Sulfonated Poly(aryl ether ketone)s Containing the Hexafluoroisopropylidene Diphenyl Moiety Prepared by Direct Copolymerization, as Proton Exchange Membranes for Fuel Cell Application[†]

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ABSTRACT: A series of sulfonated poly(aryl ether ketone) (SPAEK-6F) copolymers were prepared by aromatic nucleophilic polycondensation of hexafluoroisopropylidene diphenol with 5,5′-carbonylbis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone (DFBP) at various molar ratios. The synthesized SPAEK-6F polymers possessed high molecular weights revealed by their high viscosity, and tough and flexible membranes were obtained by casting from DMAc solution. The sulfonate or sulfonic acid content (SC) of the polymers, expressed as a number per repeat unit of polymer, was determined by ^{1}H NMR spectroscopy and was in good agreement with the initial monomer ratios. The membranes exhibited increased water uptake and swelling with increasing SC and temperature. SPAEK-6F membranes with SC ranging from 0.6 to 1.14 maintained adequate mechanical strength after immersion in water at 80 °C for 24 h. Fenton's reagent test revealed that the SPAEK-6F membranes had good stability to oxidation. The proton conductivities of the SPAEK-6F films increased with SC and temperature, reaching values above 3×10^{-2} S/cm at 80 °C for SC $\geq$ 0.75. The tensile test indicated that the SPAEK-6F membranes with SC 0.75, 0.98, and 1.14 are tough and strong at ambient conditions. Consequently, these materials proved to be promising as proton exchange membranes and may be potentially useful for application in fuel cells operated at medium temperatures.

1. Introduction

The proton exchange membrane (PEM) fuel cell (PEMFC), which typically operates in the temperature range of 60−80 °C, has been widely investigated as an automotive, stationary, and portable power source due to its low emissions and high conversion efficiency. The PEM is a proton conducting, electronically insulating polymer material, which is a critical component of the PEMFC for transferring protons from the anode to the cathode as well as providing a barrier to the fuel gas cross-leaks between the electrodes. In the past two decades, the most successful PEM materials were perfluorinated copolymers such as DuPont Nafion due to their excellent mechanical properties, chemical stability, and their high proton conductivity. Despite this, their high cost, low operating temperature (dehydration and loss of proton conductivity >80 °C), and high methanol crossover (in the case of direct methanol fuel cells) hinder their further commercial application.[1]

Hence, alternative cost-effective PEM materials with high proton conductivity able to operate at elevated temperatures (which improves FC efficiency) with lower fuel crossover are being sought. Sulfonation of aromatic polymers is one of the main approaches that enhances proton conductivity and hydrophilicity and increases solubility for easier membrane processing. These sulfonated aromatic polymers, including sulfonated poly(ether ether ketone) (SPEEK),[2−4] poly(ether sulfone) (SPES),[5] polyimides (SPI),[6] and poly(benzimidazole) (PBI),[7] are widely investigated as candidate PEM materials due to their high chemical and thermooxidative stability, good mechanical properties, and lower cost. Attaching sulfonic acid groups onto polymer backbones can be achieved either by postsulfonation of polymer or by direct copolymerization of sulfonated monomers. The hydrophobic domains formed by nonsulfonated polymer segments provide the hydrated PEMs with mechanical strength, whereas the hydrophilic domains containing the sulfonic acid group ensure the proton conductivity.[1d] The sulfonic acid groups introduced via postsulfonation are randomly distributed along the polymer backbone, which does not favor controlled chain structure. For example, postsulfonated PEEK (SPEEK)[2−4a,b] showed proton conductivity above 10^{-2} S/cm and can be potentially useful as a PEM. However, long-term immersion in hot water (80 °C) results in the loss of membrane integrity at SC > 0.6 (mequiv 560). This is mainly due to its chain structure, in which the sulfonic acid groups are randomly distributed onto the hydroquinone segments in the polymer repeat units. Consequently, the formation of zones oversaturated with fully sulfonated segments or a lack of fully hydrophobic segments could occur, having very low resistance to hot water. On the other hand, from the molecular design point of view, direct copolymerization of sulfonated monomers with other nonsulfonated aromatic monomers can ensure a better control of the polymer chain structure. This approach allows a more uniform distribution of sulfonic acid groups, better precision with targeted SC, and better control over the length of the statistical nonsulfonated segments. The

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SC of the polymers can be controlled by varying the feed ratio of sulfonated/nonsulfonated monomers. The sulfonated monomers 5,5′-carbonylbis(2-fluorobenzenesulfonate) (SDFBP) and disulfonated dihalodiphenyl sulfone were used to prepare sulfonated poly(aryl ether ketone) (SPAEK)[8−10] and sulfonated poly(aryl ether sulfone) (SPAES)[11−13] by copolymerizing sulfonated monomers with some other nonsulfonated aromatic monomers. Sulfonated PI[6] membranes were prepared in a similar way.

