

Polymer Electrolyte Membranes Derived from New Sulfone Monomers with Pendent Sulfonic Acid Groups^{\dagger}

Nanwen Li,[‡] Dong Won Shin,[§] Doo Sung Hwang,[‡] Young Moo Lee,^{*,‡,§} and Michael D. Guiver^{*,‡,⊥}

[‡]WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea, [§]School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea, and [⊥]Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Ont. K1A 0R6, Canada

Received September 11, 2010; Revised Manuscript Received October 18, 2010

ABSTRACT: New monomers containing two or four pendent phenyl groups were synthesized by bromination of bis(4-fluorophenyl) sulfone, followed by Suzuki coupling with benzeneboronic acid. The resulting monomers were converted to the corresponding sulfonated monomers having two or four pendent sulfonic acid groups, predominately at the p-phenyl position. Aromatic nucleophilic substitution (SNAr) polycondensation using the di- and tetrasulfonated monomers provided sulfonated poly(arylene ether sulfone) copolymers S2-PAES-xx and S4-PAES-xx, respectively, where xx refers to the molar ratio of the sulfonated to non-sulfonated pendent phenyl monomer. Copoly(arylene ether sulfone)s based on the corresponding nonsulfonated monomers were also synthesized for a parallel study on postpolymerization sulfonation of these copolymers. Postsulfonation occurred predominately at the para-pendent phenyl site, and the reactions were complete within a short time (about 30 min), without evidence of chain degradation. Flexible and tough membranes having high mechanical strength were obtained by solution casting of all four series of copolymers. The copolymers with two or four pendent sulfonic acid groups had high proton conductivities in the range of 44-142 mS/cm for S2-PAES-xx and 51-158 mS/cm for S4-PAES-xx at room temperature, respectively. The methanol permeabilities of these copolymers were in the range of $0.8 \times 10^{-8} - 15.0 \times 10^{-7}$ cm²/s, which is lower than Nafion (16.7 \times 10⁻⁷ cm²/s). The S4-PAES-xx membranes displayed better properties (lower water uptake and higher proton conductivities) than the S2-PAES-xx membranes, which can be attributed to the more blocky architecture of the sulfonic acid groups in the S4 membranes. A combination of high proton conductivities, low water uptake, and low methanol permeabilities for some of the obtained copolymers indicated that they are good candidate materials for proton exchange membrane in fuel cell applications.

Introduction

Polymer electrolyte membrane fuel cells (PEMFC) have attracted considerable attention as candidates for alternative power sources due to their high power density, good energy conversion efficiency, and zero emissions levels.¹⁻³ Perfluorosulfonic acid (PFSA) polymers such as Nafion (DuPont) are the most promising and state-of-the-art polymer electrolyte membranes (PEM) for PEMFC. However, the material has several shortcomings that limit its utility and performance, such as reduced proton conductivity at elevated temperatures (>80 °C), high methanol/gas diffusion, environmental incompatibility (poor recyclability), and sig-nificant manufacturing costs.^{4–6} Consequently, much progress has been made to develop novel hydrocarbon PEMs based on sulfonated aromatic polymers, which have good physical properties and are inexpensive. The most widely investigated PEMs include sulfonated derivatives of poly(arylene ether sulfone)s (SPAES),^{7,8} poly-(arylene ether ether ketone)s (SPEEK),^{9–11} poly(arylene sulfide sulfone)s (SPSS),^{12,13} poly(arylene ether nitrile)s (SPAEEN),^{14–16} polyimides (SPI),^{17–21} and polyphenylenes (PP).^{22–24} Many hydrocarbon polymers show sufficiently high conductivities only at high ion-exchange capacities (IEC)s, which causes extensive water uptake above a critical temperature (percolation threshold), or a

*To whom correspondence should be addressed. E-mail: ymlee@ hanyang.ac.kr (Y.M.L.); michael.guiver@nrc-cnrc.gc.ca (M.D.G.).

pubs.acs.org/Macromolecules

dramatic loss of mechanical properties due to dimensional swelling that render them unsuitable for practical PEM applications. The dimensional stability and proton conductivity of aromatic ionomers are crucial issues that require improvement through careful structural design.²⁵

Proton conductivity of PEMs is closely related to several parameters such as acidity, number and position of ionic groups, main chain and/or side chain structures, composition and sequence of hydrophilic and hydrophobic components, and membrane morphology.^{26–28} Among these, acidity of ionic groups and membrane morphology appear to be crucial, and they are inter-related. Kreuer et al.²⁹ reported that typical sulfonated aromatic polymers are unable to form defined hydrophilic domains, as the rigid aromatic backbone prevents the formation of continuous conducting channels and ionic clustering from occurring. Thus, various strategies have been pursued to circumvent this and to obtain efficient ionic networks for enhancing the proton conductivity.

One promising approach to enhance PEM properties and performance is to induce distinct phase separation between the hydrophilic sulfonic acid containing regions and the hydrophobic polymer main chain by positioning the sulfonic acid groups on side chains grafted onto the polymer main chain.³⁰ 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.^{31,32} For example, Jannasch and co-workers reported PEMs prepared by attaching

[†] NRCC Publication No. 52238.

flexible pendent sulfonated aromatic side chains to polysulfone, which showed proton conductivities of 11-32 mS/cm at 120 °C. Another approach to induce nanophase separation is through block copolymer architecture, whereby sulfonic acid groups are concentrated in blocks along the polymer chain. McGrath et al.³³ prepared multiblock sulfonated poly(arylene ether)s with a promising morphological structure by a two-step polycondensation. Membranes having a relatively low IEC of 0.95 mequiv/g had water uptake of 40%, but high proton conductivity of 80 mS/cm. More recently, random copolymers designed with dense localized concentrations of sulfonated units have been attracting considerable attention because of the high contrast in polarity between hydrophilic and hydrophobic units; this promotes the formation of hydrophilichydrophobic phase-separated structures. It has been found that the morphological structure of the copolymers was comparable to that of Nafion 117, which explains their high proton conductivity.^{34,35}

Another approach to enhance PEM performance is with high IEC values, but to design the highly proton conducting PEM to have less susceptibility to water swelling or solubility. Here, the selection of a suitable mechanically stable polymer as a platform is very important. The current attempts have already led to the development of some highly sulfonated polymers (with a high value of more than 2.7 mequiv/g) with good water stability, such as sulfonated poly(*p*-phenylene)s,²⁴ sulfonated poly(phenylene sulfide)s,¹ and sulfonated poly[bis(benzimidazobenzisoquinolinones)].²¹ More recently, Kreuer et al. developed a new class of sulfonated polymers with an extremely electron-poor poly(phenylene sulfone) backbone.^{36,37} These ionomers contain only strongly electron-withdrawing units $(-SO_2-)$ connecting the phenyl rings. This new class of polymers shows very high thermal, thermo-oxidative and hydrolytic stability, and distinct methanol rejection properties. Membranes with ion exchange capacities ranging from 2.32 to 2.78 mequiv/g remain insoluble in water and have proton conductivities higher than that of Nafion. Their lower solubility and degree of swelling in water compared to other sulfonated poly(arylene)s allow for the preparation of membranes with high ion exchange capacity and high proton conductivity.

