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Synthesis of Copoly(aryl ether ether nitrile)s Containing Sulfonic Acid Groups for PEM Application[†]

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ABSTRACT: Wholly aromatic poly(aryl ether ether nitrile)s containing sulfonic acid groups (SPAEEN)s, intended for fuel cells applications as proton conducting membrane materials, were first prepared via nucleophilic substitution polycondensation reactions. SPAEEN copolymers were synthesized by potassium carbonate-mediated nucleophilic polycondensation reactions of commercially available monomers: 2,6-difluorobenzonitrile (2,6-DFBN), potassium 2,5-dihydroxybenzenesulfonate (sulfonated hydroquinone SHQ), and a third monomer 4,4′-biphenol or hydroquinone in *N*-methyl-*2*-pyrrolidone (NMP) at 160 °C. The sulfonic acid group content (SC), expressed as a number per repeat unit of polymer, ranged from 0.5 to 1.0 and was obtained by changing the feed ratio of SHQ to the unsulfonated bisphenol. Membrane films in potassium salt and acid forms were obtained by casting *N,N*-dimethylacetamide (DMAc) solution of SPAEEN copolymers, followed by immersing in 2 N sulfuric acid at room temperature. FT-IR confirmed the structure of polymer in both salt and acid forms. NMR was used to determine the obtained SC values of the SPAEEN series. Glass transition temperatures (T_gs) of SPAEEN copolymers (potassium form) determined by differential scanning calorimetry (DSC) ranged from 308 to 371 °C. Decomposition temperatures (T_ds) of SPAEEN were around 300 °C for acid form and over 400 °C for potassium form. Water uptake and swelling ratio values increased with SC and temperature. All SPAEENH copolymers were mechanically stronger than Nafion117 and exhibited a reasonable flexibility. The proton conductivities of acid form membrane at different SC values were close to or higher than that of Nafion117 and reached 10^{-1} S/cm. The best compromise on PEM mechanical strength, water swelling, and proton conductivity was achieved at SC ranging from 0.5 to 0.7.

1. Introduction

During the past several years, proton conducting polymers have attracted much attention due to their considerable promise for applications in some electrochemical devices, such as displays or sensors and, which is most important, as proton exchange membranes (PEM) in PEM fuel cells (PEMFC) and direct methanol fuel cells (DMFC). In PEMFCs and DMFCs, PEMs serve as separators for the reactants and catalysts support and provide the required ionic pathway between the anode and the cathode. Therefore, their properties such as proton conductivity, water maintenance, permeability for fuel, and chemical stability are crucial for the fuel cells performance. Although perfluorosulfonic acid ionomers such as Nafion, developed by DuPont, are considered state-of-the art, their high cost, difficulty in preparation, high methanol crossover, and dramatic decrease in proton conductivity at temperatures over 80 °C due to the dehydration of membranes limit their further applications. As a response to the commercial need for less expensive and more versatile polymer electrolytes, the synthesis and characterization of new membrane materials has become an active research area.[1]

High-performance polymers are an important category of alternative candidates for PEMs. Many kinds of high-performance polymers, such as poly(aryl ether sulfone)s, poly(aryl ether ketone)s, poly(ether imide)s, polybenzimidazole, poly(phenylene oxide), poly(phenylene sulfide), etc., are well-known for their excellent thermal, mechanical, and dielectric properties and good oxidative resistance. After modification they show rather high proton conductivities[2−23] and become promising PEM materials. Wang and McGrath,[8] for example, reported the synthesis of biphenyl-based poly(arylene ether sulfone)s containing sulfonic acid groups by direct polymerization reactions of dipotassium 3,3′-disulfonate-4,4′-dichlorodiphenyl sulfone (SDCDPS), 4,4′-dichlorodiphenyl sulfone, and 4,4′-biphenol. The proton conductivity values at 30 °C of 0.11 S/cm for 40% SDCDPS copolymer and 0.17 S/cm for the 60% SDCDPS copolymer were measured. Our group[17−19] and Xiao et al.[20,21] also reported the synthesis and conductivities of poly(phthalazinone ether ketone)s and poly(phthalazinone ether sulfone)s containing sulfonic acid groups, prepared by both postsynthesis sulfonation reactions and direct polymerization reactions. Both methods gave polymers with conductivities higher than 10^{-2} S/cm at around SC 1.0 (the sulfonic acid content in repeat unit of polymers). However, this category of polymers has a tendency to swell at high humidity and elevated temperature, especially the polymers with high sulfonic acid content. As a consequence, the membranes lose the mechanical strength and their ability to function under FC conditions becomes questionable.

Aromatic poly(aryl ether nitrile)s are a new class of high-performance thermoplastic polymers that exhibit

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good mechanical properties and high chemical and thermal resistance and have already been used as matrices in advanced composites in aerospace industries.[24−38] Aromatic poly(aryl ether nitrile)s have been prepared by Kricheldorf, McGrath, and other researchers[24−38] via nucleophilic substitution polycondensation reactions of bisphenols and dihalobenzonitriles or dinitrobenzonitriles in dipolar solvents. Unlike many other poly(aryl ether)s, poly(aryl ether nitrile)s have strongly polar nitrile groups pendant on aromatic rings, which will most probably promote adhesion of the polymers to many substrates via interaction with other polar chemical groups. It is believed that for PEM applications the enhanced adhesive ability of aromatic poly(aryl ether nitrile)s to inorganic compounds is beneficial for adhesion of catalyst to the PEM. Recently, it was reported[39,40] that nitrile groups were introduced into poly(aryl ether sulfone)s containing sulfonic acid groups with the aim to decrease the swelling of membrane films via enhanced intermolecular interaction and potentially promote adhesion of the polymers to heteropolyacids in the composite membrane or to electrodes in order to improve the quality of membrane electrolyte assemblies (MEAs). The objective of the present work is the synthesis and characterization of poly(aryl ether ether nitrile)s containing various amounts of sulfonic acid groups, from the viewpoint of their further application in the FC domain as proton exchange membrane materials.

