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Comparison of PEM Properties of Copoly(aryl ether ether nitrile)s Containing Sulfonic Acid Bonded to Naphthalene in Structurally Different Ways[†]

Yan Gao,[‡] Gilles P. Robertson,[‡] Dae-Sik Kim,[‡] Michael D. Guiver,*,[‡]
Serguei D. Mikhailenko,[§] Xiang Li,[§] and Serge Kaliaguine[§]

Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada, and Chemical Engineering Department, Laval University, Quebec G1K 7P4, Canada

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ABSTRACT: The study represents a comparative investigation of three series of high molecular weight aromatic poly(aryl ether ether nitrile) copolymers (SPAEEN-*n*), containing different sulfonated naphthalene groups, where *n* (in the range 0−80 mol %) refers to molar percentage of repeat units containing the sulfonic acid function. The three series of SPAEEN-*n* copolymers were synthesized via potassium carbonate-mediated nucleophilic polycondensation reactions of commercially available monomers: 2,6-difluorobenzonitrile (2,6-BFBN), one of three dihydroxynaphthalenesulfonate (DHNS) monomers, and unsulfonated 4,4′-biphenol (BP), incorporated for the purpose of adjusting the sulfonic acid content. The incorporation of the sulfonated repeat unit into copolymers and their structures were confirmed by ^{1}H NMR and FT-IR spectroscopy. Products were solvent-cast into membranes of varying ionic content as proton exchange membrane (PEM) materials for fuel cells applications. Ion exchange capacity (IEC), thermal stabilities, swelling, and proton conducting properties of the membranes were investigated in relation to their structures and compared with those of perfluorinated ionomer (Nafion 117). Films of SPAEENH copolymers in acid form all showed high thermal stabilities with glass transition temperatures (T_g) > 224 °C and decomposition temperatures (T_d) > 264 °C. In general, the SPAEENH copolymers exhibited low moisture absorption and in some instances high proton conductivities (from 10^{-2} to 10^{-1} S/cm) comparable to that of Nafion 117 at similar water uptake, swelling, and H_2O/SO_3H ratio.

1. Introduction

Research into novel solid polymer electrolytes has become intense during the past decade due to their potential application in electrochemical devices. In particular, proton exchange membrane (PEM) materials[1,2] are currently and potentially useful in chloroalkali cells, batteries, as strong acid catalysts, and most importantly in PEM fuel cells (PEMFC)s and direct methanol fuel cells (DMFC). The latter is due to their high proton conductivity and the ability to serve as a fuel barrier.

Numerous efforts[3−23] have been made to develop alternatives to the current widely used expensive perfluorinated sulfonic ionomers (such as Nafion developed by DuPont). The objectives of these investigations were to increase the operation temperature of FCs, to lower the fuel crossover, to simplify the production process, and to decrease the cost of PEMs, thereby overcoming the corresponding drawbacks of perfluorinated ionomers, which hinder their practical applications. Chemically and thermally stable fully aromatic hydrocarbon polymers containing pendent acidic functions are considered promising as alternative PEM materials.

Many syntheses of sulfonated derivatives of poly(aryl ether)s are reported where proton conductivities in the range 10^{-3}−10^{-1} S/cm were attained. McGrath's group for instance explored dihalide monomer disulfonation and subsequent controlled copolymerization.[9] Meng et al. synthesized aromatic poly(arylene ether)s containing pendent sulfonic acid groups. The rationale for this is to reduce the PEM's hydrolytic and oxidative degradation.[13,14] Several groups, including our own, utilized this approach, enabling a better control of position and number of sulfonic acid functions in order to synthesize a series of sulfonated copoly(aryl ether ketone)s and sulfonated copoly(aryl ether sulfone)s that differ from each other by the structure of bisphenol monomers. It was found[24] that the selection of monomers has a profound influence on thermooxidative hydrolytic and dimensional stability, swelling, and many other properties of the resultant copolymers. Although the properties of sulfonated polymers made by copolymerization often exceed the characteristics of those obtained by postsulfonation, a key problem of hydrocarbon-based sulfonate polymers remains relevant. This issue concerns their strong tendency to swell under hydrothermal conditions up to complete loss of the membrane strength, particularly at high sulfonic acid content (SC) needed for high proton conductivities (≥10^{-1} S/cm).

The hydrophilicity and proton conductivity of sulfonated copolymers are related to the states of aggregation of polymer chain segments, which arises from the different structures of repeat units in polymer chains. In the case of Nafion, the hydrophobic backbone and the hydrophilic sulfonic acid groups separate into two microphase domains upon hydration.[25,26] The hydrophobic domains provide the polymer with morphological stability whereas the hydrophilic domains are responsible for transporting protons and water. Similarly, the percolation structure of poly(aryl ether ketone ketone) membranes have been examined by small-angle X-ray scattering (SAXS)[26] and showed narrower water filling channels compared with perfluorinated PEMs, which explains the lower proton conductivity of the former ones. Poly(aryl ether)s with acidic groups on short pendent side chains have been suggested as a strategy to improve the microphase separation of hydrophilic and hydrophobic domains. For example, Rikukawa et al.[12] reported that sulfonated

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* Corresponding author. E-mail: michael.guiver@nrc-cnrc.gc.ca.
[†] NRCC No. 49110.
[‡] National Research Council.
[§] Laval University.

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poly(4-phenoxybenzoyl-1,4-phenylene, Poly-X 2000) (SPPBP) with acidic groups on pendent phenyl structures showed higher and more stable proton conductivity than sulfonated PEEK (SPEEK). Other groups[27−29] also presented poly(aryl ether)s with acidic groups on short pendent side chains. The synthesis and characterization of sulfonated poly(aryl ether ether ketone ketone) (SPAEEKKH) copolymers containing pendent sulfonic acid groups prepared from the 2,3-dihydroxynaphthalene-6-sulfonate monomer were also reported in our previous work.[21]

