form polymer (Figure 1) were assigned to the proton of methyl groups in the quaternary ammonium moiety. From the ratio of the integral of these peaks to the aromatic peaks, the ionic exchange capacity (IEC) was calculated. The IEC was also measured by titration of Cl^- using silver nitrate, and there was no significant difference in IEC between the membranes fabricated from homogeneous and heterogeneous amination. The measured values were between 90 and 95% of the theoretical values determined from the DF of the brominated polymer, which was slightly higher than the results in the literature and may be due to the long soaking times employed for the titration used in this work and calculations of the polymer mass, assuming it is in the bicarbonate form after exposure to air.[11] From a recent report by Yanagi and Fukuta,[18] OH^- is neutralized quickly on exposure to air as a result of the rapid absorption of CO_2 and hydroxide/carbonate/bicarbonate exchange. After initial ion exchange of the membrane to the hydroxide form, the conductivity of the samples steadily declined over a period of 3–4 days which was ascribed to sorption of CO_2 (Figure 2). After 4 days of exposure of the membrane in water to ambient air, the conductivity of the samples was the same as for samples purposely ion exchanged to bicarbonate form. Interestingly, when the conductivities of the samples were multiplied by 3.8 to estimate the conductivity of OH^- form membranes (dashed lines) from their bicarbonate conductivity (solid lines) given the dilute solution mobility of the ions, 0.61 for HCO_3^- and 2.3 for OH^- relative to a mobility of 1 for K^+, the resulting conductivity was near the value measured at $t = 0$. This correction of the conductivity by the dilute solution mobility of the anion supports the change of conductive species from hydroxide to bicarbonate. Therefore, based on the independent investigations of Yanagi and Fukuta[18] and the data presented here, there is good evidence of conversion of AEMs to bicarbonate form from hydroxide form over the course of a few days, which causes a corresponding decrease in ionic conductivity. Because of the difficulty in characterizing membranes definitively in OH^- form by excluding CO_2 rigorously as in a glovebox, all the membranes were converted into bicarbonate form by aging in water exposed to air (with 400 ppm of CO_2) for 4 days or until its conductivity was constant. Thus, all the characterization of AEMs in this paper was based on the membranes in bicarbonate form.

The ionic conductivity as a function of ion exchange capacity on a mass basis for membranes in this study is plotted in Figure 3. A general trend was observed where the membranes converted to the ionic form in solution and then cast, homogeneous amination, had higher conductivity for a given IEC than those that underwent ionic conversion in the membrane form, or heterogeneous amination. This behavior may signal that there were some ionic interactions during the casting process, which promote ionic aggregation and thus higher conductivity. Two samples in Figure 3 seemed to not follow the general trend of increasing conductivity with IEC. These samples were both based on 100-3,

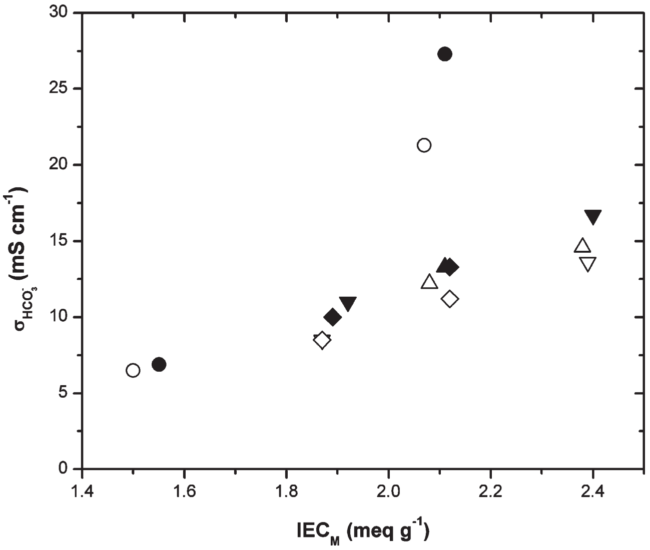


Figure 3. Anion conductivity (bicarbonate form) of the quaternary ammonium-containing poly(sulfone) samples versus IEC on a mass basis. Closed symbols represent homogeneously converted samples, and open symbols represent heterogeneously converted samples. Symbol shape indicates mol % tetramethyl bisphenol A: 100 = (●, ○), 80 = (▲, △), 60 = (▼, ▽), and 40 = (◆, ◇).

which has very high ion conductivity at intermediate ion content. The primary difference in the chemical structure of these samples versus the other membranes in this study was that they are based completely on tetramethyl bisphenol A with no 4,4′-biphenol comonomer. Thus, the ionic groups were randomly distributed along the polymer backbone chains. The IEC of the 100-3 polymers was about 2.1 mequiv g^{-1}, while the IEC of the 100-2 samples was ~1.5 mequiv g^{-1} (see Table S2 in Supporting Information). Since the lower IEC 100-2 samples did not exhibit the anomalously high conductivity as with the 100-3 samples on an IEC basis compared to the other copolymers, it can be assumed that a critical ion content was necessary to achieve high conductivities in these materials.