2. Experimental Part

2.1. Materials. All chemicals were obtained from Aldrich. SHQ was recrystallized from ~50% aqueous ethanol. NMP was vacuum-distilled, and 4,4′-biphenol was purified by sublimation before use. All other chemicals were reagent grade and used as received.

2.2. Copolymerization. Syntheses of the polymers by nucleophilic substitution reactions were based on the procedure reported by McGrath.[25] In a typical reaction, 10.1 mmol of 2,6-DFBN, 7 mmol of SHQ, 3 mmol of 4,4′-biphenol, and 15 mmol of K_2CO_3 were added into a three-neck equipped flask with a magnetic stirrer, a Dean−Stark trap, and an argon gas inlet. Then, 13 mL of NMP and 15 mL of chlorobenzene were charged into the reaction flask under an argon atmosphere. The reaction mixture was heated to 130 °C. After dehydration and removal of chlorobenzene, the reaction temperature was increased to about 160 °C. When the solution viscosity had apparently increased, the mixture was cooled to 100 °C and coagulated into a large excess of ethanol or water with vigorous stirring. The resulting polymer was designated SPAEEN-*B*70, where *B* denotes that the comonomer is 4,4′-biphenol, while *Q* denotes hydroquinone as comonomer. *n* (70) refers to the SHQ content of aromatic phenol monomers. After washing with ethanol twice, SPAEEN samples were washed with water to remove salt. SPAEEN copolymers with high SC values, that either swell or dissolve in water, were purified by dialysis for a week to remove salt, using a membrane-cellulose dialysis tube (Serva Electrophoresis, Germany) with a molecular weight cutoff value of 3500.

2.3. Copolymer Analysis and Measurement. ^{1}H NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) was the NMR solvent, and the DMSO signal at 2.50 ppm was used as the chemical shift reference. IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with membrane film samples in a diamond cell.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for measuring T_d. Polymer samples for TGA analysis were preheated to 150 °C at 10 °C/min under a nitrogen atmosphere and held isothermally for 40 min for moisture removal. Samples were then heated from 90 to 750 °C at 10 °C/min for T_d measurement. A TA Instruments differential scanning calorimeter (DSC) model 2920 calibrated with tin at 231.93 °C and zinc at 419.53 °C was used for measuring T_g. Samples in potassium form for DSC analysis were initially heated rapidly at a rate of 20 °C/min under a nitrogen atmosphere to 20 °C higher than their T_g, followed by quenching in liquid nitrogen. When the DSC cell had cooled to around 50 °C, the samples were replaced in the cell and heated at a rate of 10 °C/min to 400 °C. The procedure for samples in acid form was similar except that the initial heating rate was 10 °C/min, and the end point was below the polymer T_d point.

Intrinsic viscosities were determined using an Ubbelohde viscometer for *N,N*-dimethylacetamide (DMAc) solutions of copolymer at 25 °C.

2.4. Preparation of Membrane Films. An amount of 0.7−0.8 g of copolymer in the potassium salt form was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at about 40 °C under a constant purge of nitrogen for about 1 day. The acid form (SPAEENH-*B* or SPAEENH-*Q*) membrane films were obtained by immersing corresponding potassium form SPAEEN-*B* or SPAEEN-*Q* membrane films in 2 N H_2SO_4 for 24 h at room temperature and then in deionized water for another 24 h, during which water was changed several times. The thickness of all membrane films was in the range 40−70 μm.

2.5. Water Uptake Content and Swelling Ratio Measurements. The membrane films were dried at 100 °C overnight prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water for 24 h at predetermined temperatures. Before measuring the lengths and weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel. The water uptake content was calculated by

$$\text{uptake content (\%)} = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} \times 100\%$$

where ω_{dry} and ω_{wet} are the masses of dried and wet samples, respectively. The swelling ratio was calculated from films 5−10 cm long by

$$\text{swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100\%$$

where l_{dry} and l_{wet} are the lengths of dry and wet samples, respectively.

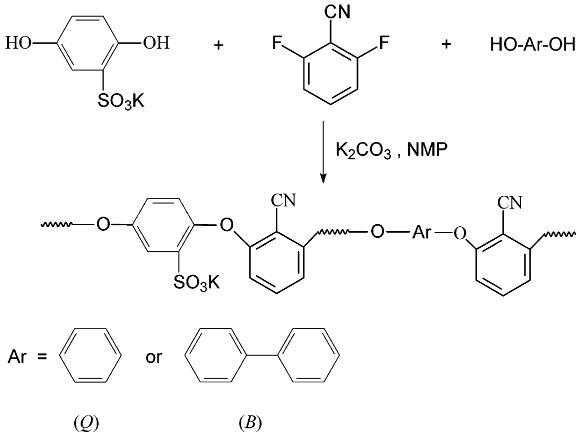
2.6. Tensile Tests. Tensile tests were performed on an Instron tensile tester (model 1123) at a strain speed of 50 mm/min at room temperature. Membrane films with typical size of 40 mm × 4 mm × 0.05 mm were used for testing.

2.7. Proton Conductivity. The proton conductivity measurements were performed on SPAEENH-*B* or SPAEENH-*Q* membrane films by ac impedance spectroscopy over a frequency range of 1−10^7 Hz with oscillating voltage 50−500 mV, using a system based on a Solatron 1260 gain phase analyzer. A 20 × 10 mm membrane sample was placed in a temperature-controlled cell open to the air by a pinhole where the sample was equilibrated at 100% RH at ambient atmospheric pressure and clamped between two stainless steel electrodes. Specimens were soaked in deionized water for 24−48 h prior to the test. The conductivity (σ) of the samples in the longitudinal direction was calculated from the impedance data, using the relationship $\sigma = d/RS$, where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re (Z) axis. The impedance data were corrected for the contribution from empty and short-circuited cell.

