

Phenyltrimethylammonium Functionalized Polysulfone Anion Exchange Membranes[†]

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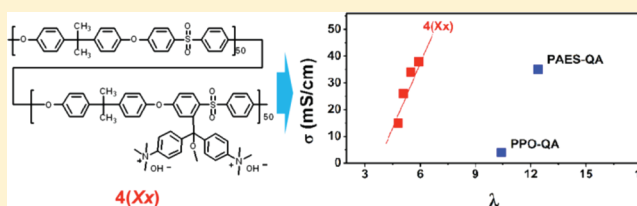
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ABSTRACT: Anion exchange membrane (AEM) materials were prepared from commercial polysulfone (PSf) by functionalization with tertiary amines via lithiation chemistry. By optimizing the reaction conditions, a degree of substitution (DS) of 0.81 could be achieved without evident polymer decomposition or cross-linking. The PSf containing pendent bis(phenyldimethylamine) substituents were then quaternized with CH_3I and ion exchange reaction to provide bis(phenyltrimethylammonium) (PTMA) polymer with hydroxide-conductive properties. Flexible and tough membranes with various ion exchange capacities (IEC)s could be prepared by casting the polymers from DMAC solutions. The ionomeric membranes showed considerably lower water uptake (less than 20%), and thus dimensional swelling in water, compared with many reported AEMs. The hydroxide conductivities of the membranes were above 10 mS/cm at room temperature. The unusually low water uptake and good hydroxide conductivity may be attributed to the “side-chain-type” structures of pendent functional groups, which facilitate ion transport. Although the PTMA substituents on the AEM were found to have insufficient long-term stability for alkaline fuel cell application, the investigation gives some insight and directions for polymeric designs by postfunctionalization.



INTRODUCTION

Aromatic poly(arylene ether sulfone)s, which include bisphenol A polysulfone (PSf), are important engineering thermoplastics because they have excellent chemical and thermal stability and mechanical strength and have been widely employed as membrane materials.^{1,2} The introduction of functional groups into PSf extends the range of potential applications of these high-performance materials with specific function and wider scope. The introduction of functionality into PSf has been accomplished by copolymerization with functionalized comonomers or by postfunctionalization of commercially available polymers. Examples of the functionalization chemistry include sulfonation,³ bromination,⁴ chloromethylation,⁵ amidoalkylation,⁶ and lithiation.^{7–9} Functionalized PSfs have been actively investigated as membrane materials for gas^{1,2,10,11} and liquid separation¹² and for fuel cells (FCs).^{13–16} For example, sulfonated polysulfones, which have been synthesized by copolymerization with a sulfonated comonomer or by postsulfonation,^{13,16} have been widely studied for proton exchange membranes (PEMs) for acidic fuel cells to provide alternatives to established Nafion that has dominated the field.^{17,18} However, the requirement for Nafion and platinum precious metal-based electrocatalysts are creating cost barriers for the widespread commercialization and adoption of acidic PEMFCs.¹³

Recently, anion (hydroxide, OH^-) exchange membranes (AEMs) have been attracting growing interest, by switching from an acidic medium to a basic one in alkaline fuel cells.^{19–23} A major advantage of alkaline fuel cells, relative to acidic fuel cells, is their enhanced reaction kinetics for both oxygen reduction and fuel oxidation, permitting the use of much less costly, non-noble-metal catalysts (e.g., Ni).^{19,24–27} Additionally, in the case of direct methanol fuel cells (DMFC), the direction of hydroxide ion conduction opposes that of methanol crossover, thereby mitigating or possibly eliminating this process.^{22,23} Some functionalized polymers have been developed as AEMs for alkaline fuel cells.^{28–31} These hydroxide-conductive functional groups were obtained by introducing quaternized ammonium (QA),^{32,33} guanidinium,^{34–36} or phosphonium groups³⁷ using chloromethylation on aromatic rings or bromination on the methyl groups of the polymers, followed by the Menshutkin reaction with tertiary amine, pentamethylguanidine, or tertiary phosphine. Some AEMs have exhibited good hydroxide conductivity. For example, Hibbs et al.²⁸ reported an AEM based on poly(phenylene), which exhibits good mechanical properties and excellent conductivity

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(50 mS/cm at 30 °C, IEC = 1.57 mequiv/g, water uptake (WU) = 122%). Zhang et al.³⁸ prepared an AEM using a partially fluorinated poly(arylene ether sulfone) system that shows remarkable conductivities in excess of 60 mS/cm at 20 °C (IEC = 2.62 mequiv/g, WU = 86%). A variety of additional AEMs based upon modification of pre-existing polymers have also been described in recent literature, which display a wide range of conductivities.^{22,23} More recently, multiblock PSf with QA groups have been synthesized, which showed enhanced hydroxide conductivity of 144 mS/cm at 80 °C (IEC = 1.93 mequiv/g, WU = 112%).^{39,40} However, the high hydroxide conductivity in these materials could be only achieved through high ionic content, leading to excessive water uptake and dimensional swelling in water, and thus loss of mechanical properties. Therefore, while many of these polymeric materials demonstrate promise and progress for AEMs and establish the feasibility for alkaline membrane electrode assemblies, conductivity improvements and water swelling controls are still necessary to reach performance approaching current acid-based PEMFC.

In the pursuit of hydrocarbon-based aromatic PEMs with improved properties, we and others have shown that one promising approach to enhance PEM properties and performance is to position the sulfonic acid groups on side chains grafted onto the polymer main chain.⁴¹ If the polymer structure contains flexible pendent side chains linking the polymer main chain and the sulfonic acid groups, nanophase separation between hydrophilic and hydrophobic domains may be improved, thus enhancing proton conductivity and mitigating water swelling.^{42–45} While there have been few reports on AEMs based on aromatic polymers with pendent quaternary ammonium (QA) groups, the strategy of utilizing a “side-chain-type” structure is also expected to be useful in AEMs. Therefore, the objective of this research is to produce AEMs containing pendent QA groups via a simple postfunctionalization of commercial PSf and to evaluate their properties.