The ionic conductivity and methanol permeability of the AEMs showed similar trends with water uptake (Figure 4) where samples over the entire range of IECs scaled in a relatively monotonic fashion with the bulk water uptake of the sample. Additionally, there was no difference between homogeneous and heterogeneously converted samples in terms of the magnitude of their methanol permeability or conductivity when plotted on a water uptake basis. Both conductivity and permeability rely on the presence of water in the membranes; therefore, the scaling of these properties with the bulk water uptake is reasonable for a given family of polymers with similar chemical structures. Figure 4 reveals that 100-3 was not a major outlier in terms of its relationship between water uptake and membrane transport properties.

Figure 4 shows 100-3, both homogeneous and membrane converted, had a relatively high ionic conductivity given their IEC. However, these polymers sorbed considerably more water than the other samples, and thus their high water uptake underpinned their increased ionic conductivity and methanol permeability. The increased water sorption of 100-3 can be rationalized given the chemical structure and the distribution of ions along the backbone chain. For a random distribution of ions on the polymer backbone, when the ionic density reached a critical level, the water uptake increased substantially, e.g., 100-2 vs 100-3. Large water uptake was suppressed by confining the placement of cationic groups on the linear polymer chain by decreasing the molar ratio of tetramethyl bisphenol A to 4,4′-biphenol. The 4,4′-biphenol residue cannot be functionalized in the bromination and amination reactions; therefore, the net effect of adding the 4,4′-biphenol to the copolymer was to exclude ions from attaching randomly to the polymer backbone and to increase the local concentration of ionic groups where tetramethyl bisphenol A residues were located. A schematic of the proposed difference in ion clustering between homopolymers of tetramethyl bisphenol A and copolymers of tetramethyl bisphenol A and 4,4′-biphenol is shown in Figure 5. Clustering of ionic groups along the backbone chain decreased the total water uptake of the membrane for a given IEC but did not seem to have an impact on ionic conductivity when the water uptake was taken into account.

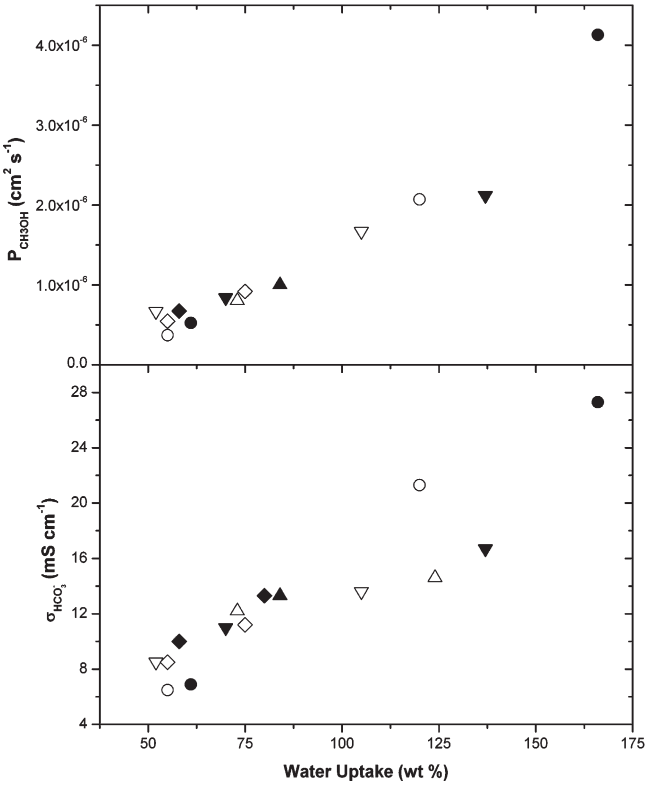


Figure 4. Methanol permeability and conductivity of tetramethyl bisphenol A-based poly(sulfone)s as a function of water uptake. Closed symbols represent homogeneously converted samples. Open symbols represent heterogeneously converted samples. Symbol shape indicates mol % tetramethyl bisphenol A: 100 = (●, ○), 80 = (▲, △), 60 = (▼, ▽), and 40 = (◆, ◇).