The hexafluoroisopropylidene diphenyl (6F-BPA) moiety has often been incorporated into polymers such as PAEK,[14] poly(ether sulfone),[12c] and polyimide. The group of McGrath[12c] recently reported the preparation of a sulfonated poly(ether sulfone) containing the 6F-BPA moiety that shows promising properties as PEM. Postsulfonated poly(ether ether ketone)s made from DFBP and 6F-BPA using chlorosulfonic acid were reported with SC ranging from 0 to 2, and the sulfonic acid groups were located on the ortho-ether position of the 6F-BPA unit.[14a] The present work reports a series of directly copolymerized sulfonated PAEKs containing the nonsulfonated 6F-BPA moiety and SDFBP, where the sulfonic acids were attached to the DFBP unit, which is less hydrophobic in comparison with 6F-BPA. Here, the incorporation of the larger rigid 6F-BPA moiety into the backbone is an attempt to increase the hydrophobicity and length of nonsulfonated segments and to improve the membranes' mechanical properties as well as the hot water stability of SPAEK-6Fs. The 6F-BPA unit also enhances the polymers' solubility and film-forming ability. The structure and some properties of the synthesized polymers were studied with particular emphasis on the PEM-related properties, such as proton conductivity, mechanical properties, water-induced swelling, and stability of cast membranes. Independently from the present work, another group recently reported the preparation of a single SPAEK-6F as a structural example in a patent application.[15]

2. Experimental Section

2.1. Chemicals and Materials. Fuming sulfuric acid (30% SO_3), dimethylacetamide (DMAc), anhydrous potassium carbonate, and 4,4′-difluorobenzophenone (DFBP) were obtained from Sigma-Aldrich Corp. 4,4′-(Hexafluoroisopropylidene) diphenol (6F-BPA) was obtained from SCM Corp. MEMBRA-CEL dialysis tubing (MWCO 3500) was obtained from Serva Electrophoresis (Germany).

2.2. Synthesis of Monomer Sodium 5,5′-Carbonylbis-(2-fluorobenzenesulfonate) (SDFBP). The monomer SDFBP-Na was prepared following the procedure described in refs 8a, 10a, and 11. Yield: 70%. FTIR and ^{1}H NMR analyses (IR (cm^{-1}): 1662 (C═O), 1592 (C═C), 1085 (Ar−SO_3Na); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.36 (dd, 9.40 Hz, 8.35 Hz, 2H), 7.74 (m, 2H), 8.07 (dd, 6.8 Hz, 2.0 Hz, 2H)) confirmed the formation of DFBP sodium sulfonate.

2.3. Synthesis of Sulfonated Poly(aryl ether ketone)s. The SPAEK-6F's were prepared by copolymerization polycondensation using equal molar amounts of monomers at concentration of 20% (w/v) solids in DMAc with an excess of anhydrous potassium carbonate.[16] Monomers DFBP, SDFBP-Na (combined total 0.5 mmol), 0.5 mmol of 6F-BPA, and 0.55 of mmol potassium carbonate were added into a 50 mL three-neck flask, equipped with a Dean−Stark trap and an argon inlet. 18 mL of DMAc and 15 mL of toluene were used as solvents. The mixture was refluxed for 2 h at 130 °C until water was removed from the reaction mixture by azeotropic distillation, and then excess toluene was distilled off. The temperature of the reaction mixture was slowly raised to 160 °C and maintained at that temperature for 24 h. Before stopping the reaction, 5 mL of DMAc was added to dilute the reaction solution, and the polymer was cooled and recovered by precipitating into ethanol and then washed with acetone and then water. Polymers with SC ≤ 1.6 in sodium salt form were washed repeatedly with deionized water until the pH reached 6−7. SPAEK-6F-100 with SC 2.0 in sodium salt form was washed by placing this polymer into water in dialysis tubing. Typically, several days of dialysis were required to obtain pH values of 6−7. The recovered polymers were dried at room temperature for 2 days and then dried in a vacuum oven at 80 °C for 24 h. The yields of all polymers were greater than 90%. IR spectra show that the aromatic C═C band at 1501 cm^{-1} corresponding to disubstitution on aromatic phenyl for nonsulfonated PAEK-6F was split into two bands at 1509 and 1482 cm^{-1} for the SPAEK-6F (e.g., SC 1.2) due to the sulfonation in the phenyl ring. New absorption bands at 1031 and 1086 cm^{-1} for SPAEK-6F sulfonate groups were assigned to symmetric and asymmetric stretching vibration of O═S═O.

2.4. Membrane Preparation. The SPAEK-6F membranes (sodium salt form) were cast onto glass plate from their DMAc solution (15 wt %) after filtration using a fine glass frit filter funnel and dried at 50 °C for 2 days and then at 120 °C under vacuum for 24 h. The SPAEK-6F membranes (in sodium salt form) were transformed to their acid form by soaking in deionized water for 1 day at room temperature and then immersion in 1.0 N HCl solution for 24 h. After that, the obtained membranes (in acid form) were immersed and washed with deionized water for 24 h. The thickness of all membrane samples was in the range of 70 and 100 μm.

X-ray fluorescence spectroscopy (model SRS3400 Bruker-AXS) was used to confirm the efficiency of conversion of selected membranes in the sodium sulfonate form to the sulfonic acid form by immersion in acid, followed by washing with deionized water.