Recently, it was found that the introduction of nitrile groups into sulfonated poly(aryl ether sulfone) and sulfonated poly(aryl ether ketone)s reduced their water uptake and swelling.[30−32] We further expanded this approach by synthesizing sulfonated poly(aryl ether nitrile)s,[33,34] a structurally new polymer with a fully nitrile-based main chain. Cast PEM films of SPAEEN exhibited considerably lower water uptake and swelling than other sulfonated poly(aryl ether)s such as sulfonated poly(aryl ether ketone)s. This may be associated with inter-/intrachain interaction through highly polar nitrile functions, which make the polymer partially cross-linked. Furthermore, proton conductivity of SPAEN was found to be in the range $10^{-2}-10^{-1}$ S/cm, which is equal to that of Nafion 117. In addition, the introduction of nitrile groups into polymer chains is supposedly beneficial for composite membrane as promoting adhesion of the polymeric matrix to inorganic fillers. Besides, it may ensure a better bonding the PEM to the electrodes in membrane electrode assembly (MEA),[30,31] which is the FC core element. In the present study, we select three inexpensive and commercially available sulfonated naphthalene-based bisphenols for the synthesis of SPAEEN copolymers. The synthesis and properties of two new series of poly(aryl ether nitrile) copolymers are compared with a previously reported series. The purpose of the study was to investigate the effect of sulfonic acid position and naphthalene segment arrangement on the properties of structurally similar aromatic poly(aryl ether nitrile) copolymers.

2. Experimental Part

2.1. Materials. 2,3-Dihydroxynaphthalene-6-sulfonate sodium salt (2,3-DHNS-6), 2,8-dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6), and 2,7-dihydroxynaphthalene-3,6-sulfonate disodium salt (2,7-DHNS-3,6) were purchased from Rintech, Inc., and recrystallized from deionized water. Dimethyl sulfoxide (DMSO) and *N*-methyl-*2*-pyrrolidone (NMP) (Sigma-Aldrich) were vacuum distilled prior to use. 4,4′-Biphenol (Sigma-Aldrich) was purified by sublimation before use. All other chemicals were reagent grade from Sigma-Aldrich and were used as received.

2.2. Copolymerization. The sulfonic acid content (SC) of the copolymers was controlled by adjusting the molar ratio of sulfonated naphthalene diol monomers (DHNS) to biphenol monomer. The SC is defined as the molar ratio of DHNS monomer to 2,6-difluorobenzonitrile (2,6-DFBN) monomer multiplied by the number of sulfonic groups in the DHNS monomer. In a typical reaction, 10 mmol of 2,6-BFBN, 4 mmol of 2,3-DHNS-6, 6 mmol of 4,4′-biphenol, and 15 mmol of K_2CO_3 were added into a three-neck flask equipped with a magnetic stirrer, a Dean−Stark trap, and an argon gas inlet. Then, 10 mL of DMSO (or NMP) and 10 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 increase of the solution viscosity became obvious, the mixture was cooled down to 100 °C and coagulated in a large excess of water or ethanol with vigorous stirring. The resulting polymer was denoted *P*-SPAEEN-40, where *n* (40) refers to the 2,3-DHNS-6 molar content of aromatic phenol monomers. The product was washed thoroughly with water or ethanol several times.

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 reference material (2.50 ppm). IR spectra of membrane film samples were recorded on a Nicolet 520 Fourier transform spectrometer in a diamond cell.

A TA Instruments apparatus (model 2950) was used for thermogravimetric analysis (TGA) of the polymers. Polymer samples were preheated to 150 °C at 10 °C/min under an air atmosphere and held isothermally for 40 min for moisture removal. Samples were then heated from 90 to 750 °C at 10 °C/min for degradation temperatures (T_d) measurement. A TA Instruments differential scanning calorimeter (DSC) model 2920 calibrated with tin (melting point = 231.93 °C) and lead (mp = 327.50 °C) was used for T_g measuring.

Intrinsic viscosities were determined using an Ubbelohde viscometer for *N*,*N*-dimethylacetamide (DMAc) solutions of copolymer at 30 °C.

2.4. Preparation of Membrane Films. An amount of 0.8−1.0 g of sulfonated copolymer in the sodium salt form was dissolved in 20 mL of DMAc and after filtration was poured onto a leveled glass plate having a circular retaining glass rim and dried at about 40 °C for about 1 day. The acid form (SPAEENH-*n*) membranes were obtained by ion exchange of corresponding sodium form of SPAEEN-*n* in 2 N H_2SO_4 for 24 h at room temperature, followed by washing in deionized water for 24 h, during which time water was changed several times.

2.5. Water Uptake Content Measurement and Swelling Ratio. The sample films were soaked in deionized water for 24 h at determined temperatures. The membrane films were then blotted and weighed immediately. After drying at 80 °C for 24 h, weighing was repeated. The water uptake was calculated as

$$\text{uptake (\%)} = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} \times 100 \qquad (1)$$

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

$$\text{swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \qquad (2)$$

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

2.6. Proton Conductivity. The proton conductivity measurements were performed on SPAEENH 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 Solartron 1260 gain phase analyzer. Prior to the proton conductivity measurements, membranes were hydrated at 98 °C in water for 36 h. To avoid excessive swelling, *P*-SPAEEN-H60 and *D*-SPAEENH-40 were pretreated in water at 80 °C instead of 98 °C, while all other *D*-SPAEENH copolymers were only soaked in water at room temperature. A 20 × 10 mm membrane sample was clamped by the edges between two pairs of stainless steel electrodes in such a manner that its faces were open to the environment. The frame with the electrodes and the 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. The proton conductivity (σ) of the samples in the longitudinal direction was calculated from the ac impedance data, using the relationship $\sigma = L/R \times w \times d$, where d, w, and L are the thickness, the width, and the length of the sample, respectively, and R was derived from the low-frequency intersect of the semicircle on a complex impedance plane with the Re (Z) axis. The impedance data were corrected for the contribution from the empty and short-circuited cell.

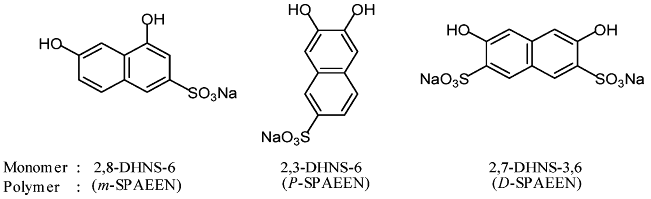
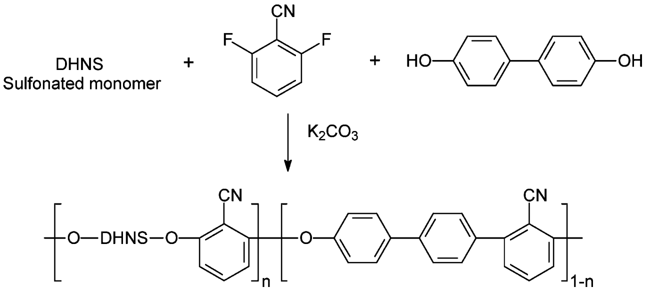


Figure 1. Investigated bisphenol structures.