In our work on polysulfone modification by lithiation,^{7–11,46} we and others have demonstrated that this synthetic method is an effective approach to postfunctionalized PSf with a wide variety of functional groups. Reaction of various electrophilic aryl and alkyl carbonyl compounds with PSf-Li yields the corresponding carbinol substituents,^{9–11} including those containing arylamines.^{46–48} Herein, we report the preparation of bis(phenyldimethylamine) functionalized PSf by facile reaction of lithiated polysulfone with Michler's ketone and subsequent conversion to bis-(phenyltrimethylammonium) (PTMA) polymer with hydroxide-conductive properties by treatment with CH₃I and ion exchange reaction. The properties of the resulting membranes, such as the stability, mechanical strength, water uptake behavior, methanol permeability, and hydroxide conductivity, are investigated.

EXPERIMENTAL SECTION

Materials. Bisphenol A polysulfone (PSf) was purchased from Solvay and dried at 110 °C for at least 24 h before using. *n*-Butyllithium (2.5 M in hexane), iodomethane, bis[4-(dimethylamino)phenyl]methanone (Michler's ketone), dimethylacetamide (DMAc), and K₂CO₃ were obtained from Sigma-Aldrich and were used as received. Anhydrous reagent grade tetrahydrofuran (THF) was freshly distilled over lithium aluminum hydride under a constant argon purge with mechanical stirring. A dry ice/ethanol bath was used for cooling reaction mixtures. For the control polymers and experiments, quaternized poly(arylene ether sulfone) (PAES-QA)³⁹

and poly(phenylene oxide) (PPO-QA)²⁰ were prepared according to previous reports.

Preparation of Bis(phenyldimethylamine)-Modified PSf 2. A typical synthetic procedure for Michler's ketone-modified PSf, illustrated by the preparation of **2** copolymers (target degree of substitution (DS) of 1.0), is shown in Scheme 1 and described as follows: A solution of PSf (8.80 g, 20 mmol) in THF (2 wt %) was cooled to -76 °C, and 1.2 mol equiv of *n*-butyllithium (9.6 mL, 24 mmol) was injected dropwise by drop funnel over a period of 15 min, during which time changes in the color and viscosity of the homogeneous reaction solution were observed. Following addition, the resulting solution of lithiated PSf (PSf-Li) was stirred for 15 min. Precooled solution of Michler's ketone (10.7 g, 40 mmol) in THF was poured promptly into the rapidly stirred PSf-Li solution, which immediately developed a deep blue color. Within 2 min, a highly viscous gel formed that gradually changed into a pearl blue heterogeneous mixture. The viscosity decreased rapidly while the reaction was gradually warmed to -10 °C over a period of 1.5 h. Then the polymer was recovered by precipitation from an ice/ethanol mixture and then washed and dried. The light blue polymeric product (**2**(X81), 10.5 g, yield 77%) had a DS of 0.62, determined by NMR.

Synthesis of PSf Containing Pendent Bis(phenyltrimethylammonium iodide) 3. The following represents a typical procedure for the synthesis of **3**(X81) containing pendent bis(phenyltrimethylammonium iodide). **2**(X81) (1.0 g, 1.4 mmol) was dissolved in DMAc (15 mL), and then K₂CO₃ (0.15 g, 1.2 mmol) and iodomethane (1 g, 6.8 mmol) were added. The reaction mixture was stirred at 30 °C for 24 h in the dark and then poured into distilled water. The precipitate was filtered off, washed with ethanol and distilled water thoroughly, and dried in vacuum oven for 24 h at 100 °C to give product with 97% of yield. ¹H NMR was used to confirm the synthesis of **3**(X81), and the degree of conversion of the tertiary amine group was close to 100%.

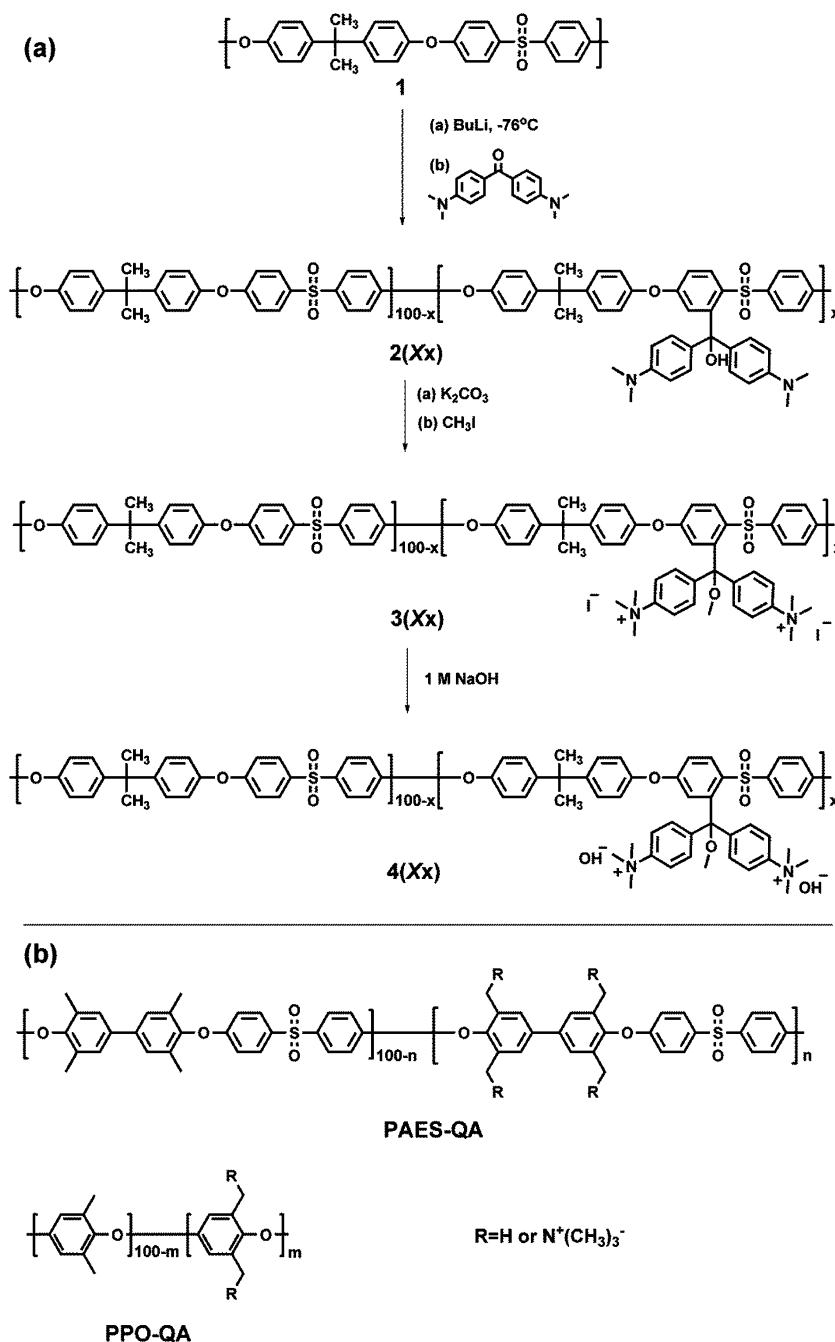
Membrane Fabrication and Anion Exchange. Cyan-colored membranes were cast from DMAc solutions (5 wt %) of **3**(X81) in a custom-built flat glass dish. The membranes were initially dried at 80 °C for 12 h and then vacuum-dried at 100 °C for 24 h. Purple-colored **4** membranes were obtained by treating **3** membranes in 1 M NaOH at room temperature for 24 h; they were washed thoroughly and immersed in deionized water for 48 h to remove residual NaOH. The resulting membranes were characterized immediately.