The activation energies for ionic conductivity and methanol permeability as a function of the water uptake are shown in Figure 6. The activation energies for these transport properties tended to decrease as the water uptake increased. The activation energies for ionic conductivity of the AEMs studied ranged from 12 to 25 kJ mol^{-1}, which are much higher than the values reported for proton exchange membranes and the values in other AEMs.[19] The high activation energies for conduction can be explained in the terms of the counterions being conduced in this work, namely bicarbonate. Bicarbonate has lower dilute solution ionic mobility compared with proton or hydroxide due to hopping type transport for both H$^+$ and OH$^-$. Bicarbonate does not undergo hopping transport; therefore, its activation energy is greater and its mobility is lower. The activation energies for methanol permeability of the materials in this work are lower than those measured for PEMs of around 20 kJ mol^{-1}.[15] Lower activation energies in the quaternary ammonium-containing membranes equate to more facile transport of methanol than

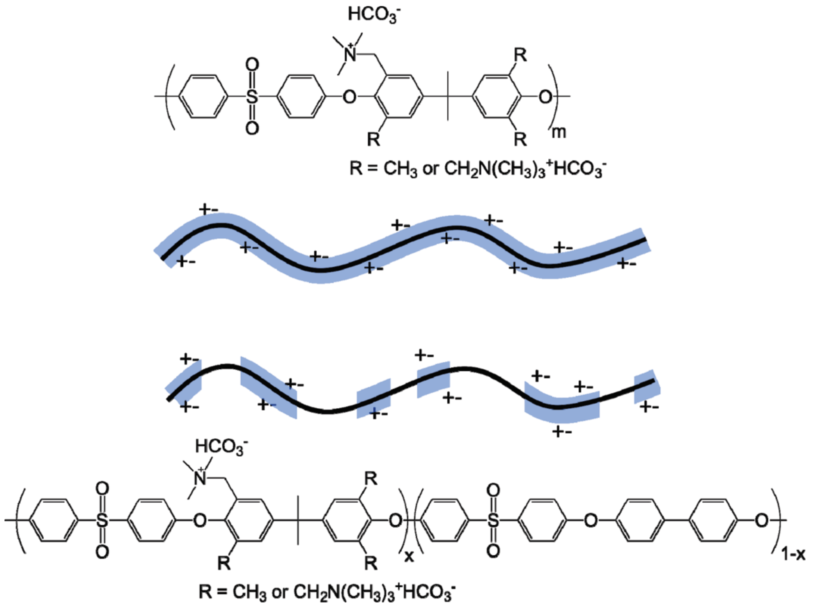


Figure 5. Proposed schematic of ion clustering in tetramethyl bisphenol A homopolymers (top) and tetramethyl bisphenol A/4,4′-biphenol copolymers (bottom).