Scheme 1. Synthesis of SPAEEN Copolymers



3. Results and Discussion

3.1. Synthesis and Characterization of *P*-SPAEEN Copolymers. Copolymers from three investigated sulfonated naphthalene-based bisphenols—2,8-DHNS-6, 2,3-DHNS-6, and 2,7-DHNS-3,6—are denoted as *m*-SPAEEN, *P*-SPAEEN, and *D*-SPAEEN individually, with the prefixes of *m*, *P*, and *D* meaning that sulfonic acid groups located either meta to ether linkage, or pendent on a phenyl ring, or accordingly disubstituted (Figure 1). The previously reported results on *m*-SPAEENs[34] are combined for comparison. The synthesis of SPAEEN copolymers is illustrated by Scheme 1, where one of the three sulfonated naphthalene-based bisphenols shown in Figure 1 is reacting with 2,6-DFBN and a biphenol, introduced to control the SC. For this synthesis solvent selection is a key parameter to effect the polymerization. Initially *N*-methyl-*2*-pyrrolidone (NMP) was used as solvent for the polymerizations. In the case of *D*-SPAEEN copolymers in the entire SC range, it led to complete precipitation of the product when only oligmers were formed. Synthesis of *P*-SPAEEN copolymers at the SC 20 and 30 was successful in NMP. However, for *P*-SPAEEN copolymers with SC > 30, products obtained in NMP could only be obtained as brittle films due to the low molecular weights, which were caused by precipitation of the growing polymer chains from polymerization solutions, hindering further chain propagation. DMSO, used for the synthesis of the other copolymers, proved to be more suitable, as high molecular weights were obtained due to the improved solubility of their growing chains in this solvent. In addition, polymerization of *P*-SPAEEN took a longer reaction time due to steric hindrance associated with 2,3-DHNS-6 monomer. The copolymers *m*-SPAEEN containing 2,8-DHNS-6 were found to be limited to SC $\leq$ 0.6, evidently owing to their angled structures, which made their chains more entangled and more difficult to propagate. In contrast, *D*-SPAEEN copolymers were most readily obtainable, which may be attributed to its stretched structure. Selected data characterizing SPAEEN-X copolymers including calculated equivalent weight per sulfonate group (EW) and ion exchange capacity (IEC) are summarized in Table 1. The resulting copolymers *P*-SPAEEN-20 through *P*-SPAEEN-60 could be dissolved in DMAc, NMP, DMSO, and *N*,*N*-dimethylformamide (DMF) and could be readily cast into membrane films.

The chemical structures of SPAEEN copolymers were characterized by FT-IR and ^{1}H NMR. FT-IR spectra shown in Figure 2 revealed the characteristic bands of the aromatic sulfonate salt at 1036 and 1107 cm^{-1} for *P*-SPAEEN and at 1080 cm^{-1} for *D*-SPAEEN. The intensity of these characteristic absorptions increased with SC. The characteristic stretching band of nitrile groups was observed at 2239 cm^{-1} for *P*-SPAEEN copolymers and at 2245 cm^{-1} for *D*-SPAEEN copolymers. The bands at 1211 and 1254 cm^{-1} are assigned to phenoxy groups. The resonances at 1463 and 1495 cm^{-1} are assigned to phenyl ring, and the bands at 1589 and 1604 cm^{-1} are attributed to C=C stretching vibrations, where the bands positions only slightly differed for the variety of copolymers under study.

The structural properties of the synthesized polymers were also investigated by liquid phase ^{1}H NMR spectroscopy with DMSO-d_6 as the solvent and reference material. Using *P*-SPAEEN copolymers as an example, Figure 3 shows three spectra of the aromatic protons for the sulfonated *P*-SPAEEN-20, -40, and -60 in sodium form. As expected, the spectra have some similarities with the SPAEEN spectra reported previously[33,34] with the chemical shifts for the benzonitrile and biphenol segments being nearly the same. The five proton signals from the naphthalenesulfonate group appear at high frequencies due to the deshielding ring current effect of the adjacent benzene rings (H-a,b,d,e) and also due to the impact of electron-withdrawing sulfonate group (H-c,d). Two-spin systems Hb-c, Hf-g, Hg-h, and Hi-j were identified by a 2D COSY experiment (not shown).

The expected SCs values derived from the synthesis feed ratios were revised by ^{1}H NMR spectroscopy, where a simple comparison of the intensities of the benzonitrile H-f,h (2.00H) resonance with the H-j signal of the biphenol segment allows to calculate the SC of the product. As an example, the intensity ratio of the H-j four proton signal to H-f,h signal for *P*-SPAEEN-60 was 1.71H, resulting in 0.42 biphenol units and hence 0.58 naphthalenesulfonate containing units. ^{1}H NMR confirmed that the expected SC values are reasonably close to the true scale.

Thermal properties of SPAEEN copolymers including glass transition temperatures (T_gs) and thermal decomposition temperatures in air (T_ds) were investigated by TGA and DSC analyses. The results are illustrated by Figures 4 and 5, respectively. Similarly to *m*-SPAEEN copolymers, *P*-SPAEEN and *D*-SPAEEN showed high thermal stabilities. The copolymers in sodium form exhibited a weight loss at ~430 °C due to main-chain degradation, while acid form copolymers displayed a weight loss in the range 264−470 °C depending on the SC, which may be attributed to sulfonic acid group degradation. All SPAEEN copolymers show sufficient thermooxidative stabilities, since PEMs are supposed to be exposed to a temperature not exceeding 150 °C in air in the process of MEA preparation. For DSC measurements, copolymers in both sodium and acid forms were initially heated at a rate of 10 °C/min to the temperature about 10 °C below their T_ds, which were derived from the TGA curves. After cooling down, they were reheated at a rate of 10 °C/min to their decomposition temperatures, and the data from the second scan were used for T_g evaluation. Figure 5 shows that T_gs of *P*-SPAEEN copolymers in sodium form are higher than for corresponding acid forms, and in both cases it increases with SC values. It is worth noting that the glass transitions become less sensitive to DSC detection with the SC increase, and the T_gs of *P*-SPAEEN-60 could not be determined for both sodium and acid forms. T_gs of *m*-SPAEEN and *P*-SPAEEN copolymers revealed a better sensitivity to DSC detection than *D*-SPAEEN. Table 2 summarizes the observed T_gs of SPAEEN copolymers, along with the extrapolated onset temperatures of the first weight loss T_d and $T_{d5\%}$. This table shows that the T_gs vary from 224 to 349