Characterization and Measurements. ¹H NMR spectra were measured at 300 MHz on a Bruker AV300 spectrometer. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 °C on 0.5 g dL⁻¹ concentrations of polymer in DMAc. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min⁻¹ at atmosphere conditions (20 °C, 50% relative humidity). To experimentally determine ion exchange capacities (IEC), the **4** membranes in the OH⁻ form were immersed in 100 mL of 0.1 M HCl standard for 48 h and then titrated with a standardized NaOH solution using phenolphthalein as an indicator.

The density of the membranes was measured by a buoyancy method. Water uptake was measured after drying the membrane in hydroxide form at 60 °C under vacuum for 24 h. The dried membrane was immersed in water and periodically weighed on an analytical balance until a constant weight was obtained, giving the weight-based (IEC_w) water uptake. The volume-based IEC (IEC_v) was obtained by multiplying the membrane density by the IEC values which were estimated from the copolymer structure. This calculation resulted in IEC_v (dry) based on the dry membrane density. The IEC_v (wet) (mequiv/cm³) was then calculated based on membrane water uptake, using the equation

$$\text{IEC}_v(\text{wet}) = \frac{\text{IEC}_w}{\frac{1}{\rho_{\text{polymer}}} + \frac{\text{WU}(\text{wt}\%)}{100 \times \rho_{\text{water}}}} \quad (1)$$

Scheme 1. (a) Synthesis of Bis(phenyltrimethylammonium) (PTMA) Functionalized Copolymers 4 by Lithiation Chemistry; (b) Chemical Structures of PAES-QA and PPO-QA for the Control Experiments



where IEC_w is the gravimetric IEC (mequiv/g) and ρ (g/cm^3) is the density.

Hydroxide conductivity (σ , $S\ cm^{-1}$) of each membrane sample (size: $1\ cm \times 4\ cm$) was obtained using $\sigma = d/L_s W_s R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The conductivity measurements under fully hydrated conditions in the longitudinal direction were carried out with the cell immersed in liquid water.

The methanol permeability was determined by using a cell consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 M) was placed on one side of the diffusion cell, and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using a Shimadzu GC-1020A series gas chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability was calculated by the equation

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (2)$$

where C_A and C_B are the methanol concentration of feed side and permeated through the membrane, respectively. A , L , and V_B are the effective area, the thickness of membrane, and the volume of

permeated compartment, respectively. DK is defined as the methanol permeability, and t_0 is the time lag.

RESULTS AND DISCUSSION

Synthesis of PSf with Pendent PTMA Groups by Lithiation Chemistry. Lithiation is a versatile method allowing the attachment of a wide variety of functional groups onto polysulfones.^{1,7–11} In the present study, a series of bis(phenyldimethylamine)-containing PSfs were prepared by the addition of Michler's ketone to PSf-Li, as outlined in Scheme 1. The Michler's ketone-modified polymers **2** having various DS were obtained as light blue powders and were soluble in most organic solvents such as chloroform, dichloromethane, dimethylformamide (DMF), DMAc, and *N*-methylpyrrolidone (NMP), but not in methanol or isopropanol. The chemical structures and DS were confirmed by ¹H NMR. As shown in Figure 1, a new singlet corresponding to the

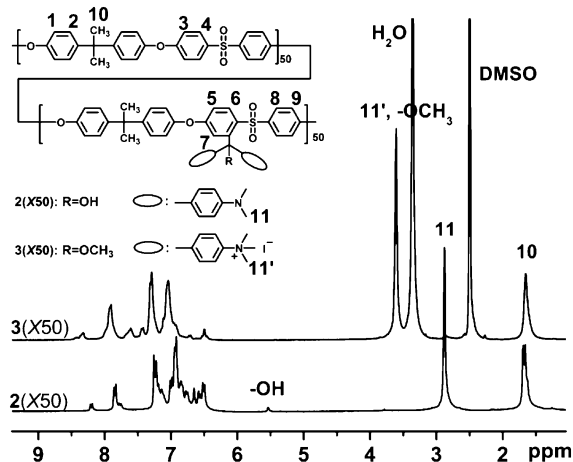


Figure 1. ¹H NMR spectra of **2**(X50) in CDCl₃ and **3**(X50) in DMSO-*d*₆ in the iodide form.

dimethylamine protons of the Michler's ketone residue was observed at 2.88 ppm. The aromatic proton signals from the Michler's ketone residue appeared at 6–7 ppm (Figure 1). The DS (Table 1) was estimated from the ratio of signal integrations of the dimethylamine protons to the 6H isopropylidene protons in the PSf chain at 1.62 ppm. Although the reaction of PSf-Li with many electrophiles has been shown to be near quantitative,^{47,48} the Michler's ketone electrophile showed lower reactivity, which resulted in a less-substituted polymer; the highest DS of 0.81 was obtained by reaction of Michler's ketone with dilithiated PSf. A likely reason for the lower than expected DS is steric hindrance of the electrophilic carbon around the sulfone linkage because the electrophilic carbon center is not easily accessible.⁴⁶ Another reason could be side reactions.