3. Results and Discussion

3.1. Synthesis and Characterization of SPAEEN Copolymers. High-performance polymers containing

Scheme 1. Synthesis of SPAEEN Copolymers



sulfonic acid groups are typically prepared either by postsulfonation reaction or direct polymerization reaction of sulfonated monomers. Direct polymerization is susceptible to possible side reactions such as degradation and cross-linking, which could occur in strongly acidic media usually used for postsulfonation. As shown in Scheme 1, SPAEEN copolymers were prepared via the nucleophilic polycondensation reactions of SHQ, 2,6-DFBN, and the third monomer, 4,4′-biphenol or hydroquinone. Since the copolymers were formed by reacting a combined amount of 1 mol of sulfonated diol (SHQ) and either 4,4′-biphenol (*B*) or hydroquinone (*Q*) with 1 mol of 2,6-DFBN, the SC is expressed as the molar ratio of SHQ units (bearing the $-SO_3Na$ group) to 1.0 M 2,6-DFBN unit. For example, the average repeat unit of SPAEEN-*Q*70 is composed of 0.7 unit of SHQ, 0.3 unit of hydroquinone (*Q*), and 1.0 unit of 2,6-DFBN. Expressed in this way, both the number of $-SO_3K$ groups per polymer repeat unit and the ratio of diol monomers (SC:1-SC) can be conveniently derived. The equivalent molecular weight (EW) and ionic exchange capability (IEC) were also calculated theoretically and listed in Table 1 for comparison. For SPAEEN with lower SC values, the polymerization reaction proceeded homogeneously. However, SPAEEN with higher SC values precipitated to the bottom of flask at the end of polymerization reactions. Table 1 lists the resulting polymers and details of the polymerization conditions. For the purpose of obtaining polymers with high proton conductivities (preferably higher than 10^{-2} S/cm), only SPAEEN copolymers with high SC values were synthesized. SPAEEN with SC values from 0.5 to 1.0 were obtained by changing the feed ratio of SHQ to unsulfonated monomer 4,4′-biphenol or hydroquinone. Both the homopolymer and copolymers exhibit intrinsic viscosities higher than 1.6 in DMAc at 25 °C, indicating the high molecular weights of resulting polymers. Although much higher molecular weight polymers could be obtained by lengthening the reaction time, polymerization reactions were stopped when obvious increases in the viscosity of reaction solutions were observed. Much longer reaction times resulted in much more viscous polymer solutions containing some gel. Such products were difficult to redissolve completely, which makes subsequent membrane film casting more complicated.

All the polymer series were transformed by solution casting into strong transparent and tough membrane films, which is usually characteristic of the polymers with high molecular weights. All obtained SPAEEN copolymers had good solubility in aprotic solvents such as NMP, DMAc, and dimethyl sulfoxide (DMSO).

Sulfonic acids or sulfonates are considered to be leaving groups that have a tendency to dissociate from their parent structure during high-temperature reactions, as has been previously observed.[41] FT-IR is a convenient method to analyze the structures of polymers containing sulfonic or sulfonate groups. It was used in this work to verify if partial or complete loss of the sulfonate groups occurs during polymerization reactions. Representative FT-IR spectra of SPAEEN in potassium form are shown in Figure 1. In the spectra of both series of SPAEEN, characteristic bands of the aromatic sulfonate salt symmetric and asymmetric stretching vibrations were observed at 1032 and 1090 cm^{-1}. In both series of SPAEEN the intensities of two characteristic absorption bands were observed to increase with SC, which confirm successful introduction of sulfonate groups into polymers. The characteristic symmetric stretching band of nitrile groups was observed at 2245 cm^{-1}. The absorption bands at 1197 and 1244 cm^{-1}, assigned to phenoxy groups, are overlapped at high SC. The absorption bands at 1458 and 1498 cm^{-1} were assigned to the phenyl ring, and a band around 1600 cm^{-1} is attributed to C=C stretching. The FT-IR spectrum of SPAEENH-100 is shown in Figure 2 together with that of the potassium form of SPAEEN-100 (obtained from the polymerization of 2,6-DFBN and SHQ) for comparative purposes. Figure 2 shows that the vibration absorptions of phenoxy groups at 1197 and 1244 cm^{-1} of SPAEEN are separate in acid form compared with potassium form. None of the samples exhibited a decrease in the intensity of the band at 2245 cm^{-1}, which is a characteristic symmetric stretching vibration of nitrile groups. In the FT-IR spectrum of SPAEENH-100, an ambiguous absorption appears around 1700 cm^{-1}. This absorption region is specific for stretching vibrations of carbonyl or carboxyl groups. The observed broad band is however believed not to be due to absorption of carboxyl groups since they are sensitive groups that show sharp absorption bands between 1650 and 1670 cm^{-1}. Thus, immersion of the SPAEEN membrane films in 2 N H_2SO_4 followed by immersion in deionized water at room temperature did not provoke a noticeable hydrolysis of nitrile groups to carboxyl groups.

The structural properties of the synthesized polymers were also studied by liquid phase ^1H NMR spectroscopy with DMSO-d_6 as the solvent. Figure 3 shows a spectrum of the aromatic protons for the highly sulfonated homopolymer SPAEEN-100 in potassium form prepared from 2,6-DFBN and sulfonated hydroquinone at 1:1 monomer ratio. Also illustrated in Figure 3 are the chemical structure of the polymer and the expected distribution of repeat unit configurations arising from the structural asymmetry of the sulfonated hydroquinone monomer. The asymmetric monomer can be introduced in the chain in two different ways where the $-SO_3K$ group will either be adjacent or opposite to the benzonitrile phenyl ring. Therefore, every polymer repeat unit will have one of the three possible configurations whereby the $-SO_3K$ groups can be symmetrically arranged (forms 1 and 3) or asymmetrically arranged (form 2, statistically predominant) about the benzonitrile phenyl ring. The evidence of this distribution of three types of repeat units was seen in the ^1H NMR spectrum of Figure 3, which can be divided into two regions: one of the higher frequencies (7.15–7.70

Table 1. Syntheses of SPAEEN Copolymers

polymer	SHQ (mmol)	second diphenol (mmol)	2,6-DFBN (mmol)	[η][a] (dL/g)	EW (IEC), g/mol SO_3 (Mequiv g^{-1})	SC from monomer ratio	SC exptl value from ^1H NMR data
SPAEEN-100	10		4	3.28	289 (3.46)	1.0	1.0
SPAEEN-*B*90	9	1	10	3.52	321 (3.12)	0.9	0.91
SPAEEN-*B*80	8	2	10	1.78	361 (2.77)	0.8	0.78
SPAEEN-*B*70	7	3	10	1.59	412 (2.43)	0.7	0.67
SPAEEN-*B*60	6	4	10	1.95	479 (2.09)	0.6	0.62
SPAEEN-*B*50	5	5	10	1.73	575 (1.74)	0.5	0.48
SPAEEN-*Q*90	9	1	10	2.85	313 (3.20)	0.9	
SPAEEN-*Q*80	8	2	10	2.03	342 (2.93)	0.8	
SPAEEN-*Q*70	7	3	10	1.79	379 (2.64)	0.7	
SPAEEN-*Q*60	6	4	10	2.38	429 (2.33)	0.6	
SPAEEN-*Q*50	5	5	10	2.88	498 (2.01)	0.5	

[a] Measured at 25 °C in DMAc.