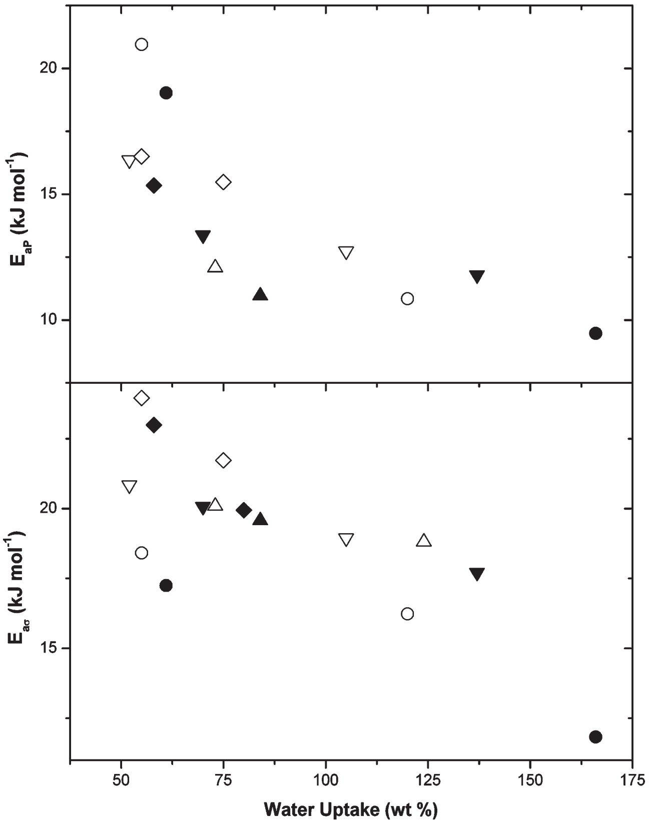


Figure 6. Activation energy for methanol permeability and bicarbonate conductivity versus water uptake. Closed symbols represent homogeneously converted samples, and open symbols represent heterogeneously converted samples. Symbol shape indicates mol % tetramethyl bisphenol A: 100 = (●, ○), 80 = (▲, △), 60 = (▼, ▽), and 40 = (◆, ◇).

in PEMs, which could be expected given the weaker water–polymer interactions in AEMs as measured by NMR and calorimetry.[9]

Ionic conductivity as a function of both hydration number, λ, and IEC in the wet state on a volumetric basis (IEC_{Vwet}) is shown in Figure 7.

The conductivity scaled with hydration number except for two outliers, which have conductivities of about 7 mS cm^{-1} at hydration numbers of 20–23. These two samples were the 100-2 polymer, which had a low concentration of ions (IEC of 1.51 mequiv g^{-1}) dispersed randomly along the polymer chain. 100-2 was different from the other samples in that it contains only tetramethylbisphenol A, which yields random placement of the ionic groups along the backbone, and it also had rather low ion content compared to 100-3 (IEC = 2.1 mequiv g^{-1}). The random placement of ions and the low ion concentration caused 100-2 to have poorer transport performance than polymers with clustered ionic arrangement or greater amounts of ions. Therefore, while the ionic clusters have not been detected in X-ray scattering experiments (see Figure S1 in Supporting Information), there seems to be morphological factors at play that promote high conductivity, through either ionic clustering on the backbone or overlap of hydrated ionic regions at high ion content.

Conclusions

A series of anion exchange membranes were prepared via the bromination of tetramethyl bisphenol A-based poly(sulfone)s followed by amination and ion exchange. By bromination of benzylmethyl-containing polymers, as opposed to the often-employed chloromethylation, the ion content of the polymer could be controlled quantitatively with relatively short reaction times. Varying the ratio of functionalizable and nonfunctionalizable monomers afforded AEMs with desirable water uptakes and conductivities with up to three ionic groups per tetramethyl bisphenol A residue. The AEMs were cast from organic solvents and yielded similar properties if converted to the ionic form in solution or in the solid state.

The structure–property relationships of these AEMs were a strong function of water uptake. The tetramethyl bisphenol A homopolymers had high conductivities at intermediate IECs on a mass basis but swelled to a large extent in liquid water. The copolymers swelled less with the incorporation of a nonfunctionalizable comonomer but had lower ionic conductivities than the homopolymers. All of the samples showed a systematic increase in conductivity with water uptake or λ. Interestingly, because of the large water uptake of these materials, the conductivity decreased with increasing ion exchange capacity in the wet state. This relationship stands in contrast to that observed for proton