Table 1. Syntheses of SPAEEN Copolymers

polymer	4,4′-BP (mmol)	2,6-DFBN (mmol)	sulfonated biphenol (mmol)	solvent for polymerization	$[\eta]^a$ (dL/g)	EW (IEC) expected g/mol SO_3 (mequiv g^{-1})	SC expected	SC from ^1H NMR data
PAEEN-0	5	5	0	NMP			0	0
m-SPAEEN-20	8	10	2	NMP	0.85^b	1480 (0.68)	0.2	0.19
m-SPAEEN-30	7	10	3	NMP	1.0^b	1005 (1.0)	0.3	0.29
m-SPAEEN -40	6	10	4	NMP	0.62^b	767 (1.3)	0.4	0.38
m-SPAEEN -50	5	10	5	NMP	0.9^b	625 (1.6)	0.5	0.50
m-SPAEEN -60	4	10	6	NMP	0.82^b	530 (1.9)	0.6	0.57
P-SPAEEN-20	8	10	2	NMP	2.3	1480 (0.68)	0.2	
P-SPAEEN-30	7	10	3	NMP	1.9	1005 (1.0)	0.3	
P-SPAEEN-40	6	10	4	DMSO	1.3	767 (1.3)	0.4	
P-SPAEEN-50	5	10	5	DMSO	1.9	625 (1.6)	0.5	
P-SPAEEN-60	4	10	6	DMSO	1.6	530 (1.9)	0.6	0.58
P-SPAEEN-70	3	10	7	DMSO	1.5	462 (2.2)	0.7	
P-SPAEEN-80	2	10	8	DMSO	0.87	411 (2.4)	0.8	
D-SPAEEN-10	9	10	1	DMSO		1492 (0.67)	0.2	
D-SPAEEN-20	8	10	2	DMSO	2.5	780 (1.3)	0.4	
D-SPAEEN-30	7	10	3	DMSO	1.4	542 (1.8)	0.6	
D-SPAEEN -40	6	10	4	DMSO	1.5	423 (2.4)	0.8	
D-SPAEEN -50	5	10	5	DMSO	2.1	352 (2.8)	1.0	
D-SPAEEN -60	4	10	6	DMSO	2.0	305 (3.3)	1.2	

[a] Measured at 30 °C in DMAc. [b] Measured at 25 °C in DMAc.

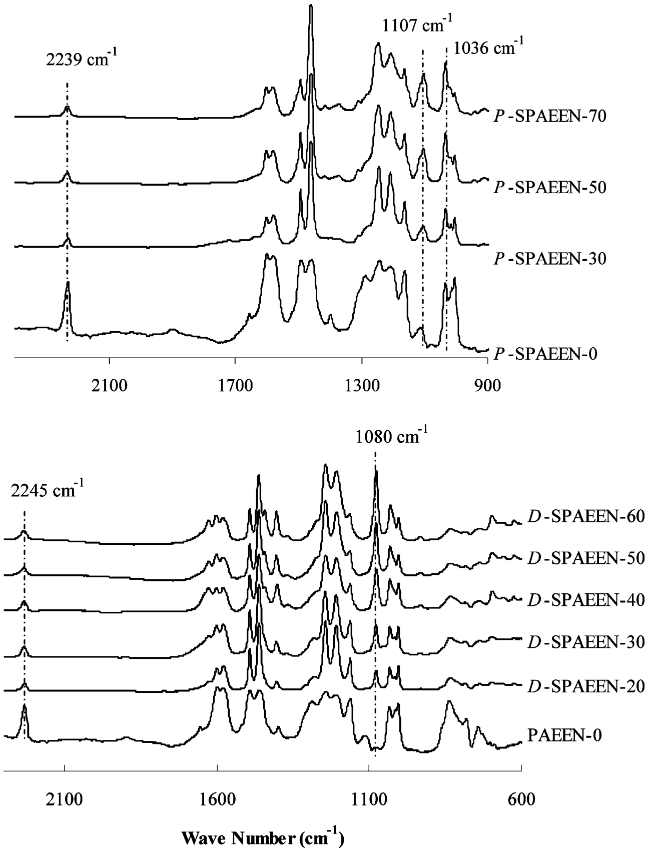


Figure 2. FT-IR spectra of SPAEEN copolymers.

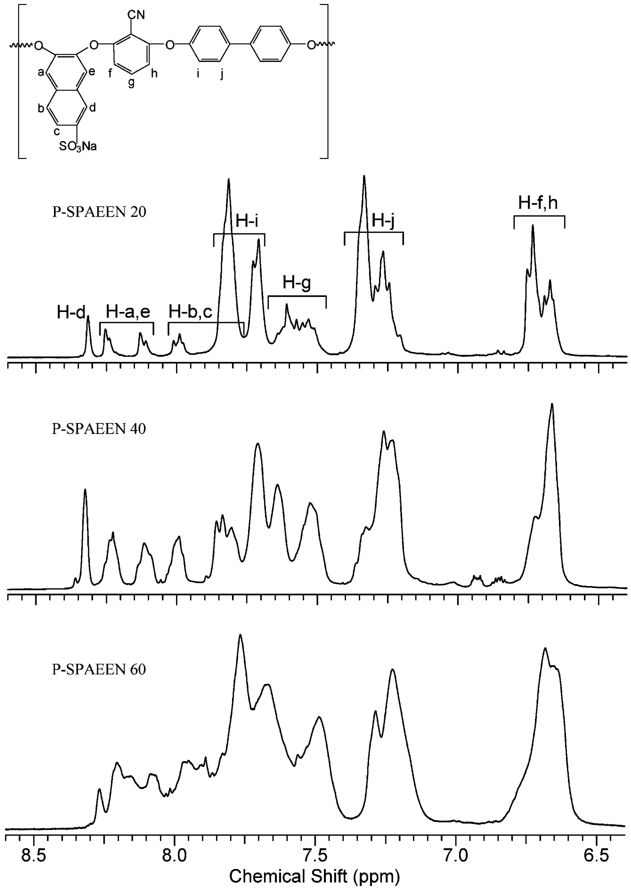


Figure 3. ^1H NMR spectrum of SPAEEN in DMSO-d_6.