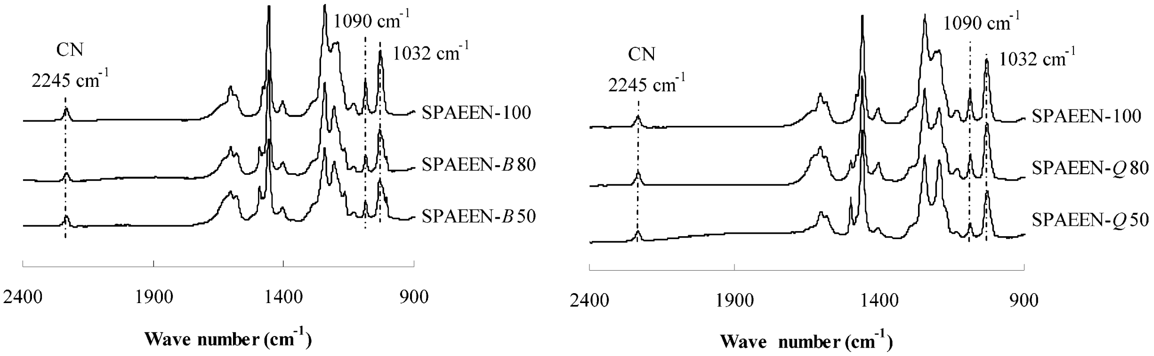


Figure 1. FT-IR spectra of SPAEEN copolymers.

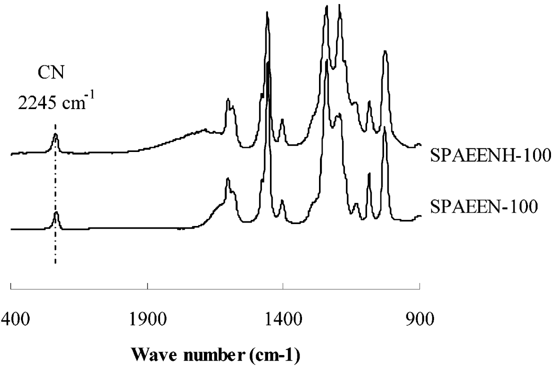


Figure 2. FT-IR spectra of SPAEEN-100 and SPAEENH-100.

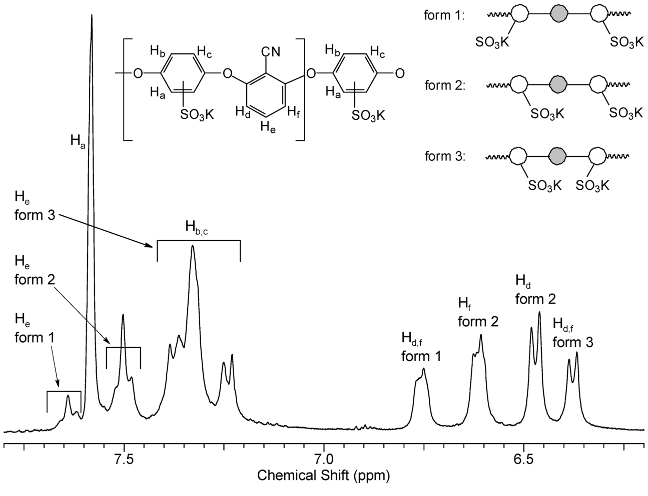


Figure 3. ^1H NMR spectrum of SPAEEN-100 in DMSO-d_6.

ppm, 4.00H) and the other of the lower frequencies (6.30−6.85 ppm, 2.00H). The four low-frequency signals on the right end of the spectrum were found to be the benzonitrile phenyl ring protons H_d and H_f which were spin-coupled ($^3J_{H-H}$, 8 Hz) with the H_e triplets (7.64, 7.50, 7.39 ppm, 8 Hz) on the left side of the spectrum. The sulfonated hydroquinone phenyl ring protons $H_{a,b,c}$ were found at higher frequency due to the effect of the electron-withdrawing sulfonic acid salt group. A 2D-ROESY spectrum was used to show that H_a was close in space to H_d and H_f for the configurations with the $-SO_3K$ groups opposite to the benzonitrile phenyl ring. Therefore, unambiguous assignment was achieved for the $H_{d,e,f}$ signals of all three possible configurations shown in Figure 3. The ROESY spectrum showed that the signal at 7.58 ppm (H_a) was close in space to two signals at 6.61 and 6.76 ppm which could only be from H_f of form 2 and $H_{d,f}$ of form 1, respectively. As expected, the signals $H_{d,e,f}$ from form 2 had higher intensities than those of forms 1 or 3 due to the statistical predominance of form 2; the distribution of forms 1, 2, and 3 was found to be 1:3:1. Electron shielding from the adjacent electron-rich $-SO_3K$ groups is responsible for the shift of H_d (form 2) and $H_{d,f}$ (form 3) toward lower frequencies.