2.5. Characterization of SPAEK-6F. Inherent viscosities of the copolymers were measured at 30 °C on 0.6 g L^{-1} solutions in DMAc. FTIR spectra were recorded on a Nicolet 520 Fourier transform spectrometer with powder samples inside a diamond cell. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova NMR spectrometer operating at a resonance frequency of 399.95 MHz for ^{1}H and of 100.579 MHz for ^{13}C. 1D and 2D NMR spectra were recorded using a 5 mm indirect detection probe as well as a 10 mm broadband probe. For each analysis, ∼5−15 wt % polymer solutions were prepared in deuterated dimethyl sulfoxide (DMSO-d_6). The chemical shift of tetramethylsilane (0.0 ppm) was used as the internal standard reference. A TA DSC 2920 differential scanning calorimetry (DSC) was employed to study the thermal transition behavior of nonsulfonated PAEK-6F sample. The sample was heated under nitrogen from room temperature to 390 °C at 10 °C/min. A TA Hi-Res TGA 2950 thermogravimetric analyzer (TGA) was employed to study the thermal stability behavior of SPAEK-6F samples. The samples were preheated under air from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to 90 °C, and then reheated from that temperature to 800 °C at 10 °C/min.

2.6. Characterization of Proton Exchange Membranes. The water uptake and swelling were obtained by measuring the difference in the weight and length between dry and hydrated membranes. Weighed films with approximate area 5 mm × 50 mm, after being dried in a vacuum oven at 120 °C for 24 h, were immersed in deionized water at different temperatures for 24 h. The liquid water on the surface of wetted membranes was removed using tissue paper before weighing. The weight gain with respect to the original membrane weight was taken as the water uptake (S), $S = (W_s - W_d)/W_d \times 100$ (%), where W_d and W_s are the weights of dry and corresponding water-swollen films, respectively. The percentage of length gain to original length was taken as the swelling ratio.

The proton conductivities of the polymer membranes were determined using AC impedance spectroscopy over a frequency range of 1−10^{-7} Hz with oscillating voltage 50−500 mV, using

Scheme 1. Synthesis of Sulfonated Poly(aryl ether ketone) (SPAEK-6F)

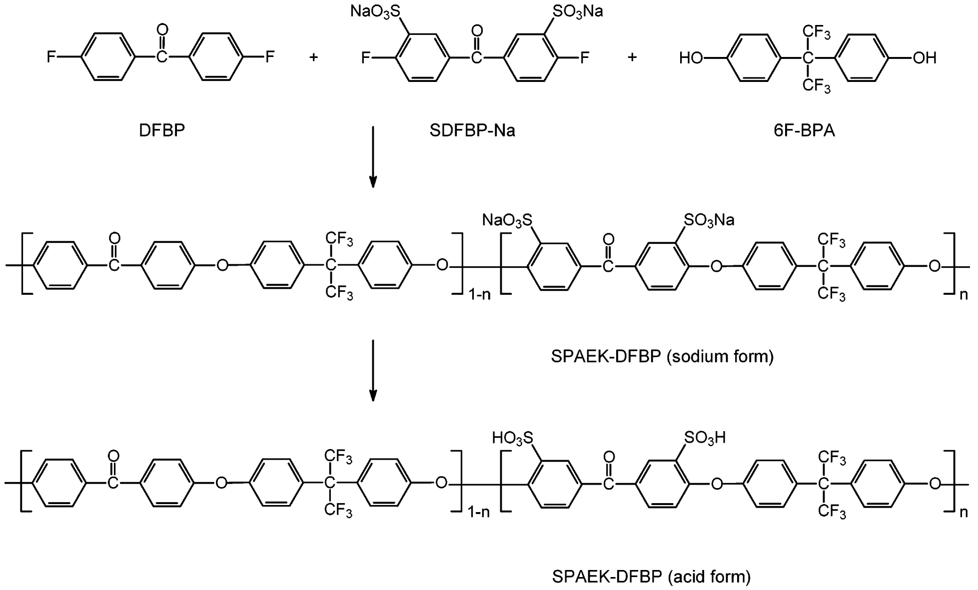

Table 1. Composition and Properties of SPAEK-6F

polymer	percentage of sulfonated monomer (mol %)[a]	SC expected from monomer feed ratio	SC from ^{1}H NMR	T_d (°C) acid form	T_d (°C) sodium form	η_{inh}[b] (dL/g)
PAEK-6F	0	0		454.9		1.08
SPAEK-6F-20	20	0.4		261.1	395.5	
SPAEK-6F-30	30	0.6	0.60	248.2	394.2	1.18
SPAEK-6F-40	40	0.8	0.75	250.2	400.6	3.47
SPAEK-6F-50	50	1.0	0.98	275.3	399.4	1.81
SPAEK-6F-60	60	1.2	1.14	254.7	407.1	1.58
SPAEK-6F-70	70	1.4	1.36	256.2	400.7	1.50
SPAEK-6F-80	80	1.6	1.58	263.7	412.3	1.05
SPAEK-6F-100	100	2.0	2.00	253.4	412.2	0.67

[a] The percentage of sulfonated monomer SDFBP = monomer SDFBP/[monomer DFBP + monomer SDFBP] × 100 as shown in Scheme 1. [b] η_{inh} was measured at a concentration of 0.6 g/dL in DMAc for sodium form of SPAEK-6Fs at 30 °C.

a Solatron 1260 gain phase analyzer. Proton conductivities in the longitudinal direction were measured. A sample of prehydrated membrane ~2 × 1 cm was clamped between two electrodes and then placed in a humidity chamber open to the air through a pinhole. The membrane between the two electrodes was exposed to allow its equilibrium with water vapor at 100% relative humidity (RH) during the experiments. The proton conductivity was calculated using $\sigma = l/Rdw$, where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and R was derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re(Z) axis. Re refers to "Real" in the complex impedance plan. The impedance data were corrected for the contribution from empty and short circuited cell.