°C for sodium form and from 224 to 385 °C for acid form. Since some acid form copolymers, such as *P*-SPAEENH-50, exhibited T_gs close to their decomposition temperatures, the reported value can only be considered as an approximation. In addition, it is noteworthy that *D*-SPAEEN was detected with T_m at 362 °C for the first scan, close to the T_m of 366 °C for unsulfonated PAEEN in its first scan. The high T_g and T_d values suggest that all *P*-SPAEENH copolymers have adequate thermal stabilities for PEM application.

3.2. Properties of Membranes. PEM materials intended for fuel cell application should provide separation between the reactants and an ionic pathway between the anode and the cathode as a core element of the membrane electrode assemblies (MEA). Therefore, their properties, such as mechanical strength, thermal stability, water swelling, proton conductivity, and adhesion to the electrodes, are crucial for the FC performance. The thermal stability of SPAEEN copolymers has been described above. The introduction of highly polar nitrile has been suggested to improve mechanical strength of the polymers and promote their potential adhesion to various substrates. Our

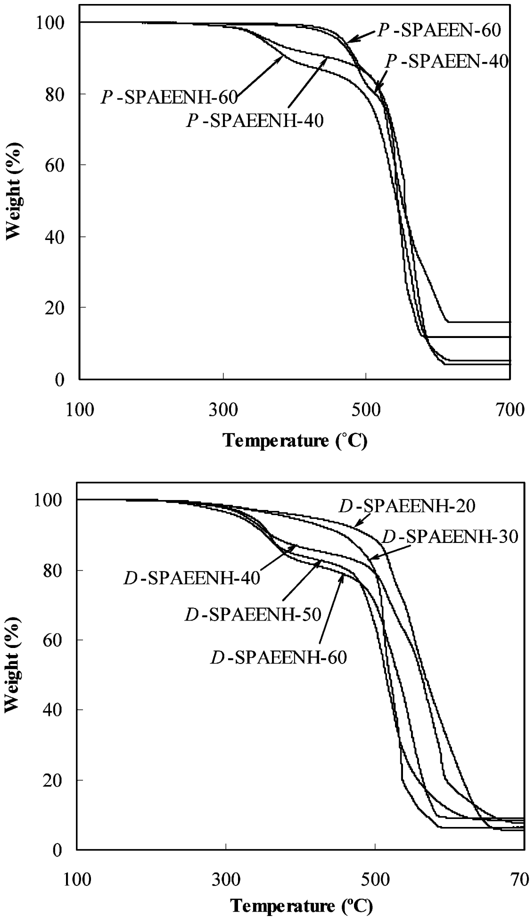


Figure 4. TGA traces of SPAEEN copolymers in air.

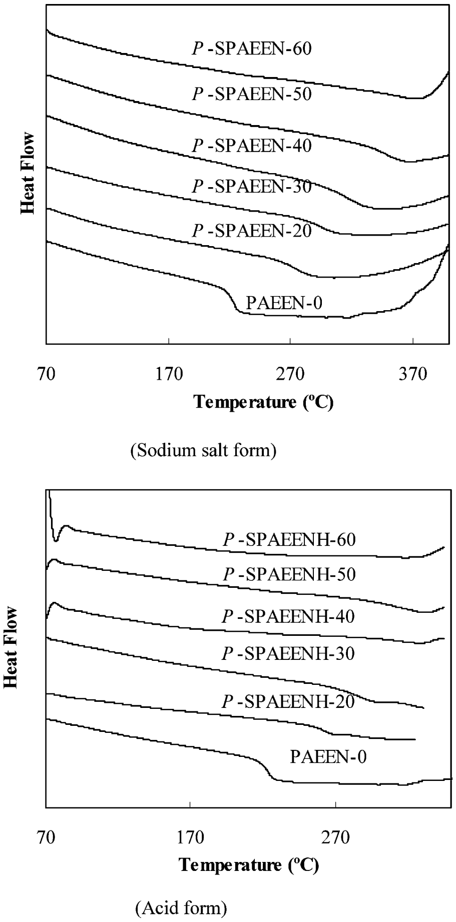


Figure 5. DSC curves of *P*-SPAEEN copolymers.

ongoing work on MEA has confirmed that the catalyst layer indeed adheres well to the SPAEENH copolymers, supporting the suggestion that nitriles facilitate electrode binding through polar interactions.

As reported before,[34] *m*-SPAEEN-based films with SC up to 0.6 maintained their shapes well and retained mechanical integrity in both dry and fully hydrated states. Cast *P*-SPAEEN-20 and *P*-SPAEEN-30 produced flexible films while *P*-SPAEEN-40 and *P*-SPAEEN-50 yielded robust membranes. The film made of *P*-SPAEEN-60 was fragile, and the *P*-SPAEEN-70-based membrane became brittle when completely dehydrated. The change in membrane mechanical properties may be related to the contents of entangled *o*-biphenol, influencing the SC and molecular weights of the polymers. However, all hydrated films of *P*-SPAEENs with SC < 60% proved to be robust. All *D*-SPAEEN copolymers with SC < 0.6 were also tough and flexible in the dry state. However, in water they swelled excessively and lost their mechanical strength or, at high SC, even dissolved, especially in hot water.