The complete analysis of the NMR spectrum from the homopolymer SPAEEN-100 greatly simplified the interpretation of the more complicated copolymer spectra. Figure 4 shows stacked spectra of three SPAEEN-*Q* (left column) and three SPAEEN-*B* copolymers (right column). The spectra clearly show the gradual decrease of the far right signal ($H_{d,f}$ of form 3) for both SPAEEN-*Q* and SPAEEN-*B* polymer derivatives with decreased SCs. That signal is expected to decrease statistically as it originates exclusively from the symmetric $H_{d,f}$ which are shielded by the adjacent $-SO_3K$ groups of form 3. On the other hand, the less shielded H_d and H_f signals around 6.75 ppm grow in intensities as the content of sulfonated monomer is replaced by either hydroquinone (SPAEEN-*Q*) or biphenol (SPAEEN-*B*) monomers. Similarly, the strong H_a signal (7.58 ppm) originating from the hydrogen at the ortho $-SO_3K$ position decreases in intensity as the sulfonated monomers are being replaced

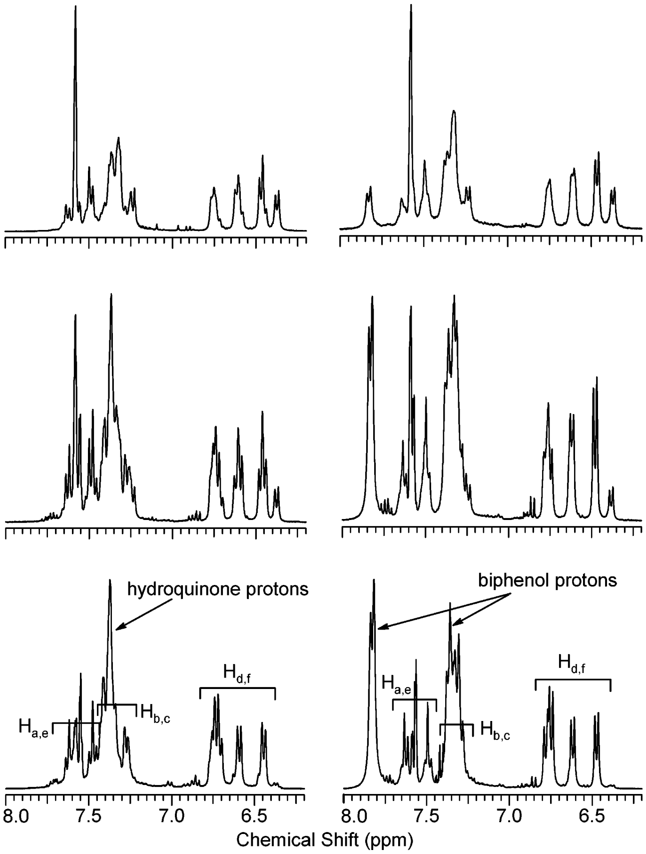


Figure 4. ^{1}H NMR spectra of SPAEEN copolymers in DMSO-d_6. Left column: SPAEEN-*Q*90 (top), SPAEEN-*Q*70 (middle), and SPAEEN-*Q*50 (bottom). Right column: SPAEEN-*B*90 (top), SPAEEN-*B*70 (middle), and SPAEEN-*B*50 (bottom).

by nonsulfonated monomers. The trend and regularity of intensity variation for all of the previously described signals is obvious. As before,[22,23] these ^{1}H NMR spectra were used to estimate the SCs by comparison of the intensities of specific signals. The advantage of ^{1}H NMR over elemental analysis resides in the fact that residual solvents or moisture in the polymers do not appear in the aromatic region of the spectra hence have no detrimental effect on SC calculations. The equations were conveniently derived because the spectra are divided in two distinct regions, *S*1 (7.0−8.0 ppm) and *S*2 (6.2−7.0 ppm), for both the copolymer derivatives. The integral (signal intensity) values of *S*1 and *S*2 were used in the calculation of the SCs as follows:

$$\text{SPAEEN-}Q\ \frac{S1}{S2} = \frac{5-n}{2} \qquad \text{SPAEEN-}B\ \frac{S1}{S2} = \frac{9-5n}{2}$$

where

$$S1 \text{ of SPAEEN-}Q \text{ (7.0−8.0 ppm)} = n \times \mathrm{H_{abc}} + \mathrm{H_e} + (1-n) \times \mathrm{H}Q = 3n + 1 + (1-n) \times 4$$

$$S1 \text{ of SPAEEN-}B \text{ (7.0−8.0 ppm)} = n \times \mathrm{H_{abc}} + \mathrm{H_e} + (1-n) \times \mathrm{H}B = 3n + 1 + (1-n) \times 8$$

$$S2 \text{ of SPAEEN-}Q \text{ and } S2 \text{ of SPAEEN-}B \text{ (6.2−7.0 ppm)} = \mathrm{H_{df}} = 2$$

$$n = \text{number of SHQ groups} = \text{SC (maximum} = 1.00)$$

The experimental SC for the SPAEEN-*Bs* copolymers were found to be within 0.02 of the calculated SC (listed in Table 1). Unfortunately, the differences between experimental and calculated SC values for SPAEEN-*Q* series were larger, possibly due to the presence of smaller signals which have a significant effect on the integration values. These signals may arise from chain end groups or from different conformations of SPAEEN-*Q* polymer chains with more restricted chain movement. Their chemical shifts would be different from the main chain proton signals, and therefore, for the SC calculation to be accurate they must all be accounted for and their intensity values assigned to the proper integral region S1 or S2. As these signals are small, difficult to identify, and overlap with other major signals, this is difficult to accomplish. The deviation between experimentally derived NMR values and calculated SC values may be a result of distinctive structural properties for this polymer in comparison with SPAEEN-*B*s. The experimental NMR results for the SCs of SPAEEN-*Q* copolymers are not reported. However, on the basis of the regularity of intensity variations of aromatic signals, observed and described above, it is believed that the SCs are close to the expected values, derived from the reaction feed ratios.