However, viscosity measurements confirmed that the PSf lithiation derivatization process did not result in any significant changes in molecular weight (Table 1), which has been observed in previous studies.^{47,48}

The copolymers **2** were converted to quaternized polysulfones by reaction with iodomethane. The mole ratio of iodomethane to phenyldimethyl amine groups was 2:1 to ensure complete quaternization of the tertiary amine units into the bis(phenyltrimethylammonium) (PTMA) substituents and –OH into –OCH₃ groups. There was no evidence of polymer chain degradation occurring under these conditions, as indicated by viscosity measurements (Table 1) and the mechanical properties of the resulting polymer membranes. The quaternized polymers **3** were isolated, which were readily soluble in common polar aprotic solvents (DMF, DMAc, and NMP), resulting in transparent solutions. Transparent and flexible cyan-colored **3** membranes were cast from DMAc solutions in the iodide form. Figure 1 shows the ¹H NMR spectrum of **3**(X50) in iodide form. Comparison of **3**(X50) with the parent copolymer **2**(X50) revealed that the signals assigned to the nonquaternized methyl groups of bis(phenyldimethylamine) (H11) disappeared in **3**(X50), while the polymer main-chain isopropylidene methyl protons (H10) remained after the quaternized reaction. A new signal assigned to the methyl groups in bis(phenyltrimethylammonium) (H11') appeared at 3.47 ppm in **3**(X50). Moreover, the disappearance of –OH protons at 5.5 ppm in **2**(X50) indicates the complete conversion of –OH to –OCH₃ (3.47 ppm) which overlap with H11'. Thus, the theoretical IEC values of **3** membranes were readily calculated by comparing the integration ratios of the isolated signals H10 and H11' and –OCH₃, as shown in Table 1.

The purple-colored anion exchange membranes **4** in the hydroxide form were obtained by treating **3** membranes in 1 M NaOH at room temperature for 24 h. An observed color change is common to many commercially available AEMs, such as the Tokuyama AMX and AMI membranes, which change color from light yellow to black after less than an hour of exposure to 1 M NaOH. The color change in the PSf-PTMA membranes is presumably due to the decomposition of PTMA under alkaline conditions during the hydroxide conversion step.¹⁹ The chemical structures before and after the hydroxide conversion were analyzed by ¹H NMR, as shown in Figure 2. After conversion in 1 M NaOH for 24 h, the aromatic proton signals between 6.4 and 8.4 ppm showed minor changes when compared with those of pristine sample in the iodide form. However, the integration of methyl protons (H11') in PTMA decreased, and the signal corresponding to H11 in phenyldimethyl amine reappeared. Thus, the IEC values estimated for **4** from the signal integration ratio were much lower than those of **3** membranes from ¹H NMR, which correlated well with the titrated values. The IEC values determined by titration were

Table 1. IEC Values and Viscosities of the Polymers

polymers	2			3		4	
	η^a	target DS	exptl DS	η^b	IEC _w (mequiv/g) (NMR)	IEC _w (mequiv/g) (NMR)	IEC _w (mequiv/g) (titration)
X35	0.58	0.5	0.35	0.88	1.24	0.98	1.01
X50	0.57	0.8	0.50	0.92	1.62	1.30	1.32
X62	0.60	1.0	0.62	1.05	1.88	1.43	1.46
X81	0.52	2.0	0.81	0.98	2.21	1.69	1.74

^aMeasured in CHCl₃ with 0.5 g/dL at 25 °C. The viscosity of PSf is 0.56 dL/g under the same test conditions. ^bMeasured in NMP with 0.5 g/dL at 25 °C.

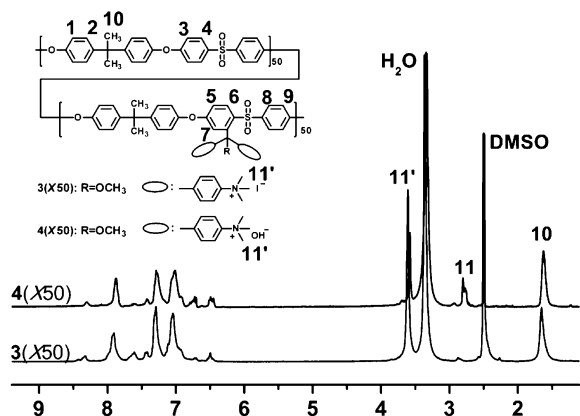


Figure 2. ^1H NMR spectral analysis of 3(X50) and 4(X50) membrane (hydroxide conversion, exposed to 1 M NaOH for 24 h) in $\text{DMSO}-d_6$.

between 73% and 83% of the theoretical IEC values of 3 membranes, suggesting some degree of instability of 4 membranes when exposed to alkaline conditions. Further investigations concerning stability will be discussed in the following section.

Water Uptake and Dimensional Swelling of 4 Membranes. Water uptake (WU) and dimensional swelling (20 and 60 °C) of the 4 membranes were measured in water and plotted as a function of IEC_w in Figure 3. Water uptake of the 4

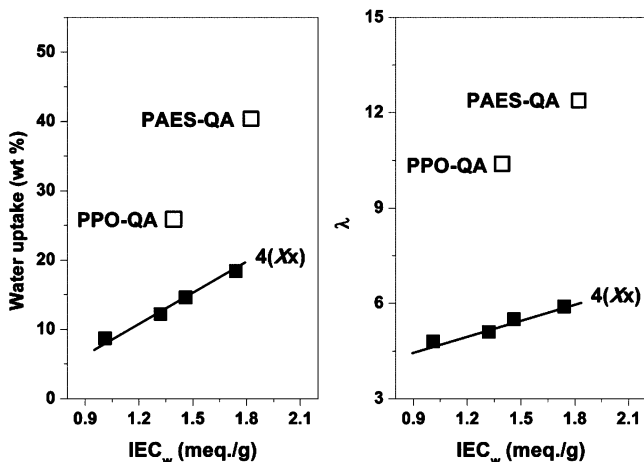


Figure 3. (a) Water uptake and (b) λ values of 4 membranes, PAES-QA and PPO-QA membranes at 20 °C in water as a function of IEC_w .

membranes, which was in the range of 8.7–18.4% at 20 °C, increased linearly with increasing IEC_w . A comparison of 4 and typical AEMs based on PAES-QA and PPO-QA revealed that the 4 membranes absorbed much less water, as shown in Figure 3a. For a better comparison among the different IEC

membranes, the number of absorbed water molecules per phenyltrimethylammonium (PTMA) group (designated as λ) was calculated (Figure 3b). Fewer water molecules per PTMA group for 4 membranes were observed even at high IEC_w levels (4(X81), $\text{IEC}_w = 1.74$ mequiv/g, $\lambda = 5.9$). These values were much lower than that of main-chain-type AEMs composed of aromatic polymers bearing quaternary ammonium groups (e.g., $\lambda > 10$) and Nafion (Table 2). The lower water uptake and λ values of the 4 membranes are considered to be related to the side-chain-type polymer structure with pendent PTMA groups which could contribute to suppression of excessive water uptake and swelling.