Mechanical tensile tests were conducted with an Instron 1123 at a head speed of 10 mm/min at ambient conditions. The relative humidity was ~65%. The specimens with thickness ~100 μm and size of 40 mm × 3 mm were used for testing.

3. Results and Discussion

3.1. Syntheses and Characterization of SPAEK-6F. As shown in Scheme 1, the sulfonated PAEK-6Fs were synthesized by polycondensation of activated aromatic halides (DFBP and SDFBP) with bisphenol 6F-BPA via the aromatic nucleophilic substitution reaction in the presence of a weak base, potassium carbonate, and a dipolar aprotic solvent, DMAc.[16] The SC of SPAEK-6F was controlled through the monomer feed ratios of SDFBP/DFBP. DMAc was used as the reaction solvent, and toluene was used to remove the water during the copolymerization. It has been reported that the nonsulfonated PAEK-6F was previously synthesized[14] using DMAc as the reaction solvent. After ~24 h of copolymerization at 160 °C, the solutions became highly viscous, and DMAc was added to dilute the reaction solution before precipitation into ethanol. Table 1 shows the nomenclature used in this paper for the prepared copolymers in the sodium salt form. In all cases the yields were >90%, and high molecular weights (M_w) were obtained as evidenced by the high η_{inh} values of >1.0 dL g^{-1} and even as high as 5 dL g^{-1} in DMAc. It is likely that the achievement of high M_w was facilitated by the good solubility of the synthesized SPAEK-6F in the DMAc reaction medium. Usually, during a polymerization, the tendency for crystallization or rigid-rod structures negatively affects the polymer solubility in the reaction medium and causes precipitation at early stage of polymerization, thus preventing a high M_w to be achieved. However, this was not the case with this series of polymers since the incorporation of the fluorinated 6F-BPA monomer into PAEK-6F enhances solubility[17] and favors the formation of amorphous polymer. Meanwhile, the introduction of the sulfonated monomer into the polymer chain also improves the solubility of the polymer because the sulfonic group (sodium form or acid form) enhances solubility in polar aprotic solvents. Thus, all synthesized SPAEK-6F samples listed in Table 1 are soluble in DMAc, DMSO, and *N*-methyl-2-pyrrolidinone (NMP).