Herein, we report on the synthesis of two novel bis(fluorophenyl) sulfone monomers containing two or four pendent phenyl or phenylsulfonic acid groups. These monomers were utilized to prepare series of sulfonated poly(arylene ether sulfone)s or poly-(phenylene sulfone)s. Selected PEM properties such as thermal and chemical stability, mechanical strength, water uptake behavior, and proton conductivity were investigated in detail.

Experimental Section

Materials. Bis(4-fluorophenyl) sulfone (DFDPS), *N*-bromosuccinimide (NBS), benzeneboronic acid, and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma-Aldrich Ltd. 4,4'-(Hexafluoroisopropylidene)diphenol (6F-BPA) was purchased from Aldrich and recrystallized twice from toluene. All other solvents and reagents (obtained from Aldrich) were reagent grade and were used as received.

3,3'-Dibromo-4,4'-difluorodiphenyl Sulfone (DBDFDPS). Bis-(4-fluorophenyl) sulfone (25.4 g, 0.1 mol) was dissolved in concentrated H₂SO₄ (150 mL) at room temperature. To this was added NBS (14.13 g, 0.22 mmol, 2.2 equiv), divided into three portions and added at 15 min intervals. The mixture was stirred vigorously at room temperature for a further 6 h and then poured into crushed ice (~500 g) to precipitate the solids. The precipitated solids were filtered, washed with water (600 mL) and then with 100 mL of *n*-hexane, and purified by recrystallization from toluene to obtain 3,3'-dibromo-4,4'-difluorodiphenyl sulfone (DBDFDPS) (39.5 g, 89%); mp 158–160 °C (DSC in N₂). ¹H NMR (300 MHz, DMSO*d*₆; ppm): 7.61–7.66 (t, 2H), 8.10–8.14 (m, 2H), 8.66 (s, 1H), 8.43–8.46 (t, 2 H).

3,3'-Diphenyl-4,4'-difluorodiphenyl Sulfone (DPDFDPS). To a 500 mL flask equipped with an Ar inlet/outlet, 16.5 g (40 mmol) of

DBDFDPS, 12.1 g (100 mmol) of benzeneboronic acid, and 300 mL of toluene were charged. The solid was completely dissolved at 50 °C with stirring. 150 mL of 10 wt % aqueous sodium carbonate solution and 1.86 g (1.6 mmol) of tetrakis(triphenylphosphine)-palladium(0) were carefully added into the solution. The reaction mixture was heated at 110 °C for 20 h, and then the solvent was evaporated to obtain a solid. The resulting solid was dissolved in dichloromethane/water mixture, and the suspended catalyst was removed by filtration. The organic phase was washed with water until neutral. The DPDFDPS monomer was obtained by evaporating the solvent and purified by recrystallization from toluene twice. Yield 84%; mp 180–181 °C (DSC in N₂). ¹H NMR (300 MHz, DMSO- d_6 ; ppm): 7.48–7.62 (m, 12H), 8.12–8.20 (m, 4H).

Bis[4-fluoro-3-(4-sulfophenyl)phenyl] Sulfone, Disodium Salt (SDPDFDPS). To a 100 mL three-necked flask equipped with a magnetic stirring device and nitrogen inlet was charged 10 g of DPDFDPS. The flask was cooled in an ice bath, and then 15 mL of concentrated sulfuric acid was slowly added with stirring. After DPDFDPS was completely dissolved, 15 mL of fuming sulfuric acid (SO₃, 30%) was slowly added to the flask. The reaction mixture was stirred at 0 °C for 0.5 h and then slowly heated to 60 °C and maintained at this temperature for an additional 2 h. After cooling to room temperature, the solution was carefully poured into 100 mL of ice-water. NaCl (33 g) was added, which produced a white precipitate identified as the disodium salt of SDPDFDPS. The powder was filtered and redissolved in 100 mL of water, and then the pH was increased to 6-7 by the addition of aqueous 2 N NaOH. An excess of NaCl was added to salt out the sodium form of disulfonated monomer. The crude product was recrystallized from water/ethanol (2:1) to give 12.5 g (yield: 89%) of white product. ¹H NMR (300 MHz, DMSO-d₆; ppm): 7.56-7.58 (d, 8H), 7.59 (2H), 8.16-8.19 (m. 4H).

3,3',5,5'-Tetrabromo-4,4'-difluorodiphenyl Sulfone (TBDFDPS). Bis(4-fluorophenyl) sulfone (12.7 g, 0.05 mol) was dissolved in concentrated H_2SO_4 (250 mL) at room temperature. To this was added NBS (37.4 g, 0.21 mmol, 4.2 equiv) divided into six portions over a period of 1 h. The mixture was stirred vigorously at room temperature for 2 h, and then the temperature was increased to 60 °C and maintained at that temperature for 12 h. The mixture was poured into crushed ice (~500 g) to precipitate the solids. The precipitated solids were filtered, washed with water several times, followed by 100 mL of *n*-hexane, and finally dried to obtain 3,3',5,5'-tetrabromo-4,4'-difluorodiphenyl sulfone (TBDFDPS) (40.5 g, 92%); mp 180–182 °C. ¹H NMR (300 MHz, CDCl₃; ppm): 8.06–8.08 (d, 4H).

3,3',5,5'-Tetraphenyl-4,4'-difluorodiphenyl Sulfone (TPDFDPS). Using similar methodology to the diphenyl analogue, the monomer with four pendent phenyl groups 3,3',5,5'-tetraphenyl-4,4'-difluorodiphenyl sulfone was prepared from 3,3',5,5'-tetrabromo-4, 4'-difluorodiphenyl sulfone (TBDFDPS) by reaction with 5 mol equiv of benzeneboronic acid at 115 °C for 24 h. The purified product was obtained by recrystallization from toluene twice. Yield 82%; mp 271–273 °C. ¹H NMR (300 MHz, CDCl₃; ppm): 7.45–7.55 (m, 12H), 7.46–7.58 (d, 8H), 8.02–8.04 (d, 4H).