Lower water uptake of 4 membranes leads to lower dimensional swelling in water (Δl), as shown in Table 2. The in-plane water swelling ratio (Δl) at 20 °C was less than 5%. These unusually small values were much lower than that of PAES-QA and PPO-QA AEMs. Unlike main-chain-type random copolymer AEMs, in which higher temperature induced excessive water uptake and dimensional swelling, the temperature had less of an influence on the 4 membranes (Table 2). Using the 4(X81) membrane ($\text{IEC}_w = 1.74$ mequiv/g) as an example, the water uptake of 22.4% and swelling ratio of 5% at 60 °C was not excessively higher than the corresponding values at 20 °C (18.4% water uptake and 4% swelling ratio), especially when compared with other copolymer systems at this temperature difference.^{29,31}

In addition, the volumetric IEC value of water absorbed membranes (IEC_v (wet)), calculated from density and water uptake measurements,⁴⁹ reflects the concentration of ions within the polymer matrix under hydrated conditions without distinguishing between those hydroxides that are mostly associated with the PTMA groups and those that are fully dissociated. It is of interest to note how this IEC_v (wet) value itself is affected by changes in base and water uptake and whether ion concentration remains constant or whether it varies. As shown in Table 2, the density decreases slightly with increasing DS, due to the lower density of PTMA groups. The IEC_v (wet) of 4 membranes at 20 °C increased from 1.14 to 1.68 mequiv/cm³, corresponding to IEC_w values increasing from 1.01 to 1.74 mequiv/g. All the values were only slightly lower than those of the corresponding IEC_v (dry) values because of the lower water uptake of 4 membranes, indicating their much lower dimensional swelling in water.

Hydroxide Conductivity and Methanol Permeability of 4 Membranes. For fuel cell operation using anion exchange membrane materials, there is a requirement for the hydroxide conductivity to be above 10⁻² S/cm and for water uptake to be less than 30%.³⁴ The hydroxide conductivity of the 4 membranes was measured in water and compared with that of PAES-QA and PPO-QA AEMs. The conductivity values reported in Table 2 are expressed in Figure 4a as a function

Table 2. Various IEC, Water Uptake, Swelling Ratio and Hydroxide Conductivities of 4 Membranes

ionomers	d (g/cm ³)	IEC_w (mequiv/g)	IEC_v (mequiv/cm ³)		WU (wt %)			Δl (%)		σ (mS/cm)
			dry	wet	20 °C	λ	60 °C	20 °C	60 °C	20 °C
4(X35)	1.26	1.01	1.27	1.14	8.7	4.8	9.4	3	3	15
4(X50)	1.22	1.32	1.61	1.40	12.2	5.1	12.9	3	3	26
4(X62)	1.20	1.46	1.75	1.49	14.6	5.5	15.8	3	4	33
4(X81)	1.19	1.74	2.05	1.68	18.4	5.9	20.8	4	5	38
PAES-QA	1.20	1.82	2.18	1.47	40.5	12.3	52.1	13	18	35
PPO-QA	1.05	1.39	1.46	1.15	25.9	10.4	28.3	7	10	4
Nafion	1.98	0.90	1.78	1.29	19.0	11.7	15.3	12	15	90

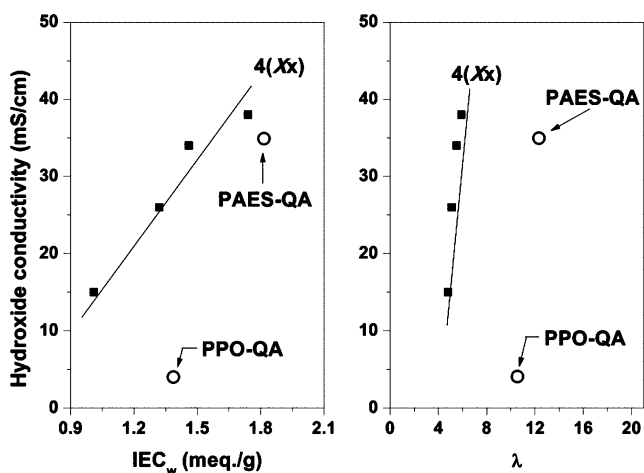


Figure 4. Conductivity of 4, PAES-QA, and PPO-QA membranes at 20 °C as a function of (a) IEC_w and (b) λ value.

of the IEC_w. Similar to the water uptake, the hydroxide conductivity of 4 membranes increased with increasing IEC values. These values were above 10^{-2} S/cm at room temperature (20 °C) which was comparable to PAES-QA and much higher than PPO-QA. Because of the side-chain PTMA groups for OH⁻ transport, it is believed that the 4 membranes are able to utilize water molecules more efficiently for ion transport. The 4(X81) membrane achieved the highest hydroxide conductivity of 3.8×10^{-2} S/cm at 20 °C.

An important finding of the present work is that the 4 membranes showed much lower water uptake but comparable conductivity compared with those of main-chain-type AEMs PAES-QA and PPO-QA. As shown in Figure 4b, the 4 membranes located on the line on the left portion of the graph have higher hydroxide conductivity but lower water absorption (λ) values. These results suggest that the present polymer design concept of a side-chain-type structure is effective for the AEMs in mitigating dimensional swelling and improving hydroxide conductivity, as already demonstrated for acid-based PEMs. Furthermore, the hydroxide conductivities of the 4 membranes showed an approximate Arrhenius-type temperature dependence, as shown in Figure 5. The 4(X81) membrane (IEC = 1.74 mequiv/g) showed the highest conductivity of 5.8×10^{-2} S/cm at 80 °C.