3.2. Thermal Properties of SPAEEN. Thermal stabilities of the SPAEEN copolymers in both potassium and acid forms were investigated by TGA analysis. T_d measurements were conducted from 90 to 750 °C at a heating rate of 10 °C/min, and the results are listed in Table 2. Table 2 shows that $T_{d5\%}$ and onset weight loss temperatures (T_d) of SPAEEN copolymers in potassium form are observed between 432 and 453 °C, indicating good thermal stabilities. In contrast with potassium forms, $T_{d5\%}$s and T_ds of copolymers in acid form are observed between 318 and 342 °C, more than 100 °C lower than potassium form. A comparison of potassium and acid forms is also shown in Figure 5. The TGA curves are similar to those of poly(aryl ether ketone)s and poly(aryl ether sulfone)s containing sulfonic acid groups[17−19,22] prepared before by our group. Polymers in potassium form exhibit only one weight-loss step in their TGA curves and in acid form exhibit a much earlier decomposition and two distinct transition steps.

T_gs of copolymers in both potassium and acid forms reported here were mainly obtained from the second scan except SPAEEN-100, for which T_g was determined in the first run. DSC curves of SPAEEN in potassium form are plotted in Figure 6. From our previous studies and from the literature,[8,17−19] it is known that glass transition is less pronounced in the DSC curves of poly(aryl ether ketone)s or poly(aryl ether sulfone)s containing sulfonate groups, compared to their parent polymers. However, SPAEEN copolymers, as can be seen from Figure 6, exhibited distinctive glass transitions in their DSC curves. All samples were amorphous, and only a single T_g is discernible on each curve. The obtained T_gs are listed in Table 2. It is seen that the T_gs of copolymers in potassium form increase with SC values varying from 308 to 371 °C for SPAEEN-*Q*s and from 339 to 371 for SPAEEN-*B*s. Compared with the unsulfonated nitrile copolymer (PEEN), which shows a T_g value at 144 °C, all the prepared SPAEEN copolymers in potassium form show more than a 1-fold increase in T_g. It was discussed previously[18] that the increase in T_gs is mainly the result of the introduction of sulfonate groups, which increases the intermolecular interactions by pendant ions, enhances molecular bulkiness, and raises the rotation activation energy of

Table 2. Thermal Properties of SPAEEN Copolymers

	T_g (°C)		$T_{d5\%}$ (°C)		T_d (°C) extrapolated onset for first weight loss	
polymer	potassium form	acid form	potassium form	acid form	potassium form	acid form
SPAEEN-100	371	ND[a]	451	325	440	327
SPAEEN-*B*90	365	ND	445	337	433	336
SPAEEN-*B*80	353	ND	442	340	427	334
SPAEEN-*B*70	339	ND	454	334	441	317
SPAEEN-*B*60	350	ND	428	328	442	316
SPAEEN-*B*50	345	ND	426	318	441	289
SPAEEN-*Q*90	357	ND	453	337	441	336
SPAEEN-*Q*80	350	ND	446	330	439	298
SPAEEN-*Q*70	333	ND	432	330	434	315
SPAEEN-*Q*60	316	ND	443	342	440	324
SPAEEN-*Q*50	308	ND	434	339	433	333

[a] ND = not detected.

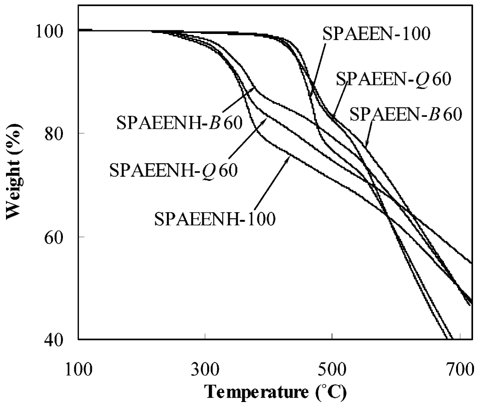


Figure 5. TGA traces of SPAEEN copolymers.

polymer molecular segment. This can be expressed as $T_g \propto cq/\alpha$, where c is the concentration of ionic repeat unit in backbone, q is the cation charge, and α is the distance of closest approach between the centers of charge of the anion and cation.[42] Furthermore, cluster formation due to the separation of hydrophilic and hydrophobic domains also contributed to the increase in T_g.[21] For SPAEEN-*Q* copolymers T_gs continually goes down when SC decreases. However, for SPAEEN-*B* copolymers, the T_g dependence on the SC is not the same. From SPAEEN-100 to SPAEEN-*B*50, T_gs decrease with decreasing SC values initially and then begin to increase at a certain SC value. To explain this, it should be taken into consideration that a decrease in the content of sulfonate groups is achieved by decrease in the feed ratio of SHQ to biphenol during synthesis. However, the increase in polymer rigidity is caused by replacement of short benzene ring by long rigid biphenyl between two ether linkages, which results in an increase in T_gs of SPAEEN-*B* copolymers. Therefore, when the content of biphenyl structures in polymer chain reaches a high enough value, the change in T_gs depends not only on SC values but is also influenced by backbone structure. The weak transitions occurring between 100 and 200 °C in the DSC curves of SPAEEN with high SC values were caused by evaporation of residual water, strongly bound by the copolymers, which is difficult to remove completely. Glass transitions for SPAEEN in acid form were not observed.

3.3. Water Uptake and Swelling Ratio. The proton conductivity and mechanical stability of PEMs are strongly related to the presence of water. In sulfonated poly(aryl ether ketone) or sulfonated poly(aryl ether sulfone),[8,43] hydrophilic sulfonic acid clusters are distributed in continuous hydrophobic domains. These domains swell with imbibed water and are interconnected to form continuous ionic pathways. Water uptake and swelling ratio of SPAEEN as determined by measuring the changes in weight and length are listed Table 3. The water uptake and swelling ratio increase with SC or IEC values and temperature. At room temperature, membrane films, in both potassium salt and acid forms, show gradual increases in water uptake up to a certain SC value then increase sharply. At 80 °C, SPAEEN copolymers with SC values lower than 0.7 for SPAEEN-*B*s and 0.6 for SPAEEN-*Q*s show moderate water uptake and swelling. SPAEENH copolymers with higher SC values swelled too much or completely dissolved in hot water. Membrane films in acid form have higher water uptake and swelling ratio values than in salt form due to hydrogen bond interactions between H_2O and sulfonic acid groups. Compared with Nafion117 (IEC = 0.91 mmol/g) membrane, which shows a water uptake of 35% at room temperature,[44] SPAEENH copolymers absorbing similar proportion of water have much higher IEC values. In other words, SPAEENH with the same sulfonic acid content (or IEC values) have lower water uptake values than Nafion117. We believe that part of the reason that the copolymers imbibe less water than Nafion117 at room temperature is the result of the high rigidity of the aromatic chain of SPAEENH and the lower acidity of the sulfonic acid groups compared with Nafion. In addition, the strong ionic interaction between sulfonic acid groups increases rigidity of network structure. A combination of these two effects results in the restriction of free volume for water adsorption and a decrease in the water uptake of SPAEENH copolymers. At elevated temperatures, the polymer chain mobility and the free volume for water adsorption increase. As a result, the rigid network structure of the membrane is weakened or even destroyed for copolymers with high SC, since in hot water the ionic interactions between macromolecules is gradually replaced by hydrogen bonding between H_2O and sulfonic acid groups.