Bis[4-fluoro-3,5-bis(4-sulfophenyl)phenyl] Sulfone, Tetrasodium Salt (STPDFDPS). TPDFDPS was sulfonated using fuming sulfuric acid as before at 60 °C for 2 h. The crude product was recrystallized from water/ethanol (3:1) to give the STPDFDPS (yield: 85%) of white monomer. ¹H NMR (300 MHz, DMSO-*d*₆; ppm): 7.61–7.64 (d, 8H), 7.73–7.76 (d, 8H), 8.26–8.29 (d, 4H).

Synthesis of Copoly(arylene ether sulfone) (2-PAES-60). To a round-bottomed flask equipped with a Dean–Stark trap, DFDPS (0.2034 g, 0.8 mmol), DPDFDPS (0.4877 g, 1.2 mmol), 6F-BPA (0.6726 g, 2 mmol), and K_2CO_3 (0.3312 g, 2.4 mmol) were charged. Then, 1-methyl-2-pyrrolidinone (NMP) (6 mL) and toluene (4 mL) were added into the flask under nitrogen. The reaction mixture was stirred at 140 °C for 2 h. After removal of toluene, the reaction temperature was increased to 165 °C, and the reaction was continued for 16 h. After cooling to room temperature, the mixture was poured into methanol. The resulting fiber

was filtered and washed with water and hot methanol. The polymer was dried in vacuo at 100 °C for 8 h to give 2-PAES-60. The yield was 0.96 g (95%).

The copolymer 4-PAES-20 was prepared by a similar methodology using 3,3',5,5'-tetraphenyl-4,4'-difluorodiphenyl sulfone (TPDFDPS), DFDPS, and 6F-BPA at 165 °C for 20 h.

Synthesis of Sulfonated Poly(arylene ether sulfone). A series of sulfonated poly(arylene ether sulfone)s were synthesized with different molecular structures and sulfonic acid content (SC). As an example, the synthesis of S4-PAES-20 is as follows: 0.6726 g (2 mmol) of 6F-BPA, 0.4068 g (1.6 mmol) of DFDPS, 0.3516 g (0.4 mmol) of STPDFDPS, and 0.3312 g (2.4 mmol) of potassium carbonate were charged to a three-necked 100 mL flask equipped with a condenser, a Dean-Stark trap, a nitrogen inlet, and a mechanical stirrer. Then, distilled DMSO (5 mL) and toluene (3 mL) were added to the flask, and the reaction mixture was heated at 145 °C with stirring. The solution was allowed to reflux at 145 °C while the toluene azeotropically removed the water in the system. After 4 h, the toluene was removed from the reaction by slowly increasing the temperature to 168 °C. The reaction was allowed to proceed for another 20 h. The resulting viscous solution was cooled to room temperature and poured into isopropanol (IPA). The resulting fiber was filtered and washed with IPA and water. The copolymer was dried at 120 °C in vacuo for at least 24 h.

Postpolymerization Sulfonation of Polymer. To a round-bottomed flask equipped with a dropping funnel, 1 g of 2-PAES-60 or 4-PAES-20 was charged. Then, dry dichloromethane (20 mL) was added into the flask, and the mixture was cooled to 5-10 °C. To the mixture was added dropwise a solution of chlorosulfonic acid (0.6 mL, 3 mmol) in dry dichloromethane (20 mL) at 5 °C, and the mixture was stirred at this temperature for 30 min. After the reaction, the mixture was poured into hexane. The resulting polymer was washed with water. The polymer was dried in vacuo at 100 °C for 10 h to give PS2-PAES-60 or PS4-PAES-20.

Polymer Electrolyte Membrane Preparation. Since the copolymers in the acid form were more amenable to casting films than those in the salt form, they were first acidified. Copolymers (powder) in the sodium sulfonate form were treated with 2.0 N sulfuric acid at room temperature for 2 days for proton exchange. The proton-exchanged copolymers were thoroughly washed with deionized water and then dried in vacuum at 120 °C for 24 h. The acidified copolymers could be readily dissolved as 5–8 wt % solutions in DMSO at 60 °C. The solutions at 60 °C were filtered and cast onto glass plates and left to dry at 80 °C for 20 h. Tough, ductile ionomer membranes were obtained with a controlled thickness in the range of 30–50 μ m. The PEMs were dried in a vacuum oven at 120 °C for 24 h.

Measurements. ¹H NMR spectra were measured on a 300 MHz Bruker AV 300 spectrometer using DMSO- d_6 or CDCl₃ as solvent. The inherent viscosities were determined from 0.5 g dL⁻¹ solutions of polymer in NMP with an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The glass-transition temperature (T_g) was determined on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen protection. T_g is reported as the temperature at the middle of the thermal transition from the second heating scan.

The proton conductivity (σ , S/cm) of each membrane film (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s W_s R$ (d: 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/gainphase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough, Hampshire, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions 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 following equation:

$$C_{\rm B}(t) = \frac{A}{V_{\rm B}} \frac{DK}{L} C_{\rm A}(t-t_0) \tag{1}$$

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. t_0 is the time lag.

Characterization Methods. The density of membrane was measured from a known membrane dimension and weight after drying at 100 °C for 24 h. Water uptake was measured after drying the membrane in acid form at 100 °C under vacuum overnight. The dried membrane was immersed in water at 20 °C and periodically weighed on an analytical balance until a constant water uptake weight was obtained. From this, the volume-based water uptake (WU) was obtained. A volume-based IEC (IEC_v) was obtained by multiplying the membrane density by the IEC_w values, which were estimated from the copolymer structure. This calculation resulted in IEC_v (dry) based on the dry membrane density. An IEC_v (wet) was then calculated based on membrane water uptake.³⁸

From the conductivity and density data, proton diffusion coefficient (D_{σ}) was calculated using the Nernst–Einstein equation where *R* is gas constant, *T* is the absolute temperature (K), *F* is the Faraday constant, and $c(H^+)$ is the concentration of proton charge carrier (mol/L).

$$D_{\sigma} = \frac{RT}{F^2} \frac{\sigma}{c(\mathrm{H}^+)} \tag{2}$$

Results and Discussion

Synthesis and Characterization of the Monomers. Two new types of difluorodiphenyl sulfone monomers having two or four pendent phenyl groups were prepared as shown in Scheme 1. They could be polymerized either in the non-sulfonated form as 3,3'-diphenyl-4,4'-difluorodiphenyl sulfone (DPDFDPS) and 3,3',5,5'-tetraphenyl-4,4'-difluorodiphenyl sulfone (TPDFDPS) or in the sulfonated form. The monomers were synthesized by bromination of 4,4'-difluorodiphenyl sulfone using NBS. The reactions were conducted in concentrated sulfuric acid as solvent and catalyst and at different temperatures, giving dibrominated and tetrabrominated compounds DBDFDPS and TBDFDPS, respectively.