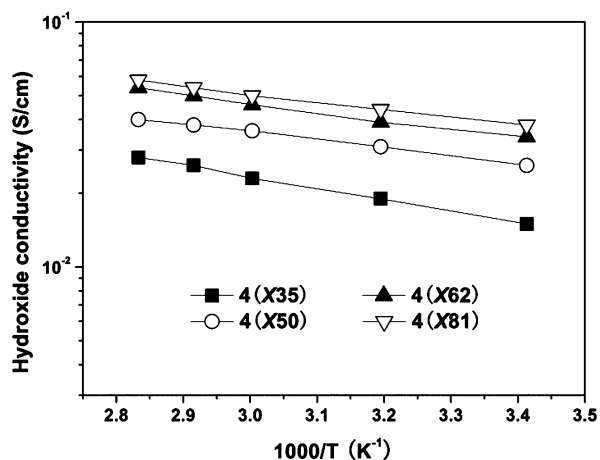


Figure 5. Hydroxide ion conductivity of 4 membranes in water as a function of temperature.

However, all alkali-based 4 membranes show much lower ion conductivity compared to that of the acid-based Nafion 112 (9.0×10^{-2} S/cm at 20 °C). The conductivity of ions is a function of both the ion mobility and the concentration of charge carriers. The 4 membranes displayed comparable or higher bulk concentrations of potential charge carriers in each case, e.g. IEC_v(wet), but lower ion conductivity. The major difference in conductivity between Nafion 112 and 4 membranes can be rationalized by considering the mobility or dissociation of the sulfonic acid and quaternary ammonium functional groups ($H^+ = 4.76$ and $OH^- = 2.69$ relative to K^+ in infinitely dilute solution at 298 K).^{51,52} The sulfonic acid in Nafion is a super acid, while quaternary ammonium substituents are weak bases with pK_b values of about 4.³³ The dissociation of weakly basic quaternary ammonium groups presents a considerable theoretical barrier for efficient hydroxide conduction AEMs.

Polymer electrolyte membranes intended for direct methanol fuel cells (DMFC) must possess both sufficiently high ion conductivities and be effective barriers for methanol crossover from the anode to the cathode compartment. Methanol permeability through polymer electrolyte membranes often follows a similar relationship to ion conductivity; that is, ion conductivity has a strong trade-off in its relationship with methanol permeability. Nafion has good proton conductivity due to strongly interconnected ionic domains structure and high proton mobility, but its high methanol permeability is a shortcoming in its application in DMFC. The 4 membranes exhibited comparatively lower methanol permeability to Nafion, as shown in Figure 6. The permeability values for

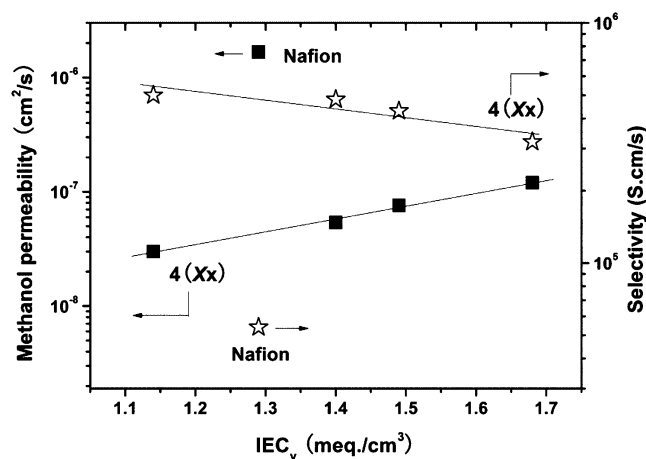


Figure 6. Performance trade-off plot of the IEC_v values vs the methanol permeability (■) and selectivity (☆).

2 M methanol at room temperature were in the range of 3×10^{-8} to 1.2×10^{-7} cm²/s, which were almost 2 orders of magnitude lower than that of Nafion (1.67×10^{-6} cm²/s). Although the 4 membranes have lower ion conductivities than Nafion, the conductivities are sufficiently high to achieve much better selectivity, which is the ratio of ion conductivity to methanol permeability (Figure 6).

Thermal and Alkaline Stabilities and Mechanical Properties. The TGA curves of 4 membranes are shown in Figure 7. A two-step degradation profile was observed for all membranes in their hydroxide form. There was no weight loss up to 150 °C because all the samples were preheated at 120 °C

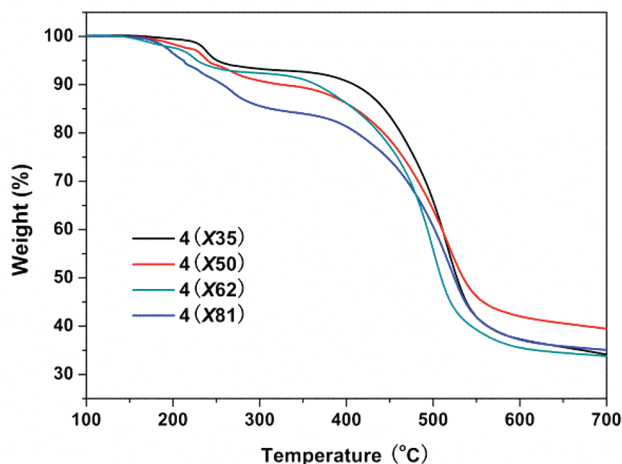


Figure 7. TGA curves for copolymer 4 membranes from measurements run at 10 °C/min in N₂.

for 20 min to remove absorbed water. As shown in Figure 7, the first weight loss occurred at about 180 °C, which is associated with the degradation of the quaternary ammonium groups. Furthermore, the membranes with lower IEC values displayed better thermal stability than those with higher IEC values. For example, the 5% decomposition temperature of 4(X35) is about 220 °C, which is much higher than that of the 4(X81) membrane (ca. 170 °C). The second weight loss at around 400–500 °C is related to the degradation of the polymer chain. The decomposition temperature of the polymer backbone was similar to that of the parent polymer,⁷ suggesting that the decomposition of the quaternary ammonium groups did not trigger degradation of the polymer backbone, which was observed in some aromatic AEMs.⁵⁰

As mentioned above, the degradation of PTMA functionalized 4 membranes occurs under high pH conditions probably via (i) Hoffmann elimination and (ii) direct nucleophilic substitution.^{19,22,23} To further evaluate the stability and degradation mechanism of the 4 membranes, 4(X50) membrane with IEC of 1.32 mequiv/g was treated with 4 M NaOH aqueous for different exposure times. The membranes maintained their toughness, flexibility, and appearance after stability tests as long as 800 h, suggesting no decomposition of PSf main chain. The chemical structures before and after the tests were analyzed by use of ¹H NMR spectroscopy (Figure 8). The signals for the methyl protons in the PTMA substituents in the tested membranes become smaller, while the integrations of methyl and aromatic protons (6.4–6.8 ppm) in phenyldimethylamine increase with increasing the time. Since there are no other signals assignable to methyl or methylene protons observed in Figure 8, which are assumed to appear if a Hoffmann elimination degradation mechanism were to occur, the major degradation mode of 4 membranes under these stability testing conditions is most likely to be direct nucleophilic substitution, that is, the elimination of methanol to revert to the phenyldimethyl amine substituent. After an initial period of transient behavior for 80 h, the IEC and conductivity showed a constant but slow decline, as shown in Figure 9. The IEC value after the test of 800 h was estimated to be 0.46 mequiv/g, which was ~35% of the initial IEC value of 1.32 mequiv/g, suggesting the 4 membranes have insufficient long-term stability for anion exchange membrane fuel cell application. The long-term instability of PTMA groups in the 4