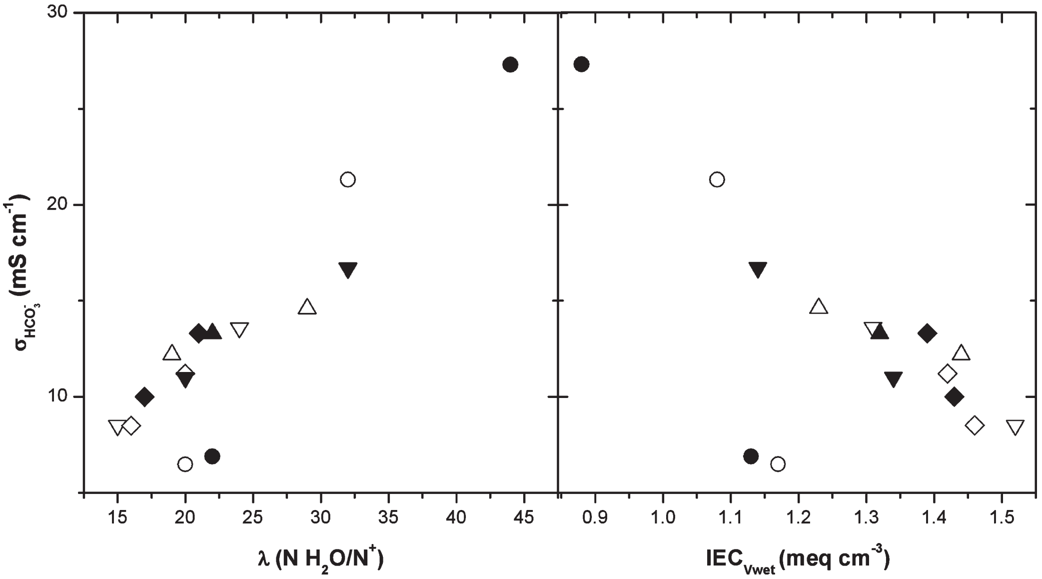


Figure 7. Conductivity versus hydration number and volumetric ion exchange capacity for the hydrated membranes. Closed symbols are homogeneously converted samples, and open symbols are heterogeneously converted samples. Symbol shape indicates mol % tetramethyl bisphenol A: 100 = (●, ○), 80 = (▲, △), 60 = (▼, ▽), and 40 = (◆, ◇).

exchange membranes, where the conductivity usually increases with IEC_{Vwet}. In anion exchange membranes, increased water content seems to promote high conductivity even at low volumetric polymer-bound cation concentration. This unique relationship between ion content, water uptake, and conductivity could be a result of anion conduction, bicarbonate in this case, being more reliant on the presence of high concentrations of loosely bound water versus a strong dependence on fixed volumetric ion concentration. This observation underscores some of the challenges in developing highly conductive anion exchange membranes with low water uptake and robust mechanical properties.

Acknowledgment. The authors thank the Office of Naval Research under Grant N00014-08-1-0730 for support of this work. The Penn State Materials Research Institute and Penn State Institutes of Energy and the Environment are acknowledged for infrastructure support. We thank Kui Xu from Professor Qing Wang's lab in the Department of Materials Science and Engineering at Penn State for the GPC measurements.

Supporting Information Available: Tables listing the degree of functionalization for multiple bromination reactions, sample properties in numerical form, and small-angle X-ray scattering data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187–200.
(2) Varcoe, J. R.; Slade, R. C. T.; Yee, E. L. H.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. *Chem. Mater.* **2007**, *19*, 2686–2693.
(3) Zschocke, P.; Quellmalz, D. *J. Membr. Sci.* **1985**, *22*, 325–332.
(4) Sata, T.; Tsujimoto, M.; Yamaguchi, T.; Matsusaki, K. *J. Membr. Sci.* **1996**, *112*, 161–170.
(5) Bauer, B.; Strathmann, G.; Effenberger, F. *Desalination* **1990**, *79*, 125–144.
(6) Hao, J. H.; Chen, C.; Li, L.; Yu, L.; Jiang, W. *Desalination* **2000**, *129*, 15–22.
(7) Hwang, G. J.; Ohya, H. *J. Membr. Sci.* **1998**, *140*, 195–203.
(8) Hwang, G. J.; Ohya, H. *J. Membr. Sci.* **1998**, *149*, 163–169.
(9) Hibbs, M. R.; Hickner, M. A.; Alam, T. M.; McIntyre, S. K.; Fujimoto, C. H.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2566–2573.
(10) Wright, M. E.; Toplikar, E. G.; Svejda, S. A. *Macromolecules* **1991**, *24*, 5879–5880.
(11) Xu, T.; Zha, F. F. *J. Membr. Sci.* **2002**, *199*, 203–210.
(12) Xu, T.; Yang, W. *J. Membr. Sci.* **2001**, *190*, 159–166.
(13) Hibbs, M. R.; Cornelius, C. J. *Polym. Prepr.* **2007**, *48*, 198–199.
(14) Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827–1836.
(15) Hickner, M. A.; Fujimoto, C. H.; Cornelius, C. J. *Polymer* **2006**, *47*, 4238–4244.
(16) Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* **2005**, *38*, 5010–5016.
(17) Kim, Y. S.; Einsla, B.; Sankir, M.; Harrison, W.; Pivovar, B. S. *Polymer* **2006**, *47*, 4026–4035.
(18) Yanagi, H.; Fukuta, K. *ECS Trans.* **2008**, *16*, 257–262.
(19) Slade, R. C. T.; Varcoe, J. R. *Solid State Ionics* **2005**, *176*, 585–597.