The reactions proceeded cleanly and in high yield, and the degree of bromination was readily controlled by adjusting the temperature and the amount of NBS. Following this, Suzuki coupling reactions of DBDFDPS or TBDFDPS with benzeneboronic acid produced 3,3'-diphenyl-4,4'-difluorodiphenyl sulfone (DPDFDPS) or 3,3',5,5'-tetraphenyl-4,4'-difluorodiphenyl sulfone (TPDFDPS), respectively, both in high yields (>84%). The structures were confirmed by ¹H NMR analysis, as shown in Figure 1. Subsequently, the DPDFDPS and TPDFDPS were readily sulfonated with fuming sulfuric acid at 60 °C for 2 h to give sulfonated monomers SDPDFDPS and STPDFDPS,

Scheme 1. Synthetic Route To Prepare SDPDFDS and STPDFDPS Monomers



respectively. Under these conditions, the sulfonate substitution reaction occurred predominately at the *para*-position to the pendent phenyl groups because electronic and steric hindrance effects render this position more reactive than other sites. ¹H NMR characterization confirmed the structures of SDPDFDPS and STPDFDPS, as shown in Figure 1. The signals at about 7.54 and 7.76 ppm were assigned to the pendent phenyl group of STBDFDPS, while those at 8.26 ppm were assigned to the protons in the phenyl sulfone ring.

Synthesis of Sulfonated and Non-sulfonated Poly(phenyl sulfone)s and Copoly(arylene ether sulfone)s. The original intention for the preparation of these monomers was for the preparation of poly(phenyl sulfones) having pendent phenylsulfonic acid units. Kreuer and co-workers reported the synthesis of sulfonated poly(phenyl sulfone)s having high proton conductivity, chemical and oxidative stability, and low water uptake, ^{36,37} as shown in Scheme 2. Although the poly(phenyl sulfone) PEMs exhibit some attractive properties such as high conductivity and oxidative stability, the structural repeat unit leads to IEC values that are excessively high, resulting in films that have poor mechanical properties. Using the same polymerization methodology, it was intended to use non-sulfonated pendent-phenyl sulfone monomers to produce pendent-phenyl poly(phenyl sulfone), which could be subsequently sulfonated and which would have a lower IEC value and potentially a higher molecular weight (Scheme 2). In spite of numerous polymerization attempts, the precursor poly(sulfide sulfone) had low viscosity and low molecular weight and thus could not be fabricated into flexible and tough membranes. The inability to obtain high molecular weight was attributed to steric hindrance effects, whereby the larger thiolate nucleophile has hindered access

to the fluorine atom because of the bulky *ortho*-substituted pendent phenyl groups.

Instead, sulfonated poly(arylene ether sulfone)s containing two or four pendent sulfonic acid groups (S2-PAES-*xx* or S4-PAES-*xx*, where *xx* is the molar percentage of sulfonated monomers in the total amount of difluorodiphenyl sulfone monomers) were synthesized successfully by SNAr polycondensation in DMSO. Copolymers having different molar percentages of pendent group were obtained by adjusting the feed ratios of SDPDFDPS or STPDFDPS to DFDPS (Scheme 3).

Characterization results are listed in Table 1. Two nonsulfonated copoly(arylene ether sulfone)s (2-PAES-60 and 4-PAES-20) were also synthesized in NMP for a comparative study of alternative route by postpolymerization sulfonation (Scheme 4).

All the polymerization reactions by both routes proceeded smoothly, with no evident cross-linking, even after prolonged polymerization times at temperatures in the range of 160– 200 °C. The sulfonated copolymers in the acid form were readily soluble in polar aprotic solvents such as DMF, DMAc, NMP, and DMSO. It should be pointed out that the sulfonated copolymers in the salt form showed poor solubility in common organic solvents, resulting in opaque solutions and membranes. However, tough, flexible, and transparent membranes of copolymers were obtained by solvent casting the sulfonated copolymer in the sulfonic acid form.

Postpolymerization Sulfonation of Copoly(arylene ether sulfone)s. Electrophilic sulfonation using reagents such as chlorosulfonic acid preferentially introduces sulfonic acid groups on electron-rich sites of aromatic rings. However, if vigorous sulfonation conditions are employed, such as high reaction temperatures and extended reaction times, polymer chain degradation may occur, resulting in a loss of mechanical strength. Therefore, it is very important to carefully control the reaction conditions for introducing sulfonic acid group onto phenyl rings to avoid adverse side reactions. Our



Figure 1. ¹H NMR spectra of non-sulfonated and sulfonated monomers in DMSO-*d*₆ (TPDFDPS in CDCl₃).

earlier work has shown that pendent phenyl rings attached to electron-donating polymer chain sites can be preferentially sulfonated at the para position, without obvious chain degradation occurring during sulfonation.³⁹⁻⁴³ In the present study, the copolymers 2-PAES-60 and 4-PAES-20, having pendent phenyl groups on the electron-withdrawing site of the polymer chain were sulfonated on the para-phenyl position with chlorosulfonic acid to produce PS2-PAES-60 and PS4-PAES-20, respectively ("postsulfonation" is distinguished by PS). On the basis of experimental IEC_w values, a 5-fold molar excess of chlorosulfonic acid was necessary for complete sulfonation. The reaction proceeded smoothly in dichloromethane solution at 5-10 °C, and most of the product precipitated out of the mixture within 10 min. However, the reaction was continued for an additional 20 min to ensure completion. The sulfonated copolymers were isolated as white powders and were soluble in DMSO, NMP, DMF, and DMAc. There was no evidence of chain degradation occurring under these conditions, as indicated by viscosity measurements and the mechanical properties of the resulting sulfonated polymer membranes. Figure 2 shows the ¹H NMR spectra of PS2-PAES-60 and PS4-PAES-20 in the sulfonic acid forms. In comparison with the spectra of the parent copolymers 2-PAES-60 and 4-PAES-20, new signals H-5 assigned to the protons adjacent to the sulfonic acid group appeared at about 7.68 and 7.56 ppm, respectively. The comparative signal integration of H-5 indicated complete sulfonation (100% degree of sulfonation) on each pendent phenyl ring. In the ¹H NMR spectrum of polymers with four pendent phenyl groups, H-7 and H-7', H-8 and H-8' are not magnetically equivalent. This is because the steric hindrance of the bulky phenyl groups prevents the benzene ring of the neighboring phenoxy moiety from rotating freely. Moreover, H-7' appeared farthest upfield at 6.61 ppm (Figure 2b) due to the ring current effect caused by the neighboring benzene ring. The spectra of the sulfonated