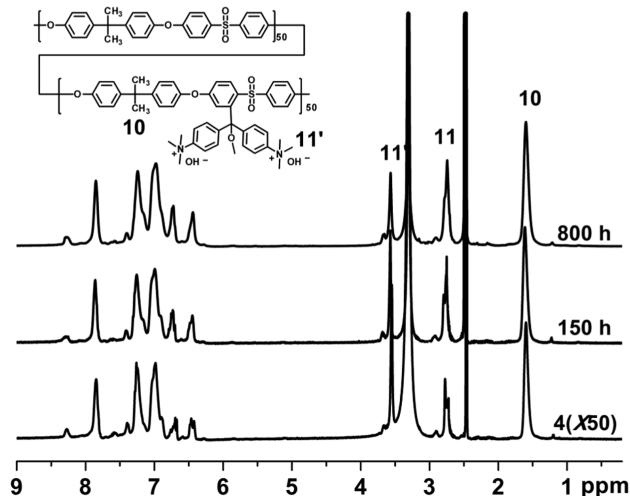


Figure 8. ¹H NMR spectra of 4(X50) in DMSO-*d*₆ (IEC = 1.30 mequiv/g) after stability tests in 4 M NaOH at room temperature for 150 and 800 h.

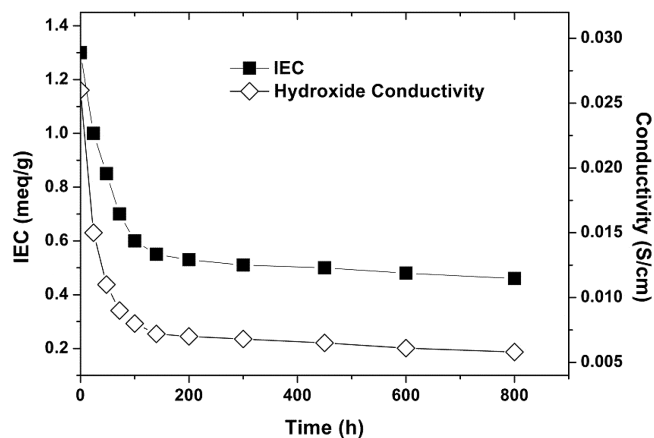


Figure 9. Decline in IEC values and hydroxide ion conductivity with time for the 4(X50) membrane (IEC = 1.30 mequiv/g) in 4 M NaOH at room temperature.

membranes is probably attributable to the low electron cloud density of the nitrogen atom, brought about by the electron-withdrawing phenyl, which could be attacked readily by hydroxide ion.^{35,53–56}

The mechanical properties for the 4 membranes are shown in Table 3. The membranes displayed values of tensile stress at

Table 3. Mechanical Properties of the 4 Membranes at 20 °C and 50% RH

sample	IEC (mequiv/g)	tensile strength (MPa)	Young's modulus (GPa)	elongation at break (%)
4(X35)	1.01	65.8	1.72	12.6
4(X50)	1.32	63.6	1.62	10.3
4(X62)	1.46	67.3	1.67	13.2
4(X81)	1.74	60.2	1.58	9.0

maximum load of 60.2–67.3 MPa, Young's moduli of 1.58–1.72 GPa, and values of elongation at break of 9.0–13.2%. These results indicate that the 4 membranes were tough and

ductile, without any decomposition occurring during their preparation by lithiation chemistry.