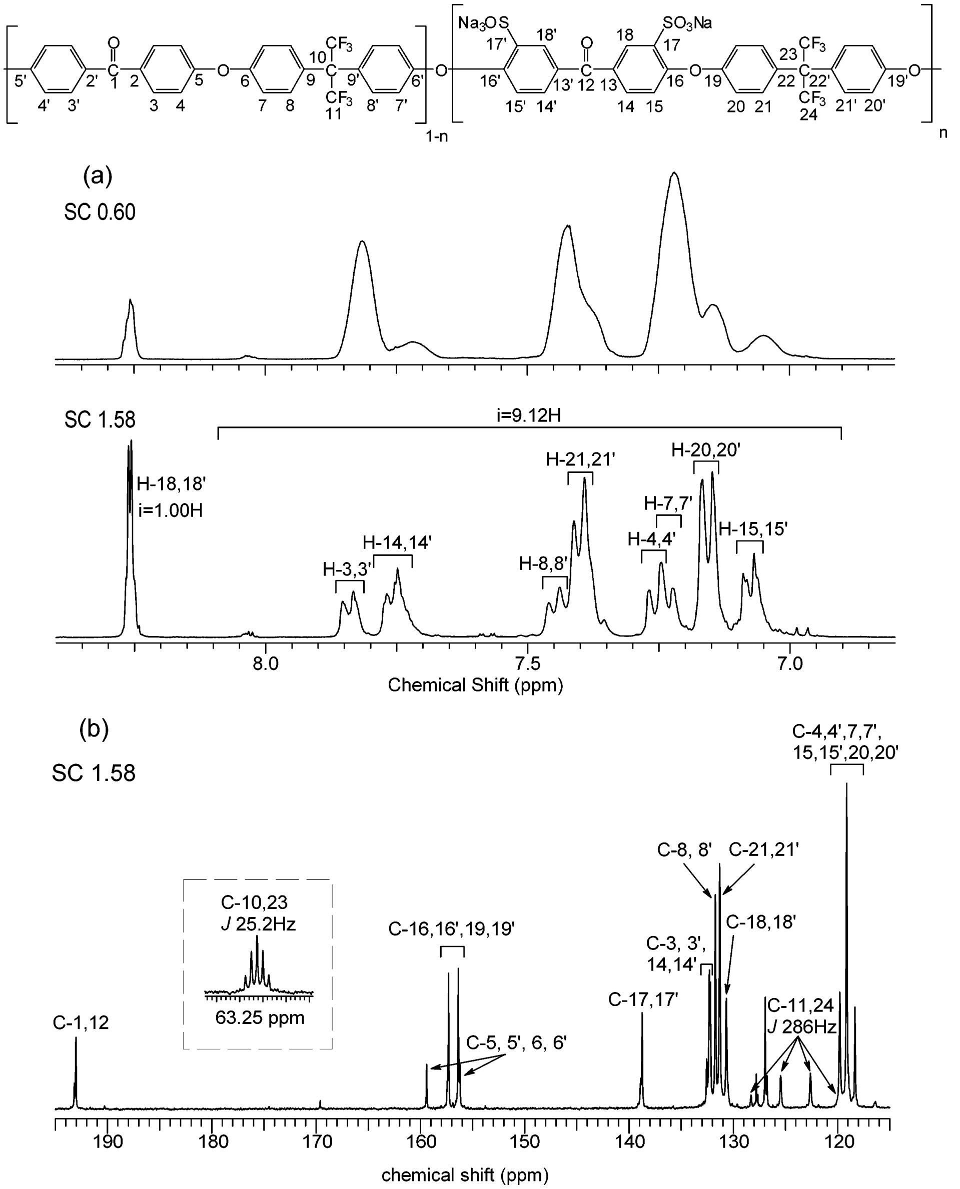

Figure 1. (a) ^{1}H NMR spectra of SPAEK-6F (SC 0.60 and 1.58) in DMSO-d_6. (b) ^{13}C NMR spectrum of SPAEK-6F-80 (SC 1.58) in DMSO-d_6 (^{1}H noise decoupled).

NMR spectroscopy (1D ^{1}H, ^{13}C, and 2D ^{1}H−^{1}H, ^{1}H−^{13}C correlation) was used as the principal method for characterization of the polymers in the sodium salt form. Polymer samples were dissolved in DMSO-d_6 for spectroscopic measurements. Stacked spectra comparing low and high SC polymers (SC 0.60 and 1.58) displayed in Figure 1a show improved line resolution for the higher SC polymer as a result of its better solubility in DMSO-d_6. The signal intensities of ^{1}H NMR spectra were used to derive the experimental SC ($0 < \mathrm{SC} \leq 2$), defined as the average number of $-\mathrm{SO_3Na}$ groups per polymer repeat unit (RU). Each signal was assigned to a single or to a group of aromatic protons of sulfonated (S_{RU}) or nonsulfonated RU (NS_{RU}). The SC was measured by comparing the intensities of the S_{RU} aromatic signals H-18,18′ with the intensities of the NS_{RU} aromatic signals H-3,3,3′,3′. The following equation explains how the SC is derived from these signal intensities:

$$\mathrm{SC} = 2 \times \left[\frac{S_{\mathrm{RU}}}{S_{\mathrm{RU}} + NS_{\mathrm{RU}}}\right] \therefore \mathrm{SC} = 2 \times \left[\frac{(2 \times i_{18})}{(2 \times i_{18}) + i_3}\right]$$

where $[S_{\mathrm{RU}}/S_{\mathrm{RU}} + NS_{\mathrm{RU}}]$ = the ratio of S_{RU} per average polymer RU, i_{18} = intensity of H-18,18′, and i_3 = intensity of H-3,3,3′,3′.

For example, the SC calculation of the SC 1.58 SPAEK-6F in Figure 1a was derived from the ratio of the signal intensity of the two protons H-18,18′ (i_{18} set to 1.00H) to that of the H-3,3,3′,3′ (i_3 0.54H). The experimental SC values are in close agreement with those expected from the monomer feed ratio, as shown in Table 1. The ^{13}C NMR spectrum of the SC 1.58 polymer is shown in Figure 1b. Assignment of several carbon signals was accomplished using one bond ^{1}H−^{13}C correlation. Carbon atoms linked to oxygen or sulfur atoms (C=O, C−O, C−S) were discerned by their well-known and expected chemical shifts. Other minor signals from quaternary carbon atoms were left unassigned.

Unsulfonated PAEK-6F is an amorphous polymer with T_g 173.6 °C as measured by DSC. PAEK-6F exhibits a T_g significantly higher than that of PEEK (~150 °C), which is attributed to increased stiffness of the polymer chain by incorporating 6F-BPA into the

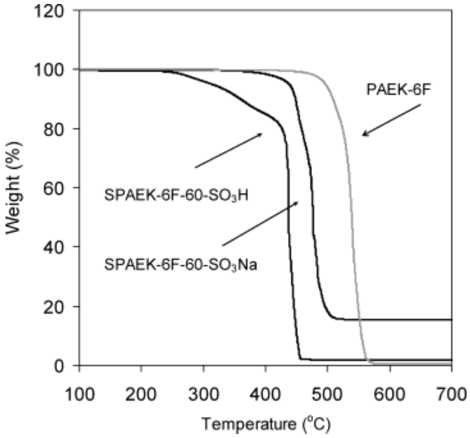

Figure 2. Typical TGA curves of SPAEK-6F.