Scheme 2. Synthetic Route to Sulfonated Poly(phenylene sulfone) Reported by Kreuer et al.^{36,37} and the Originally Intended Sulfonated Poly(phenylene sulfone) with Pendent Phenylsulfonic Acid Groups of the Present Work



Scheme 3. Synthesis of S2-PAES-xx and S4-PAES-xx by Copolymerization with Sulfonated Monomers (SDPDFDPS and TDPDFDPS) I. Copolymerization







IEC



Table 1. Characterization of Copolymers

		ILC							
copolymer	$\eta_{\rm inh} \left({\rm dL/g} ight)^a$	calc NMR		$T_{\rm g}$	$T_{\rm d} (5\%)^c$	tensile strength (MPa)	elongation at break (%)	methanol permeability $(10^{-6} \text{ cm}^2/\text{S})$	
S2-PAES-40	0.62	1.19	1.16	240	349	60.7	12.5	0.10	
2-PAES-60	0.48^{b}	0	0	174	446	73.2	10.6		
PS2-PAES-60	0.65	1.64	1.59	241	350	57.8	11.2		
S2-PAES-60	0.58	1.64	1.62	246	342	58.7	9.8	0.28	
S2-PAES-70	0.69	1.84	1.86	258	335	54.9	11.8	0.62	
S2-PAES-80	0.71	2.02	1.98	274	332	51.2	9.5	1.50	
4-PAES-20	0.46^{b}	0	0	176	447	55.2	12.5		
PS4-PAES-20	0.56	1.18	1.21	239	351	49.6	10.2		
S4-PAES-20	0.57	1.18	1.16	239	352	50.2	14.5	0.08	
S4-PAES-30	0.62	1.63	1.59	260	349	45.9	12.3	0.22	
S4-PAES-35	0.58	1.82	1.78	272	334	46.7	9.6	0.51	
S4-PAES-40	0.59	2.00	2.01	286	332	42.2	8.8	0.98	
$a0.5 \text{ g dL}^{-1}$ in	DMSO at 30 °C.	b 0.5 g dL	⁻¹ in NMP a	t 30 °C. ^{<i>c</i>}	5% weight loss	temperature in N ₂ ga	s (acid form memb	orane).	

polymers, whether derived from sulfonated monomers or by postsulfonation, were essentially equivalent.

Thermal and Mechanical Properties. The TGA curves of non-sulfonated (2-PAES-60 and 4-PAES-20) and sulfonated copolymers membranes are shown in Figure 3. The 5% weight loss temperatures of 2-PAES-60 and 4-PAES-20 membranes are above 430 °C and followed similar degradation profiles. A two-step degradation profile was observed for all sulfonated copolymers in their acid form (Figure 3). There was no weight loss up to 200 °C because all the samples were preheated at 150 °C for 20 min to remove absorbed water. The first weight loss occurred above 300 °C, which is associated with the degradation of the sulfonic acid groups, and this initial weight loss increased with increasing DS. The high decomposition temperature suggests that sulfonic groups attached to pendent phenyls have high thermal stability. The main weight loss at around 500-600 °C is related to the degradation of the polymer chain.

The T_{g} s of the non-sulfonated copolymers 2-PAES-60 and 4-PAES-20 were around 170 °C, and the sulfonated copolymers

S2-PAES-xx and S4-PAES-xx were above 250 °C (Table 1) but lower than the decomposition temperature. The high thermal stability presents the possibility of preparing membrane electrode assemblies (MEA) by hot pressing. The T_{gs} of sulfonated copolymers are much higher than those of non-sulfonated ones, since chain rigidity is increased through hydrogen bond interactions of sulfonic acid groups. The T_{gs} of S2-PAES-xx or S4-PAES-xx increase with increasing proportions of sulfonated monomers in the copolymers. At the same sulfonic acid content, S4-PAES-xx polymers with four pendent phenyl groups had higher T_g values than those of corresponding S2-PAES-xx analogues because the presence of two bulky phenyl substituents around the ether linkage further hinders polymer chain rotation and thus increases chain rigidity. Supporting evidence for restricted chain rotation is shown by the nonequivalence of ortho-ether protons in the ¹H NMR spectrum (Figure 2b).

Good mechanical properties of the membranes are one of the necessary requirements for their effective use in DMFC or PEMFC applications. Films in the dry state had tensile stress at maximum load of 42.2–73.2 MPa and elongation at

Scheme 4. Synthesis of 2-PAES-60 and 4-PAES-20 Copolymers and Corresponding PS2-PAES-60 and PS4-PAES-20 by Postpolymerization Sulfonation



break of 8.8–14.5%, as shown in Table 1. Compared with the data of Nafion, having tensile stress of 32 MPa and elongation at break of 301.5% in the dry state, the SPAES materials showed higher tensile strength and the lower elongation than Nafion. The mechanical properties indicate that the copolymer films were strong and flexible, suitable for DMFC or PEMFC.

Water Uptake. Water uptake (weight and volume based) of PEMs is an important parameter for IEC, proton conductivity, dimensional stability, mechanical strength, and membrane– electrode compatibility of the membrane. For a more realistic comparison of the water uptake among the different membranes, volumetric IEC (IEC_v, mequiv/cm³), which is defined as molar concentration of sulfonic acid groups per unit volume containing absorbed water, was calculated. Table 2 compares the density, IEC, and water uptake (weight and volume based) of the copolymer membranes and Nafion. The water uptake of

SPAES increased with IEC_w and IEC_v (dry), due to the increased hydrophilicity, as shown in Figure 4. The highest water uptake (wt %) was 62.6% and 50.8% at 20 °C for the highest IEC_w membranes S2-PAES-80 (2.02 mequiv/g) and S4-PAES-40 (2.0 mequiv/g), respectively, which was 3 times higher than that of Nafion membrane. Moreover, the S4-PAES-*xx* membranes showed a slightly lower water uptake trend than the S2-PAES-*xx* membranes of the same SC. This effect can be attributed to the higher local concentrations of hydrophilic sulfonic acid groups of S4-PAES-*xx* membranes because of the blocky nature of these units.