It should be also mentioned that unlike sulfonated poly(phthalazinone ether sulfone) previously prepared in our group[18] or other sulfonated poly(aryl ether)s, which showed some brittleness in the dry state at high SC, all SPAEEN copolymers even up to SC1.0 (IEC 3.46) showed good film-forming properties and yielded membranes that were tough and flexible. This could be the result of the good proportion of the flexible ether linkage in polymer backbone and the rigid polar chemical groups as a side substitute instead of in the polymer backbone.

3.4. Tensile Properties. Tensile properties of SPAEENH copolymers were tested at room temperature during 2 days, and the results are tabulated in Table

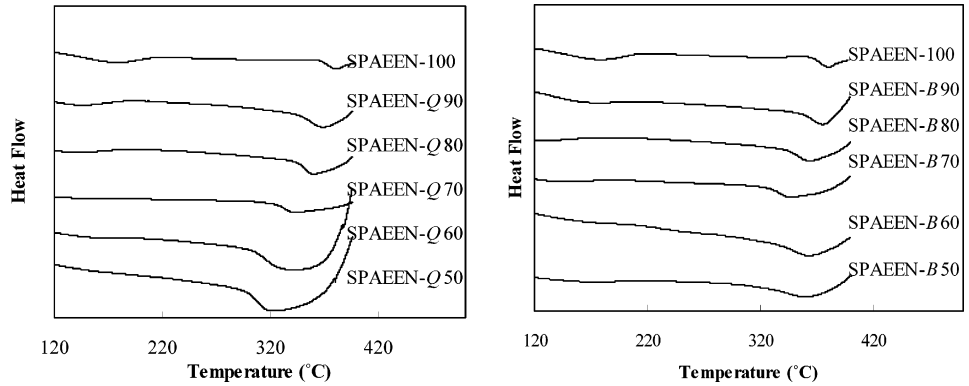


Figure 6. DSC curves of SPAEEN copolymers in potassium sulfonate form.

Table 3. Water Uptake and Swelling Ratio of SPAEEN Copolymers[a]

	room temperature				80 °C			
	water uptake (%)		swelling ratio (%)		water uptake (%)		swelling ratio (%)	
polymer	potassium form	acid form	potassium form	acid form	potassium form	acid form	potassium form	acid form
SPAEEN-100	190	SW	51	SW	D	D	D	D
SPAEEN-*B*90	61	250	14	61	PD	D	PD	D
SPAEEN-*B*80	32	81	11	28	PD	D	PD	D
SPAEEN-*B*70	19	51	3.9	17	190	SW	42	SW
SPAEEN-*B*60	16	22	0.61	9.1	29	58	9.5	17
SPAEEN-*B*50	7.7	19	0.50	6.9	13	36	0.92	11
SPAEEN-*Q*90	76	520	23	110	PD	D	PD	D
SPAEEN-*Q*80	42	160	16	52	880	SW	130	SW
SPAEEN-*Q*70	25	90	10	30	690	S	120	S
SPAEEN-*Q*60	22	50	2.8	16	140	410	31	75
SPAEEN-*Q*50	15	31	2.2	9.4	34	96	5.6	26

[a] D = dissolved; PD = partially dissolved; SW = swelled.

Table 4. Tensile Properties of SPAEENH Copolymers

polymer	tensile strength (MPa)	elongation at break (%)	tensile strength at break (MPa)
SPAEEN-*B*90	67	63	61
SPAEEN-*B*80	64	65	71
SPAEEN-*B*70	77	70	81
SPAEEN-*B*60	81	45	74
SPAEEN-*B*50	82	16	72
SPAEEN-*Q*90	51	39	71
SPAEEN-*Q*80	66	37	71
SPAEEN-*Q*70	73	24	67
SPAEEN-*Q*60	80	21	73
SPAEEN-*Q*50	75	25	71
Nafion 117	10	623	15

4. In general, all SPAEENH copolymers exhibited good tensile strengths ranging from 51 to 82 MPa, which decreased with increasing SC values. The elongations at break ranged from 16% to 70%, increasing with the SC values. Since SPAEENH-100 swelled excessively during the process for conversion from salt to acid form and then wrinkled when dry, the film dimension was difficult to measure accurately. Thus, tensile properties of SPAEENH-100 were not reported. However, its tensile curve also exhibited the same trend. For comparison, Nafion117 was also tested for tensile properties under the same conditions, and the results are also listed in Table 4. All SPAEENH copolymers exhibited tensile strength values severalfold higher and less elongation at break compared with Nafion117. In addition, all SPAEENH copolymers showed yield behavior, while Nafion117 exhibited a continuous increase in tensile strength before break. In other words, Nafion117 exhibited tensile behavior between elastomer and thermoplastic whereas the SPAEENH copolymer exhibited thermoplastic behavior.

3.5. Proton Conductivity. In our previous study,[23] X-ray fluorescence spectroscopy confirmed that all the sodium sites were effectively converted into sulfonic acid using the method described in experimental part. Proton conductivities of the acid form of SPAEEN-*Q* and SPAEEN-*B* copolymers were measured at 100% relative humidity as a function of SC and temperature and are shown in Figures 7 and 8, respectively. For comparison, the proton conductivity of Nafion117 measured under the same experimental conditions is also shown in the figures.