polymer backbone. The TGA curve of SPAEK-6F showed a single step thermal degradation at ∼440 °C, indicating that the incorporation of 6F-BPA did not forfeit thermal stability[17] due to the strong C−F bond. The TGA experiments were performed at a heating rate of 10 °C min^{-1} in air since the air environment is similar to fuel cell operating conditions. In contrast to unsulfonated PAEK-6F, SPAEK-6F exhibited two distinct thermal degradation steps (Figure 2). In similarity with SPEEK,[3a,d] the SPAEK-6F polymer in the acid form shows the first weight loss step at∼ 260 °C (Table 1) which is believed to be associated mainly with the loss of sulfonic groups and the second weight loss step starting at about 380 °C, which is related to decomposition of the main chain of SPAEK-6F. The main-chain degradation temperature of SPAEK-6F is lower than that of unsulfonated PAEK-6F because of the acid-catalyzed chain degradation caused by SO_3H (Figure 2). The high initial thermal degradation temperature of SPAEK-6F (acid form) indicates their thermal stability may be adequate for application in PEMFC. Compared with the acid form of SPAEK-6F, the sodium form of SPAEK-6F showed a much higher thermal stability and starting thermal degradation temperature of ∼400 °C (Figure 2 and Table 1).

3.2. Water Uptake, Oxidative Stability, Proton Conductivity, and Mechanical Strength of Membranes. Water uptake and swelling of membranes are closely related to their proton conductivity and the mechanical strength. PEMs in fuel cells generally operate at temperatures close to 80 °C or higher. Thus, the swelling and water uptake were determined as functions of temperature. It has been reported that in the presence of water perfluorosulfonic polymers such as Nafion exhibit hydrophobic/hydrophilic nanophase separation,[1d] whereby the sulfonic acid groups form hydrophilic hydrated domains contributing to the proton conductivity and the perfluorinated backbone forms a well-networked hydrophobic domain providing mechanical strength. A similar percolation structure was also found in sulfonated poly(ether ketone) (PEEKK),[1d] but with narrower (compared with Nafion) water-filled channels, which arose due to the higher rigidity of the backbone and the direct attachment of sulfonic acid groups to the polymer backbone. Figure 3a,b and Table 2 display water uptake (wt %) and linear swelling (%) of SPAEK-6F membranes in the acid form. Figure 3a clearly shows that the water uptake continues to increase with SC and temperature and particularly sharply increases for SPAEK-6F-70 with SC 1.36. However, most of the SPAEK-6F membranes with SC ≤ 1.14 were observed to be stable and have adequate mechanical strength for PEMs before and after swelling in water at 80 °C. For example, the SPAEK-6F-50 (SC 0.98, calcd mequiv 610) membrane did not show excessive water uptake and maintained excellent mechanical strength after immersion in hot water at 80 °C for 24 h. In comparison with SPEEK (SC 0.6, calcd mequiv 560) the SPAEK-6F-60 and -50 (with similar calcd mequiv 500−600, Table 2) had much better mechanical stabilities in hot water. However, the SPAEK-6F-70 (SC 1.36) membrane had excessive water uptake and lost its mechanical integrity after 24 h water exposure at 80 °C. At higher SCs, the mechanical properties of the films deteriorated further. The SPAEK-6F-80 membrane (SC 1.58) formed a gel after immersion in water at room temperature, and the SPAEK-6F-100 (SC 2.0) readily dissolved in water. A slow increase in water uptake with SC for hydrated SPAEK-6F-20, -30, and -40 membranes with the retention of mechanical strength may be an indication of the formation of a percolation structure, but with more branched and dead end channels in these polymers at low SC,[1d] and at lower SC, a hydrophobic backbone domain essentially prevails. The properties of SPAEK-6F-50 and -60 membranes with SC 0.98 and 1.14 may be an indication of a continuum percolation structure due to their high water uptake and the mechanical strength of the hydrated membranes. In the case of SPAEK-70, the hydrophobic domain cannot provide adequate mechanical strength due to the very high water uptake at 80 °C. Figure 3b shows the linear swelling at 80 °C for the membranes SPAEK-6F-

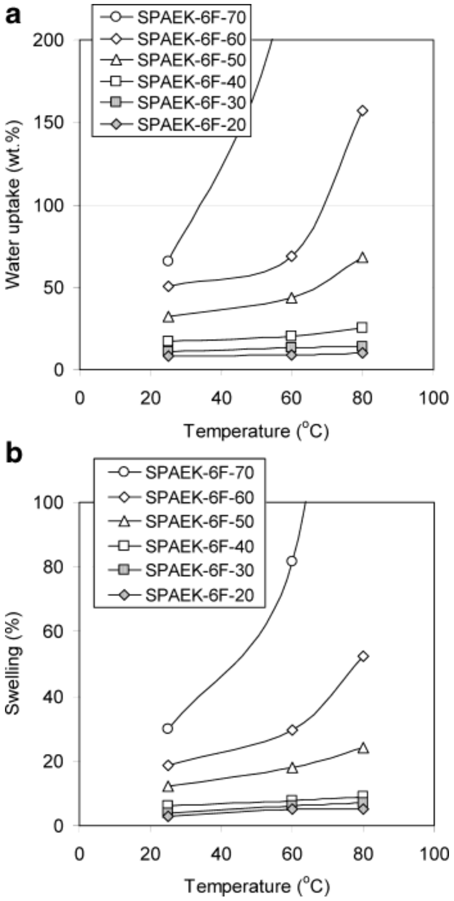

Figure 3. Water uptake (a) and swelling (b) of SPAEK-6F as functions of temperature.