The group of McGrath[24] observed a noticeable influence of the bisphenols' structure on water uptake by sulfonated poly(aryl ether sulfone)s and attributed it to the differences in hydrophobicity of various bisphenols. In the present investigation the difluorobenzonitrile and 4,4′-biphenol moieties form the hydrophobic domains of identical structures in all three studied SPAEEN copolymers. They, however, differ from each other by their hydrophilic domains, comprised of bisphenol moieties with sulfonate groups in structurally different positions and naphthalene skeletons differently linked to the main chain. From this viewpoint SPAEEN copolymers can be considered as quasi-isomers, which is to be taken into account in examination of PEM swelling behavior. It can be seen from Figure 6 that after 24 h of immersion *P*-SPAEENH membranes absorbed from 4.0% to 168% of water with linear expansion from 1.6% to 49% depending on the SC and temperature. *D*-SPAEENH copolymers exhibit higher water absorption starting at 8.8% and ending by complete dissolution in hot water at high SC. Their dimensional changes started at 2%. The swelling ratios and conductivities of some *P*- and *D*-SPAEEN are compared in Table 3 with the data previously obtained for *m*-SPAEEN.[34] It can be seen from Table 3 that *P*-SPAEENH copolymers show slightly higher values of water swelling than *m*-SPAEENH copolymers for the same EW values, especially at high SC. The number of water absorbed per sulfonic acid (H_2O/SO_3H) is in line with the trend of water uptake and swelling. Since *D*-SPAEENH copolymers have slightly higher EW values than corresponding *m*-SPAEENH and *P*-SPAEENH copolymers with the same SC values, their comparison based on SC is not fully justified. However, it still can be seen that *D*-SPAEENH copolymers have the lowest water uptake and swelling ratios among the three SPAEENH copolymers at similar equivalent weights (Figure 7). The pendent naphthalenesulfonic acid segment in *P*-SPAEENH copolymers has a kinetic diameter of 9.1 Å, as was estimated from ACD/3D Viewer (v.10.0) calculation, which is much bigger than the value of 6.0 Å of angled naphthalenesulfonic acid segment in *m*-SPAEENH. Thus, *P*-SPAEENH copolymers have the largest interchain spaces for water molecules in the membrane's hydrophilic domains, and therefore, the number of water absorbed per sulfonic acid of *P*-SPAEENH is higher than *m*-SPAEENH copolymers of similar EW values. Among the three SPAEENH copolymers studied, *D*-SPAEENH has the least contorted main chain with the smallest kinetic diameter (5.1 Å) of the naphthalenesulfonic acid

Table 2. Thermal Properties of SPAEEN Copolymers

	T_g (°C)		$T_{d5\%}$ (°C)		T_d (°C) extrapolated onset for first weight loss	
polymer	Na form	acid form	Na form	acid form	Na form	acid form
PAEEN-0	224		–		–	
m-SPAEEN-20	233	230	477	390	521	264
m-SPAEEN-30	261	244	468	361	504	290
m-SPAEEN-40	310	247	449	352	491	290
m-SPAEEN-50	313	260	467	341	489	297
m-SPAEEN-60	336	–[b]	463	344	512	310
P-SPAEEN-20	274	261	461	372	486	345
P-SPAEEN-30	296	285	432	363	456	327
P-SPAEEN-40	317	311	469	365	462	328
P-SPAEEN-50	349	324	471	363	459	332
P-SPAEEN-60	ND[a]	ND	468	356	452	323
D-SPAEEN-20	228	ND	–	370	–	415
D-SPAEEN-30	224	ND	–	330	–	386
D-SPAEEN-40	ND	ND	–	301	–	328
D-SPAEEN-50	ND	ND	–	320	–	305
D-SPAEEN-60	ND	ND	–	335	–	331

[a] ND = not detected. [b] Not measured.

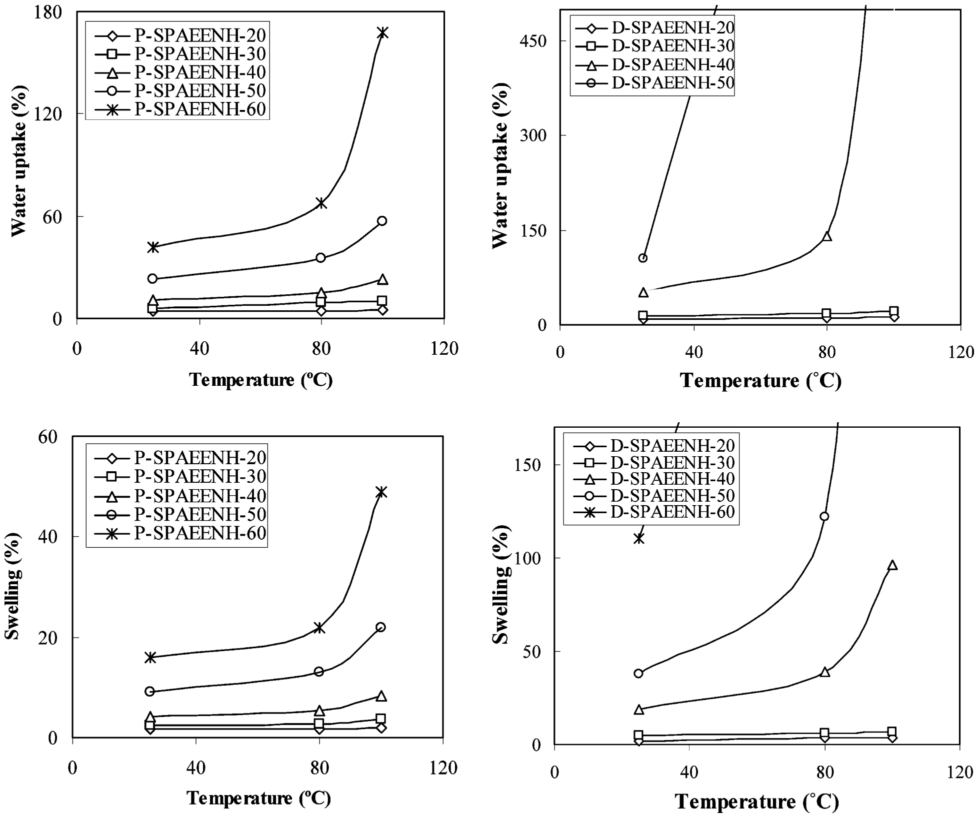


Figure 6. Water uptake and swelling of SPAEENH copolymers.

segment Thus, *D*-SPAEENH copolymers having the least interchain free volume should exhibit the lowest swelling ratios at similar equivalent weights, as indeed is evidenced by Table 3 (compare *m*- and *P*-SPAEENH-60 and *D*-SPAEENH-30). The *P*-SPAEENH copolymers with SC ≤ 0.5 exhibited dimensional swelling of less than 25% and are adequately stable even in boiling water. The copolymers with SC ≤ 0.6 are dimensionally stable up to 80 °C. *D*-SPAEENH-30 is dimensional stable up to 100 °C, and *D*-SPAEENH-40 swelled excessively at 80 °C.