The IEC_v (wet) reflects the concentration of ions within the polymer matrix under hydrated conditions, without distinguishing between those protons that are mostly associated with the sulfonic acid groups and those that are fully dissociated. The IEC_v (wet) value itself is affected by changes in acid and water uptake and whether ion concentration remains constant



Figure 2. Comparative ¹H NMR spectra of non-sulfonated and sulfonated copolymers in DMSO- d_6 .



Figure 3. TGA curves for the non-sulfonated and sulfonated PAES powders from measurements run at 10 °C/min in N₂.

or whether it varies. The IEC_v (wet) of S4-PAES-*xx*, measured at 20 °C, increased from 1.43 to 1.69 mequiv/cm³, corresponding to IEC_w values increasing from 1.18 to 2.0 mequiv/g. The IEC_v (wet) of S2-PAES-*xx* also increased from 1.32 to 1.59 mequiv/cm³ as IEC_w increased from 1.18 to 2.0 mequiv/g. However, for highly sulfonated copolymers, the IEC_v (wet) values of S2-PAES-70 and S2-PAES-80 were lower than those of the less sulfonated S2-PAES-40 and S2-PAES-60 membranes. For S2-PAES-40, S2-PAES-60, and all the S4-PAES-*xx* membranes measured at 20 °C, the increased sulfonic acid group concentration of the dry polymer was retained after

equilibration with water, while hydration of S2-PAES-70 and S2-PAES-80 resulted in excessive swelling and dilution of the ion concentration. This is observed in Figure 5, whereby the slope of the S2-PAES-xx curves at 20 °C reverses direction due to high water uptake (vol %) and reduced IEC_v (wet). At 80 °C, both series of membranes showed a reverse direction due to ion dilution caused by swelling of membranes.

The IEC_v is plotted as a function of temperature in Figure 6. Similar to Nafion, the IEC_v values decrease with increasing temperature due to increased water volume within the polymer matrix. The S2-PAES-40 membrane showed approximately the same trend in IEC_v values as Nafion over the temperature range, since the differences in gravimetric IEC were counterbalanced by the differences in density (1.98 g/cm³ for Nafion and 1.39 g/cm³ for S2-PAES-40). The other membranes displayed higher IEC_v than the Nafion membranes when the temperature was lower than 60 °C. The IEC_v (wet) of SPAES membranes with high IEC_w (> 1.8 mequiv/g) decreased sharply at elevated temperatures, to values lower than Nafion, which indicated that these membranes swelled excessively in water. The S2-PAES-xx and S4-PAES-xx membranes shared a similar dependency of the IEC_{v} upon temperature, but the latter ones exhibited slightly higher IEC_v values, which is the result of their relatively lower water uptake.

Proton Conductivity. The higher IEC_w membranes have higher proton conductivity at all temperatures investigated, as shown in Figure 7. Compared to Nafion membranes with similar IEC_w values, SPAES membranes showed predictably lower proton conductivities, in common with most aromatic ionomers, which derives from a combination of lower proton acidity of arylsulfonic acid and less effective phase separation.⁴⁴ Similar to Figure 5, proton conductivities of copolymers decrease when expressed in terms of IEC_v , reflecting the phenomenon of ion dilution in the swelled polymer matrix (Figure 7).

As shown in Table 2, with increasing IEC_w values for S4-PAES-xx from 1.18 to 2.0 mequiv/g, proton conductivities increased from 51 to 158 mS/cm at 20 °C and from 106 to 311 mS/cm at 80 °C. These values are slightly higher than the corresponding copolymer S2-PAES-xx with the same SC values, which indicates that the more blocky sulfonic acidcontaining segments in the polymer chain are more effective in proton conduction. Therefore, the S4-PAES-xx membranes exhibit higher relative proton conductivity and lower relative water uptake (vol %) than the S2-PAES-xx membranes, as shown in Figure 8.

Figure 9 displays proton conductivities as a function of temperature. The proton conductivities of the SPAES membranes increased with increasing temperature. The highest proton conductivity of 360 mS/cm was obtained for S4-PAES-40 with IEC_w of 2.0 mequiv/g at 100 °C, which is much higher than that of Nafion 112 (184 mS/cm) measured under the same conditions.

To further elucidate the proton-conducting properties of the SPAES membranes, the proton diffusion coefficients (D_{σ}) through the membranes were estimated from the proton conductivity and the IEC_v in hydrated membranes.^{45,46} A general trend of the dependency of D_{σ} on the temperature was obtained, as shown in Figure 10. At lower temperatures, SPAES membranes showed lower or similar D_{σ} values compared to Nafion, in spite of the higher IEC_v of SPAES. These results are consistent with the fact that the SPAES membranes having higher IEC_w showed lower proton conductivity. However, membranes with lower the IEC_v values that resulted from excessive matrix swelling and high water uptake have much higher D_{σ} values at higher temperatures compared with Nafion. The high D_{σ} could be attributed to increased water content at higher temperatures, leading to

					water uptake					
			IEC _v ^{<i>a</i>} (mequiv/cm ³)		wt % ^b		vol % ^c		proton conductivity (mS/cm)	
copolymer	density (g/cm ³)	$IEC_W \ (mequiv/g)$	dry	wet	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C
S2-PAES-40	1.39	1.19	1.65	1.32	18.2	24.5	25.3	34.0	44	82
S2-PAES-60	1.41	1.64	2.31	1.59	32.2	43.1	45.1	60.8	75	153
PS2-PAES-60	1.40	1.60	2.25	1.58	30.2	39.5	42.3	55.3	78	157
S2-PAES-70	1.43	1.84	2.63	1.57	47.3	76.8	67.6	109.8	95	195
S2-PAES-80	1.45	2.02	2.93	1.54	62.6	134.2	90.8	194.6	142	298
PS4-PAES-20	1.39	1.20	1.67	1.43	12.1	14.9	16.8	20.7	49	108
S4-PAES-20	1.40	1.18	1.65	1.43	11.4	14.0	15.1	19.4	51	106
S4-PAES-30	1.42	1.63	2.31	1.65	28.4	37.1	40.3	52.7	83	164
S4-PAES-35	1.43	1.82	2.60	1.67	39.1	64.8	55.9	92.7	112	209
S4-PAES-40	1.45	2.00	2.90	1.69	50.8	115.2	73.8	167.0	158	311
Nafion 112	1.98	0.90	1.78	1.29	19.0	28.6	37.6	56.6	90	174

^{*a*}Based on volume of dry and/or wet membranes (IEC_v(wet) = IEC_v(dry)/(1 + 0.01WU)). ^{*b*}WU (wt %) = ($W_{wet} - W_{dry}$)/ $W_{dry} \times 100$. ^{*c*}WU (vol %) = (($W_{wet} - W_{dry}$)/ δ_w)/(W_{dry}/δ_w) × 100 (W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively; δ_w is the density of water (1 g/cm³), and δ_m is the membrane density in the dry state).