Table 2. Water Uptake and Swelling Ratio of SPAEK-6Fs and Proton Conductivities at Different Temperatures

polymer	SC exptl (^{1}H NMR)	mequiv g/mol SO_3H calcd	water uptake (%) at 25 °C	swelling (%) at 25 °C	water uptake (%) at 80 °C	swelling (%) at 80 °C	H_2O/SO_3H		σ (S/cm)	
							25 °C	80°C	25 °C	80 °C
SPAEK-6F-20		1365	8	3	10	5	6	8	9.5×10^{-4}	2.8×10^{-3}
SPAEK-6F-30	0.60	937	11	4	14	7	6	7	4.5×10^{-3}	1.1×10^{-2}
SPAEK-6F-40	0.75	723	17	6	25	9	7	10	1.3×10^{-2}	3.0×10^{-2}
SPAEK-6F-50	0.98	610	32	12	68	24	11	23	3.9×10^{-2}	8.0×10^{-2}
SPAEK-6F-60	1.14	519	50	19	157	52	14	45	4.6×10^{-2}	1.1×10^{-1}
SPAEK-6F-70	1.36	458	92	30	2400	250	56	610	8.0×10^{-2}	1.6×10^{-1}
SPAEK-6F-80	1.58	406							8.2×10^{-2}	
SPAEK-6F-100	2.00	337								
Nafion 117		1100	19	13	30	20	12	18	7.5×10^{-2}	9.6×10^{-2}

40, -50, and -60, which range from 9% to 52% compared with 20% for Nafion117.

The stability of SPAEK-6F to oxidation was investigated by immersing the films into Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C, which is one of the standard tests for oxidative stability. SPAEK-6F-70 and -60 films dissolved after 50 and 90 min, respectively, whereas the SPAEK-6F-50 and -40 films dissolved after 240 and 390 min, respectively. SPAEK-6F-30 film remained undissolved after 24 h. Except for SPAEK-6F-70, all other membranes retained their mechanical strength after 1 h treatment, indicating they possess high oxidative stability similar to the results observed from sulfonated polyimides[6c−e] and sulfonated copolymer poly(aryl ether ketone ketone).[10b]

The proton conductivities (σ) of the membranes were measured in the longitudinal direction by AC impedance spectroscopy. Since the SPAEK-6F series were initially synthesized and cast into membranes in the sodium sulfonate form and then converted to the sulfonic acid form by immersion of the membranes in dilute acid, X-ray fluorescence spectroscopy was used to determine whether this conversion was efficient and complete. Membranes of polymers SPAEK-6F-30 and SPAEK-6F-60 before and after transformation from sodium sulfonate form to sulfonic acid form were measured for sodium content. First, a sodium standard of 6.5 μg on paper had a peak of 0.16 kcps, corresponding to 4 times background reading. SPAEK-6F-30 SO_3Na and SPAEK-6F-60 SO_3Na membrane samples had peaks of 17.9 and 31.0 kcps, respectively. After conversion to the acid form by treatment in 1.0 N HCl for 24 h followed by washing and immersion in deionized water for 24 h, the membrane samples had peaks of 0.06 kcps, corresponding to readings slightly above background noise. This confirmed that the acidification and washing protocol was effective in converting all the sodium sites to sulfonic acid sites. Before measurement of proton conductivity, all membranes were initially hydrated by immersion in deionized water for 24 h at room temperature. Figure 4 shows that the proton conductivities increased both with SC and with temperature. Indeed, a higher SC resulted in higher water uptake and higher proton conductivity. The proton conductivity increased from 1.1×10^{-2} S/cm for SPAEK-6F-30 (SC 0.6) to 1.6×10^{-1} S/cm for SPAEK-6F-70 (SC 1.36) at 80 °C (Table 2). All SPAEK-6F samples with SC $\geq$ 0.75 had $\sigma > 1.3 \times 10^{-2}$ S/cm at 25 °C and around 1×10^{-1} S/cm at 80 °C (Table 2), which is very close to the proton conductivity of Nafion117 (especially at around 80 °C) and considered to be adequate for PEM operation in a fuel cell at medium temperature. When considering both proton conductivity and water uptake data, the membranes in the range SPAEK-6F-40, -50, and -60 have the best combination of properties for application in PEM for FC at elevated temperatures. SPAEK-50, SPAEK-60, and Nafion 117 show similar proton conductivity ($\sim 1 \times 10^{-1}$ S/cm) at 80 °C, which may be an indication that percolation in the hydrophilic domain of these two polymers is possibly similar to that of Nafion 117, as pointed in ref 1d. However, SPAEK-6F-50 and -60 have higher H_2O/SO_3H ratios (23 and 45, respectively) than the one (18) of Nafion 117. It is also noteworthy that the proton conductivities of the present membranes (e.g., SPAEK-50 and -60) show a more marked increase with temperature than the ones of Nafion 117 membranes. This is attributed to the lower hydrophobicity of SPAEK-6F polymer backbone compared with the perfluorinated backbone of Nafion as well as a relatively strong interactions between the water molecules and sulfonic acid groups,[1a] which would result in improved water retention and high proton conductivity at elevated temperature.