All SPAEEN membrane films showed room temperature proton conductivities higher than 10^{-2} S/cm, which makes them placed among the promising PEMs as representing a practical interest for use in fuel cells. As expected, membrane proton conductivity increases with sulfonic acid groups' content. The membranes with lower IEC values, SPAEEN-*B*50, SPAEEN-*B*60, SPAEEN-*Q*50, and SPAEEN-*Q*60, showed room temperature proton conductivities comparable to that of Nafion117. The films with higher IEC values, SPAEEN-*B*70, SPAEEN-*B*80, SPAEEN-*B*90, SPAEEN-*Q*70, and SPAEEN-*Q*80, showed room temperature proton conductivities higher than that of Nafion117, in some cases even exceeding 0.1 S/cm. SPAEEN-*Q*90 (not shown in Figure 7) showed unexpectedly lower proton conductivity than SPEEN-*Q*70 and SPAEEN-*Q*80, although its proton conductivities was still higher than 10^{-2} S/cm. This apparent inconsistency is attributed to its higher water uptake and swelling ratio. From Table 3, it can be seen that SPAEEN-*Q*90 exhibited high water absorption and a more substantial dimensional change than other samples. This large dimensional change resulted in a large decrease in the SC content per unit of volume of wet membrane. In other words, although

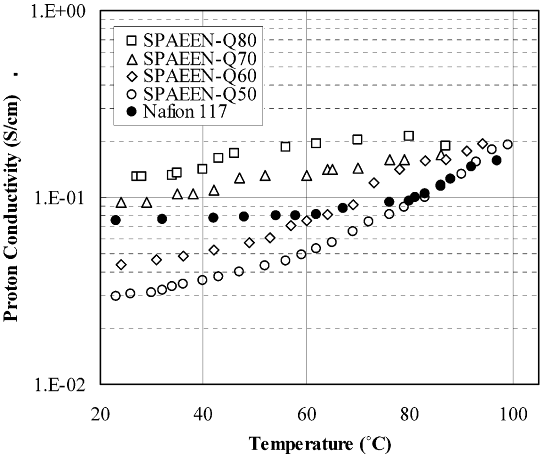


Figure 7. Proton conductivities of SPAEEN-*Q* copolymers.

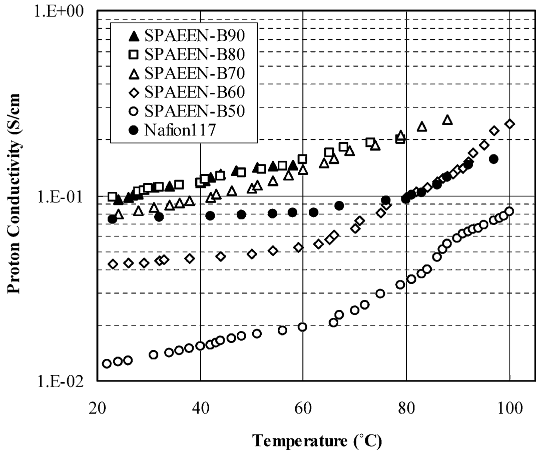


Figure 8. Proton conductivities of SPAEEN-*B* copolymers.

it has a high SC value, the sulfonic acid groups in the excessively swollen membrane are highly diluted, resulting in a decrease in its proton conductivity. Figure 7 also illustrates the fact that a higher proton carrier concentration in dry membranes does not necessarily ensure higher proton conductivity in humidified material. Thus, high proton conductivities of PEMs cannot be pursued solely by increasing the IEC values. SPAEEN-100 swelled excessively even at room temperature; its proton conductivity could not be measured. However, since the entire SPAEEN copolymer series up to SPAEEN-100 showed good membrane-forming properties and could be cast into tough and flexible membrane films in the dry state, there may be application for the materials having high SC in a nonaqueous environment which would not cause excessive swelling.

In general, proton conductivities increased with temperature, and the SPAEEN-*Q* series showed higher proton conductivities than the SPAEEN-*B* series at the same SC values, which may be explained by the difference in their equivalent molecular weights. Compared with Nafion117, SPAEEN copolymers exhibited a more sensitive change in proton conductivities with temperature which suggests that SPAEEN copolymers have higher activation energy for proton conductivity that Nafion117.

4. Conclusion

Wholly aromatic sulfonated poly(aryl ether ether nitrile)s (SPAEEN)s were prepared via K_2CO_3-mediated direct polymerizations of commercially available monomers: 2,6-difluorobenzonitrile (2,6-DFBN), potassium 2,5-dihydroxybenenesulfonate (SHQ), and a third monomer 4,4′-biphenol or hydroquinone, in NMP. The sulfonic acid group content (SC) in the copolymers was controlled by varying the ratio of the sulfonated diol monomer to either biphenol or hydroquinone diol monomers. The resulting copolymers had high T_gs ranging from 308 to 371 °C in potassium salt form and were thermally stable up to at least 289 °C in acid form. SPAEEN copolymers were organic soluble and could be cast into membrane films that were tough and flexible in the dry state, even at high IEC values. The SPAEEN membranes with high IEC are superior to sulfonated (aryl ether ketone)s and sulfonated (aryl ether sulfone)s, which are often brittle at high IEC values when dry. SPAEENH copolymers were readily prepared from inexpensive commercially available chemicals via one-pot reactions. All SPAEENH copolymers exhibited reasonable flexibility and high tensile strength. Both potassium and acid form sulfonated membrane films show continuous increases in water uptake and swelling ratio with SC and temperature, and the acid form membrane films show higher and more rapid increases than those in the potassium form. SPAEEN copolymers obtained from high sulfonated diol monomer ratios swelled excessively or dissolved in water. The copolymers showed similar or slightly higher room temperature proton conductivities compared with that of Nafion117. Nitrile groups are also anticipated to promote adhesion of the polymers to catalyst or to carbon black in the membrane electrolyte assemblies (MEA) and might be beneficial for preparation of the composite membrane, increasing bonding to embedded second phase.[37] This combination of desirable properties makes SPAEENH copolymers potentially good candidate for proton conducting membrane materials for fuel cells applications.

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