Figure 4. Water uptake dependence of weight IEC (IEC_w) and volumetric IEC (IEC_v) values of copolymer membranes.

increased dissociation of the protons from the SO_3^- groups. In addition, the D_σ values obtained for S4-PAES-*xx* were similar to those of the S2-PAES-*xx* membranes in spite of the former's higher IEC_v. The results are not contradictory to the above-mentioned conductivity data. It is assumed that the blocky and pendent sulfonic acid groups change the size and shape of the hydrophilic ionic domains through which proton transport occurs, which results in the high D_σ values of S4-PAES-*xx* membranes. This result reveals that the more blocky S4-PAES-*xx* membranes do indeed provide a less encumbered proton conducting pathway, from which it can



Figure 5. Water uptake dependence of volumetric IEC values (IEC_v (wet)) of copolymer membranes in the wet state.



Figure 6. Volumetric IEC_v of SPAES and Nafion 112 in water as a function of temperature.

be inferred that the ionic domains are very dense and well distributed.

Methanol Permeability and Selectivity. Polymer electrolyte membranes intended for DMFC must both possess high proton conductivity and be an effective barrier for methanol crossover from the anode to the cathode compartment. The methanol permeability through the polymer electrolyte membranes often



Figure 7. $IEC_w(a)$ and $IEC_v(b)$ dependence of proton conductivity of the SPAES membranes.



Figure 8. Relative proton conductivity vs relative volume water uptake.

follows a similar relationship to proton conductivity. That is, the proton conductivity has a strong trade-off in its relationship with the methanol permeability. Nafion not only has good proton conductivity due to strongly interconnected ionic domains structure but also has high methanol permeability. The S2-PAES and S4-PAES copolymers exhibited comparatively lower methanol permeability to Nafion. The methanol permeability values for 10% methanol concentration at room temperature were in the range of 0.08×10^{-6} – 1.5×10^{-6} cm²/s, which is lower than the value of 1.67×10^{-6} cm²/s for Nafion. Although S2-PAES-40 and S4-PAES-20 have lower *ex situ* proton conductivities than Nafion 112, it is sufficient to achieve



Figure 9. Proton conductivity of SPAES membranes in water as a function of temperature.



Figure 10. Proton diffusion coefficient of SPAES and Nafion 112 membranes as a function of volumetric IEC_v in the water.



Figure 11. Performance trade-off plot of the ${\rm IEC}_{\rm w}$ values vs the selectivity.

improved DMFC performance through its low methanol permeability (i.e., better selectivity) (Figure 11). Selectivity, which is the ratio of proton conductivity to methanol permeability, is often used to evaluate the potential performance of DMFC membranes. It is a useful predictive parameter of performance, providing the proton conductivity is sufficiently high. The selectivity is plotted as a function of IEC_w in Figure 11. The selectivity of SPAES membranes decreases rapidly as the IEC_w values increase. The S4-PAES-*xx* membranes displayed higher selectivity than the S2-PAES-*xx* membranes due to the higher proton conductivity and lower methanol permeability.

Conclusions

Novel difluorodiphenyl sulfone monomers containing two or four pendent phenyl groups have been successfully synthesized in high yields by sequential bromination and Suzuki coupling. The non-sulfonated monomer could either be polymerized and the resulting polymer sulfonated or the monomer could be sulfonated and then polymerized. ¹H NMR spectroscopy confirmed that the pendent phenyl groups in either the monomers or the polymers could be completely sulfonated predominately at the para-phenyl site in a short time. The polymer electrolyte membranes showed excellent thermal stability and mechanical properties. The nature of the hydrophilic segments in the polymer electrolyte membranes significantly affected the proton transport and other properties. The S4-PAES-xx membranes, comprising a more blocky higher local concentration of sulfonic acid groups, showed lower water uptake and low methanol permeability but higher proton conductivities than their S2-PAES-xx counterparts having the same sulfonic acid content. This infers that a local and high density of sulfonic acid groups in the pendent phenyl is important for optimum percolation. For example, S2-PAES-60 and S4-PAES-30 with similar IEC_w values exhibited proton conductivity of 190 and 210 mS/cm, respectively, at 100 °C, higher than that of Nafion 117. The highest conductivity, i.e., 360 mS/cm, was obtained for S4-PAES-40 at 100 °C. The methanol permeability values of S2-PAES-60 and S4-PAES-30 were 2.8 \times 10^{-7} and 2.2×10^{-7} cm²/s, respectively, which is several times lower than Nafion. The combination of high thermal stability, good relative proton conductivity, and low methanol transport makes S2-PAES-60 and S4-PAES-30 attractive as PEM materials for fuel cells applications.

Originally, attempts were made to prepare highly sulfonated poly(phenyl sulfone) with pendent sulfonic acid groups and high IEC values using these monomers. However, the precursor poly(sulfide sulfone) had low viscosity and molecular weight and thus could not be fabricated into flexible and tough membranes. The lower molecular weight was attributed to a steric hindrance effect, which results from a combination of the bulky pendent phenyl groups and the larger thiolate nucleophile. We are currently exploring other reaction conditions in order to increase the molecular weight.

Acknowledgment. This research was supported by the WCU (World Class University) program, National Research Foundation (NRF) of the Korean Ministry of Science and Technology (No. R31-2008-000-10092-0), which we gratefully acknowledge.