Compared with our previously prepared sulfonic acid-containing poly(aryl ether ether ketone ketone)s (SPAEEKKH) based on 2,3-DHNS-6 monomer (Table 3), *P*-SPAEENH show much lower water uptake and considerably improved dimensional stability. SPAEEKKH with EW = 575 g/mol SO_3, which is less than that of *m*- and *P*-SPAEENH60, swelled excessively already at 80 °C and dissolved in boiling water. At the same time *P*-SPAEEN-H60 with EW 530 g/mol SO_3 showed water uptake of only 68% and 168% and linear expansion of 22% and 49% at 80 and 100 °C, respectively. The difference in membranes' behavior can be explained by the different molecular structures of the polymers. The nitrile groups pendent on aromatic rings of SPAEENH have much stronger polarity and basicity compared with ketone links in SPAEEKKH polymer main chain. This obviously enhances inter-/intramolecular interactions in SPAEENH copolymers, consequently improving the dimensional stability of the membrane films. An attempt was made to confirm the percolating network structure of the SPAEEN polymers by transmission electron microscopy, as was undertaken in refs 25 and 26 for explanation of membrane behavior from the viewpoint of phase separation and electro-

Table 3. Comparisons on Swelling and Conductivity of Different Polymers

		room temperature			80 °C			100 °C		
polymer	EW calcd g/mol SO_3	swelling ratio (%)	nH_2O per SO_3H	conductivity (S/cm)	swelling ratio (%)	nH_2O per SO_3H	conductivity (S/cm)	swelling ratio (%)	nH_2O per SO_3H	conductivity (S/cm)
m-SPAEENH-50	625	6.2	6.3	3.5×10^{-2}	10	8.7	6.4×10^{-2}	12	13	7.8×10^{-2}
m-SPAEENH-60	530	7.5	7.1	8.3×10^{-2}	15	13	1.4×10^{-1}	24	20	1.5×10^{-1}
P-SPAEENH-50	625	9.1	8.0	3.9×10^{-2}	13	12	8.8×10^{-2}	22	20	1.3×10^{-1}
P-SPAEEN-H60	530	16	13	7.9×10^{-2}	22	20	1.5×10^{-1}	49	49	2.0×10^{-1}
D-SPAEENH-30	542	4.9	6.0	1.5×10^{-2}	6.1	6.3	2.9×10^{-2}	6.8	6.9	3.7×10^{-2}
D-SPAEENH-40	423	19	9.4	8.0×10^{-2}	39	35	1.5×10^{-1}	96	235	1.8×10^{-1}
SPAEEKKH-100[21]	575	17	13	–	*a*	–	–	*b*	–	–
Nafion 117	1100	13	12	7.5×10^{-2}	20	18	9.6×10^{-2}	–	–	1.6×10^{-1}

[a] Excessively swollen. [b] Dissolved.

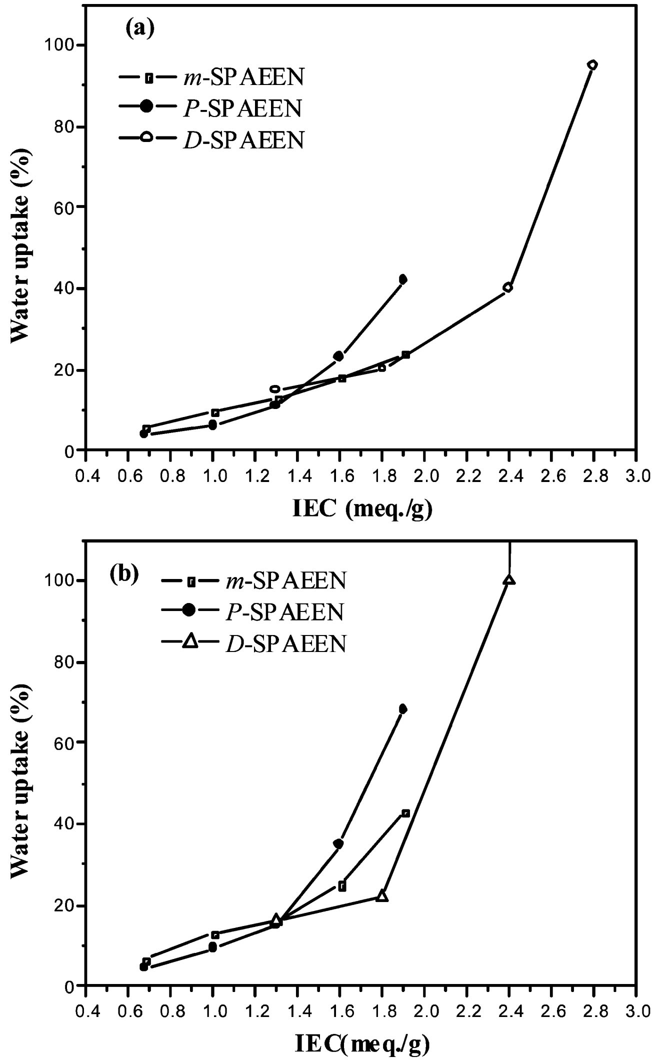


Figure 7. Water uptake vs IEC at (a) room temperature and (b) 80 °C.