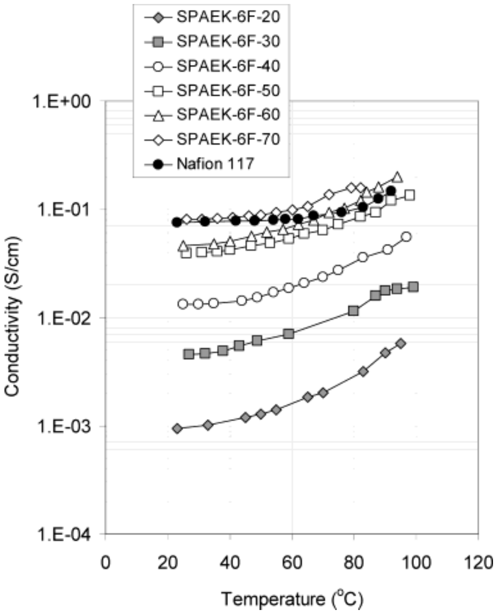

Figure 4. Proton conductivities of SPAEK-6F films as functions of temperature.

It is essential for PEMs to possess adequate mechanical strength under dry and humidified conditions. Here, the tensile test of membranes was conducted at ambient conditions with relative humidity (RH) ~ 65%, and the results are shown in Figure 5. For comparison, the Nafion 117 was also tested under the same conditions. Nafion 117 membrane showed a Young's modulus of 234 MPa, elongation at break 327%, and the maximum stress of 27 MPa at break, which are quite similar to the results from Nafion product information reported by DuPont[18] at similar ambient conditions. The initial Young's modulus for the membranes of SPAEK-6F-40,

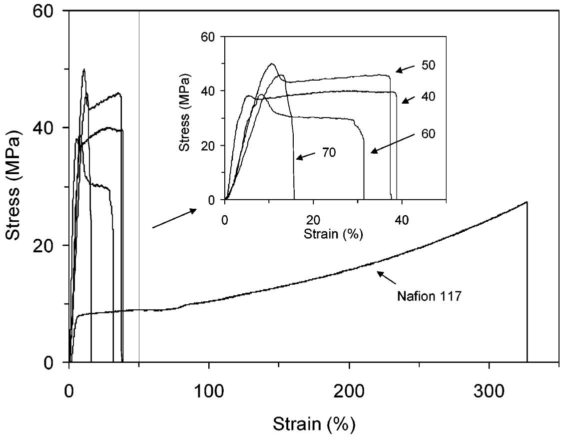

Figure 5. Stress vs strain curves for SPAEK-6F-40, -50, -60, and -70 and Nafion 117 at 25 °C and 65% RH. Inset is an enlargement of the SPAEK-6F sample region.

-50, -60, and -70 are 1.3 GPa, 662 MPa, 755 MPa, and 502 MPa, respectively, which are higher than the ones of Nafion 117. All four SPAEK-6F (-40, -50, -60, -70) curves from Figure 5 show elongation at break of 39%, 37%, 30%, and 15%, and SPAEK-6F (-40, -50, -60) curves show yield behavior and yield strength ranging from 35 to 50 MPa. These data indicate these three membranes are strong and tough at RH 65% and are very promising. The Young's modulus and elongation at break of these membranes mainly decrease with the increase of SC (from 0.75 to 1.36), which indicates the better mechanical properties of membranes with lower SC.

4. Conclusions

A novel series of sulfonated poly(aryl ether ketone) (SPAEK-6F) copolymers were prepared by aromatic nucleophilic polycondensation of 6F-BPA with 5,5′-carbonylbis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone at various molar ratios. The SPAEK-6Fs in acid form were thermally stable up to ~260 °C in air. The water uptake and swelling properties of prepared films were also studied, and the proton conductivities were measured at different temperatures. Hydrated membranes with SC ≤ 1.14 show good mechanical integrity, even when hydrated at 80 °C. The membranes also showed stability to oxidation, as evaluated by Fenton's reagent. The proton conductivities of SPAEK-6F membranes with SC from 0.6 to 1.36 were from 4.5×10^{-3} to 8.0×10^{-2} S/cm at 25 °C and up to from 1.1×10^{-2} to 1.6×10^{-1} S/cm at 80 °C, respectively. The tensile test indicated that the SPAEK-40, -50, and -60 membranes are tough and strong at ambient conditions. Combined proton conductivity, water swelling data, and mechanical properties suggest that SPAEK-6F-40, -50, and -60 membranes have the properties most suitable for PEMs for application in FC at elevated temperatures.

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(18) From Nafion PFSA membranes product information by DuPont, the tensile (Young's) modulus is 249 MPa, and the maximum tensile strength is 43 MPa in machine direction (MD) and 32 MPa in transverse direction (TD) at 23 °C and 50% RH. Its elongation at break is 225% in MD and 310% in TD at 23 °C and 50% RH.

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