References and Notes

- Tant, M. R.; Mauritz, K. A.; Wilkes, G. L. *Ionomers*; Chapman & Hall: New York, 1997.
- (2) Carrette, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* 2001, *1*, 5–39.
- (3) Costamagna, P.; Srinivasan, S. J. Power Sources 2001, 102, 253– 269.
- (4) Roziere, J.; Jones, D. J. Annu. Rev. Mater. Res. 2003, 33, 503-555.
- (5) Lakshmanan, B.; Huang, W.; Olmeijer, D.; Weidner, J. W. Electrochem. Solid-State Lett. 2003, 6, A282–A285.
- (6) Mathias, M. F.; Makharia, R.; Gasteiger, H. A.; Conley, J. J.; Fuller, T. J.; Gittleman, C. J.; Kocha, S. S.; Miller, D. P.; Mittelsteadt, C. K.; Xie, T.; Yan, S. G.; Yu, P. T. *Interface* 2005, 14, 24–36.
- (7) Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J. Membr. Sci. 2002, 197, 231–242.
- (8) Chikashige, Y.; Chikyu, Y.; Miyatake, K.; Watanabe, M. Macromolecules 2005, 38, 7121–7126.
- (9) Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K.; Kaliaguine, S. J. Membr. Sci. 2004, 229, 95–106.

- (10) Gil, M.; Ji, X.; Li, X.; Na, H.; Hampsey, J. E.; Lu, Y. J. Membr. Sci. **2004**, *234*, 75–81.
- (11) Shang, X.; Tian, S.; Kong, L.; Meng, Y. J. Membr. Sci. 2005, 266, 94–101.
- (12) Schuster, M.; Kreuer, K.-D.; Andersen, H. T.; Maier, J. Macromolecules 2007, 40, 598–607.
- (13) Bai, Z.; Dang, T. D. Macromol. Rapid Commun. 2006, 27, 1271– 1277.
- (14) Sumner, M. J.; Harrison, W. L.; Weyers, R. M.; Kim, Y. S.; McGrath, J. E.; Riffle, J. S.; Brink, A.; Brink, M. H. J. Membr. Sci. 2004, 239, 199–211.
- (15) Gao, Y.; Robertson, G. P.; Kim, D.-S.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Macromolecules* **2007**, *40*, 1512– 1520.
- (16) Kim, Y. S.; Kim, D. S.; Liu, B.; Guiver, M. D.; Pivovar, B. S. J. Electrochem. Soc. 2008, 155, B21–B26.
- (17) Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359–373.
- (18) Miyatake, K.; Zhou, H.; Matsuo, T.; Uchida, H.; Watanabe, M. *Macromolecules* **2004**, *37*, 4961–4966.
- (19) Yin, Y.; Suto, Y.; Sakabe, T.; Chen, S.; Hayashi, S.; Mishima, T.; Yamada, O.; Tanaka, K.; Kita, H.; Okamoto, K.-I. *Macromolecules* **2006**, *39*, 1189–1198.
- (20) Li, N.; Cui, Z.; Zhang, S.; Li, S. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 2820–2832.
- (21) Li, N.; Zhang, S.; Liu, J.; Zhang, F. Macromolecules 2008, 41, 4165–4172.
- (22) Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. Solid State Ionics 1998, 106, 219–225.
- (23) Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* 2005, *38*, 5010–5016.
- (24) Wu, S. Q.; Qiu, Z. M.; Zhang, S. B.; Li, Z. Y. Polymer 2006, 47, 6993–7000.
- (25) Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y. S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D.; Zelenay, P.; More, K.; Stroh, K.; Zawodzinski, T.; Boncella, J.; McGrath, J. E.; Inaba, M.; Miyatake, K.; Hori, M.; Ota, K.; Ogumi, Z.; Miyata, S.; Nishikata, A.; Siroma, Z.; Uchimoto, Y.; Yasuda, K.; Kimijima, K. I.; Iwashita, N. *Chem. Rev.* 2007, 107, 3904–3951.
- (26) Rikukawa, M.; Sanui, K. Prog. Polym. Sci. 2000, 25, 1463-1502.
- (27) Ghassemi, H.; McGrath, J. E.; Zawodzinski, T. A. Polymer 2006, 47, 4132–4139.
- (28) Bae, B.; Miyatake, K.; Watanabe, M. *Macromolecules* **2009**, *42*, 1873–1880.
- (29) Kreuer, K. D. J. Membr. Sci. 2001, 185, 29-39.
- (30) Einsla, B. R.; McGrath, J. E. Am. Chem. Soc. Div. Fuel Chem. 2004, 49, 616–618.
- (31) Lafitte, B.; Puchner, M.; Jannasch, P. Macromol. Rapid Commun. 2005, 26, 1464–1469.
- (32) Lafitte, B.; Jannasch, P. Adv. Funct. Mater. 2007, 17, 2823-2834.
- (33) Ghassemi, H.; McGrath, J. E. Polymer 2006, 47, 4132–4139.
- (34) Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z.; Holdcroft, S.; Hay, A. S. *Macromolecules* **2008**, *41*, 281–284.
- (35) Matsumura, S.; Hlil, A. R.; Du, N.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z.; Holdcroft, S.; Hay, A. S. J. Polym. Sci., Part A: Polym. Chem. 2008, 44, 3860–3868.
- (36) Schuster, M.; Kreuer, K. D.; Andersen, H. T.; Maier, J. Macromolecules 2007, 40, 598–607.
- (37) Schuster, M.; de Araujo, C. C.; Atanasov, V.; Anderson, H. T.; Kreuer, K. D.; Maier, J. *Macromolecules* **2009**, *42*, 3129–3137.
- (38) Kim, Y. S.; Einsla, B.; Sankir, M.; Harrison, W.; Pivovar, B. S. Polymer 2006, 47, 4026–4035.
- (39) Liu, B.; Robertson, G. P.; Guiver, M. D. Am. Chem. Soc. Polym. Mater. Sci. Eng. Prepr. 2006, 95, 206–207.
- (40) Liu, B.; Robertson, G. P.; Kim, D.-S.; Guiver, M. D.; Hu, W.; Jiang, Z. Macromolecules 2007, 40, 1934–1944.
- (41) Liu, B.; Kim, Y. S.; Hu, W.; Robertson, G. P.; Pivovar, B. S.; Guiver, M. D. J. Power Sources 2008, 185, 899–903.
- (42) Kim, Y. S.; Guiver, M. D. Macromolecules 2009, 42, 957-963.
- (43) Liu, B.; Robertson, G. P.; Kim, D.-S.; Sun, X.; Jiang, Z.; Guiver, M. D. Polymer 2010, 51, 403–413.
- (44) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. Chem. Rev. 2004, 104, 587–611.
- (45) Peckham, J. T.; Schmeisser, J.; Rodgersa, M.; Holdcroft, S. J. Mater. Chem. 2007, 17, 3255–3265.
- (46) Tsang, E. M. W.; Zhang, Z.; Shi, Z.; Soboleva, T.; Holdcroft, S. J. Am. Chem. Soc. 2007, 129, 15106–15107.