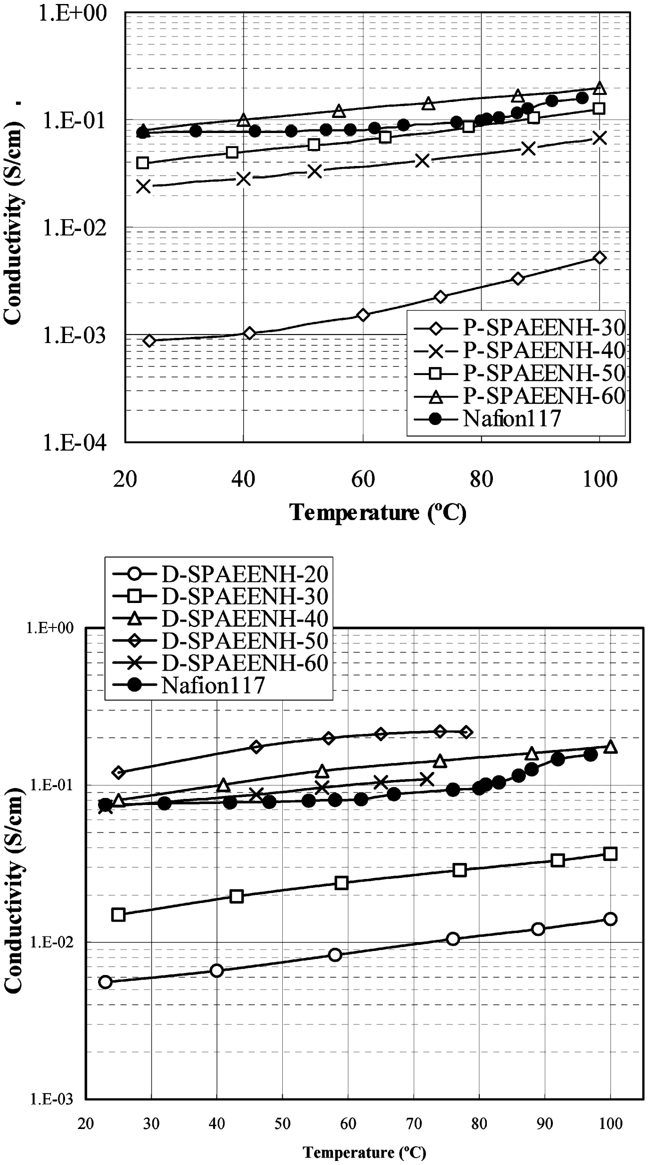


Figure 8. Proton conductivity of SPAEENH copolymers.

aggregation of protonated chain segments that form ionic pathways. Unfortunately, in our experiments the film samples were fully dehydrated under TEM high vacuum, and no ionic channels were observed.

The proton conductivities of *P*- and *D*-SPAEENH copolymers along with that of Nafion 117 were measured at 100% RH and plotted as functions of temperature in Figure 8. The conductivities of *P*-SPAEENH copolymers increased both with SC and with temperature, and at SC = 0.4–0.6 they were above 10^{-2} S/cm even at room temperature. This makes these membranes of practical interest for PEMFC application. *P*-SPAEENH-50 and -60 exhibited still higher proton conductivities from 3.9×10^{-2} to 2.0×10^{-1} S/cm, which is comparable to that of Nafion 117 (7.5×10^{-2}–1.6×10^{-1} S/cm from RT to 100 °C), with similar water uptake and dimensional swelling. Moreover, as seen in Table 3, *P*-SPAEENH-60 shows similar H_2O/SO_3H ratio to that of Nafion 117 while with slightly higher proton conductivities. *D*-SPAEENH copolymers also show an increase in proton conductivity both with temperature and with SC, but starting from SC = 1.0 the conductivity could not be measured above certain temperature because of excessive membrane swelling at 100% RH. At SC = 0.6−0.8 *D*-SPAEENH displays proton conductivities exceeding 10^{-2} S/cm. Dimensional swelling of SPAEENH copolymers are listed in Table 3 along with their proton conductivities. It can be seen that *P*-SPAEENH films generally show somewhat higher conductivities along with higher H_2O/SO_3H ratios than corresponding *m*-SPAEENH films at the same SC values and similar temperatures, which is consistent with their higher water uptake and swelling. In general, one should expect that the dependence of proton conductivity on the SC and temperature correlates with that of H_2O/SO_3H ratios and swelling. It should be noted that as a rule the precision of conductivity measurements is negatively affected by swelling due to membrane geometrical changes in the course of conditioning at 100% RH and at temperatures above ambient. Besides, *D*-SPAEENH-40, absorbing much more water than other PEMs, obviously has lesser concentration of the proton generating sites, as its bulk is more diluted by water. Indeed, the concentration of the acid functions in *D*-SPAEENH-40 is only 25% higher than in *m*- and *P*-SPAEENH-60. However, this brought about a much higher water absorption, exceeding 2−4 times that of *m*- and *P*-polymers and resulting in a decrease of SO_3H concentration by 1.5−3 times.

Apart from the above reasoning, some considerations based on chemical structure of the polymers can be also taken into account. The proton conductivity of a membrane, in general, depends on the proton concentration, their ability to dissociate, and their mobility. These factors in turn depend on the polymer equivalent weight and water uptake (influencing concentration of the charge carriers), on the temperature (influencing mobility), and on the position and structure of the acid sites (influencing proton dissociation). In *m*- and *P*-SPAEENH polymer chains, sulfonic acid groups are located either at the *meta* position to the ether linkage or on a benzene ring, long-distanced from the ether linkage. Therefore, SO_3H function in these polymers is less affected by the electron-donating ether group. At the same time in *D*-SPAEENH chain the SO_3H group is located ortho to ether linkage, which makes this function partially deactivated. Thus, proton dissociation occurs less readily in *D*-SPAEENH than in *m*- and *P*-SPAEENH. Along with other factors, such as higher water absorption, molecular weight, microstructural aspects, and different microphase distribution, this may greatly contribute to the overall proton transport in the polymers under study.

4. Conclusion

Three series of poly(aryl ether ether nitrile) copolymers containing sulfonic acid groups bonded to naphthalene in structurally different ways have been prepared from commercially available monomers via one-step polycondensation reactions. They were solvent-cast into dry membranes, having different mechanical properties, varying from flexible and robust to fragile depending on the SC. All SPAEENH copolymers have good thermal stabilities with $T_d > 264$ °C and $T_g > 224$ °C. The films prepared from *m*- and *P*-SPAEENH exhibited lower water uptakes and dimensional swelling than *D*-SPAEENH films, but more pronounced correlation of the proton conductivities with water content. *P*-SPAEENH films show somewhat higher swelling and proton conductivities than *m*-SPAEENH films due to their increased intermolecular distance. The meta linkage of the sulfonic acid function with respect to the ether group in *m*-SPAEENHs and a long-distanced connection in *P*-SPAEENHs results in a relatively less deactivated $-SO_3H$ group, which contributed to higher proton conductivities compared with *D*-SPAEENH films. The two former membranes show proton conductivities close to or higher than those of Nafion 117 at similar H_2O/SO_3H ratio. The various advantages of the polymers under study, such as low cost of the initial monomers, high thermal stability, low dimensional swelling, and high proton conductivity, make *m*- and *P*-SPAEENH copolymers with SC in the range 0.5−0.8 notably promising as PEM materials for fuel cells applications.

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