CONCLUSIONS

In summary, we have demonstrated a new synthetic method for the incorporation of side-chain quaternary ammonium (QA) functional groups into a commercially available polymer using lithiation chemistry, without evident polymer decomposition and cross-linking. The resulting PTMA functionalized polymers exhibited unusually low water uptake and methanol permeability but high hydroxide conductivity. The 4(X81) membrane with IEC of 1.74 mequiv/g showed the highest hydroxide conductivity (58 mS/cm) at 80 °C. Long-term stability tests over 800 h indicate that the PTMA groups do not have sufficient stability under alkaline conditions, for the probable reason that the lower electron cloud density of nitrogen atoms allows attack more readily by hydroxide ion. However, from a polymer design perspective, the results suggest that side-chain quaternary ammonium functional substituents can enhance hydroxide conductivity and mitigate water swelling in AEMs. The introduction of other kinds of tertiary amine-containing compounds such as guanidine, which could be introduced into PSf by the same lithiation approach, could help to improve the stability of quaternary ammonium groups.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Guiver, M. D.; Robertson, G. P.; Yoshikawa, M.; Tam, C. M. In *Membrane Formation and Modification*; ACS Symposium Series No. 744; Pinnau, I., Freeman, B., Eds.; American Chemical Society: Washington, DC, 1999; Chapter 10, pp 137–161.
- (2) Guiver, M. D.; Robertson, G. P.; Rowe, S.; Foley, S.; Kang, Y. S.; Park, H. C.; Won, J.; Thi, H. N. L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2103–2124.
- (3) Iojoiu, C.; Maréchal, M.; Chabert, F.; Sanchez, J. Y. *Fuel Cells* **2005**, *5*, 344–354.
- (4) Guiver, M. D.; Kutow, O.; ApSimon, J. W. *Polymer* **1989**, *30*, 1137–1142.
- (5) Warshawsky, A.; Kahana, N.; Deshe, A.; Gottlieb, H. E.; Arad-Yellin, R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2885–2905.
- (6) Kahana, N.; Arad-Yellin, R.; Deshe, A.; Warshawsky, A. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3303–3315.
- (7) Guiver, M. D.; ApSimon, J. W.; Kutow, O. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 123–127.
- (8) Kerres, J.; Cui, W.; Reichle, S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2421–2438.
- (9) Brownstein, S. K.; Guiver, M. D. *Macromolecules* **1992**, *25*, 5181–5185.
- (10) Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S. *Macromolecules* **2005**, *38*, 9670–9678.
- (11) Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S.; Lee, K. J. *Macromolecules* **2003**, *36*, 6807–6816.
- (12) Park, H. B.; Freeman, B. D.; Zhang, Z.; Sankir, M.; McGrath, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 6019–6024.
- (13) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587–4612.
- (14) Harrison, W. L.; Hickner, M. A.; Kim, Y. S.; McGrath, J. E. *Fuel Cells* **2005**, *5*, 201–212.
- (15) Jannasch, P. *Fuel Cells* **2005**, *5*, 248–260.
- (16) Park, C. H.; Lee, C. H.; Guiver, M. D.; Lee, Y. M. *Prog. Polym. Sci.* **2011**, *36*, 1443–1498.
- (17) Diat, O.; Gebel, G. *Nat. Mater.* **2008**, *7*, 13–14.
- (18) Curtin, D. E.; Lousenberg, R. D.; Henry, T. J.; Tangeman, P. C.; Tisack, M. E. *J. Power Sources* **2004**, *131*, 41–48.
- (19) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187–200.
- (20) Xu, T. *J. Membr. Sci.* **2005**, *263*, 1–29.
- (21) Hickner, M. A. *Mater. Today* **2010**, *13*, 34–41.
- (22) Merle, G.; Wessling, M.; Nijmeijer, K. *J. Membr. Sci.* **2011**, *377*, 1–35.
- (23) Couture, G.; Alaeddine, A.; Boschet, F.; Ameduri, B. *Prog. Polym. Sci.* **2011**, *36*, 1521–1557.
- (24) McLean, G. F.; Niet, T.; Prince-Richard, S.; Djilali, N. *Int. J. Hydrogen Energy* **2002**, *27*, 507–526.
- (25) Spindel, J. S.; Wieckowski, A. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2654–2675.
- (26) Dillon, R.; Srinivasan, S.; Arico, A. S.; Antonucci, V. *J. Power Sources* **2004**, *127*, 112–126.
- (27) Fang, J.; Shen, P. K. *J. Membr. Sci.* **2006**, *285*, 317–322.
- (28) Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromolecules* **2009**, *42*, 8316–8321.
- (29) Varcoe, J. R.; Slade, R. T. C.; Yee, E. L. H.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. *Chem. Mater.* **2007**, *19*, 2686–2693.
- (30) Herman, H.; Slade, R. T. C.; Varcoe, J. R. *J. Membr. Sci.* **2003**, *218*, 147–163.
- (31) Danks, T. N.; Slade, R. T. C.; Varcoe, J. R. *J. Mater. Chem.* **2003**, *13*, 712–721.
- (32) Yan, J.; Hibbs, M. R. *Macromolecules* **2010**, *43*, 2349–2356.
- (33) Hibbs, M. R.; Hickner, M. A.; Alam, T. M.; McIntyre, S. K.; Fujimoto, C. H.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2566–2573.
- (34) Wang, J.; Li, S.; Zhang, S. *Macromolecules* **2010**, *43*, 3890–3896.
- (35) Kim, D. S.; Labouriau, A.; Guiver, M. D.; Kim, Y. S. *Chem. Mater.* **2011**, *23*, 3795–3797.
- (36) Zhang, Q.; Li, S.; Zhang, S. *Chem. Commun.* **2010**, *46*, 7495–7497.
- (37) Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 6499–6502.
- (38) Wang, J. H.; Zhao, Z.; Gong, F. X.; Li, S. H.; Zhang, S. B. *Macromolecules* **2009**, *42*, 8711–8717.
- (39) Zhao, Z.; Wang, J.; Li, S.; Zhang, S. *J. Power Sources* **2011**, *196*, 4445–4450.
- (40) Tanaka, M.; Fukasawa, K.; Nishino, E.; Yamaguchi, S.; Yamada, K.; Tanaka, H.; Bae, B.; Miyatake, K.; Watanabe, M. *J. Am. Chem. Soc.* **2011**, *133*, 10646–10654.
- (41) Liu, B.; Robertson, G. P.; Kim, D. S.; Sun, X.; Jiang, Z.; Guiver, M. D. *Polymer* **2010**, *51*, 403–413.
- (42) Lafitte, B.; Puchner, M.; Jannasch, P. *Macromol. Rapid Commun.* **2005**, *26*, 1464–1469.
- (43) Lafitte, B.; Jannasch, P. *Adv. Funct. Mater.* **2007**, *17*, 2823–2834.
- (44) Kim, D. S.; Robertson, G. P.; Kim, Y. S.; Guiver, M. D. *Macromolecules* **2009**, *42*, 957–963.
- (45) Li, N.; Shin, D. W.; Hwang, D. S.; Lee, Y. M.; Guiver, M. D. *Macromolecules* **2010**, *43*, 9810–9820.
- (46) Kerres, J.; Ullrich, A.; Hein, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2874–2888.
- (47) Guiver, M. D.; Robertson, G. P.; Foley, S. *Macromolecules* **1995**, *28*, 7612–7621.
- (48) Robertson, G. P.; Guiver, M. D.; Bilodeau, F. O.; Yoshikawa, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1316–1329.
- (49) Kim, Y. S.; Einsla, B.; Sankir, M.; Harrison, W.; Pivovar, B. S. *Polymer* **2006**, *47*, 4026–4035.

(50) Tanaka, M.; Koike, M.; Miyatake, K.; Watanabe, M. *Polym. Chem.* **2011**, *2*, 99–106.

(51) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999.

(52) Vanysek, P. Ionic conductivity and diffusion at infinite dilution. In *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2002.

(53) Fenton, G. W.; Ingold, C. K. *J. Chem. Soc.* **1929**, 2342–2357.

(54) Zanger, M.; Vanderwerf, C. A.; McEwen, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3806–3807.

(55) Einsla, B. R.; Chempath, S.; Pratt, L.; Boncella, J.; Rau, J.; Macomber, C.; Pivovar, B. *Electrochem. Soc. Trans.* **2007**, *11*, 1173–1180.

(56) Chempath, S.; Einsla, B. R.; Pratt, L. R.; Macomber, C. S.; Boncella, J. M.; Rau, J. A.; Pivovar, B. S. *J. Phys. Chem. C* **2008**, *112*, 3179–3182.