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Sulfonated Poly(aryl ether ketone)s Containing Naphthalene Moieties Obtained by Direct Copolymerization as Novel Polymers for Proton Exchange Membranes

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ABSTRACT: A series of sulfonated poly(aryl ether ketone)s (SPAEKs) were prepared by aromatic nucleophilic polycondensation of 2,6-dihydroxynaphthalene with 5,5′-carbonyl-bis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone. The structure and degree of sulfonation (DS) of the SPAEKs were characterized using ^{1}H NMR spectroscopy. The experimentally observed DS values were close to the expected values derived from the starting material ratios. The thermal stabilities of the SPAEKs were characterized by thermogravimetric analysis, which showed that in acid and sodium salt forms they were thermally stable in air up to about 240 and 380 °C, respectively. Transparent membranes cast from the directly polymerized SPAEKs exhibited good mechanical properties in both dry and hydrated states. The dependence of water uptake and of membrane swelling on the DS at different temperatures was studied. SPAEK membranes with a DS from 0.72 to 1.60 maintained adequate mechanical properties after immersion in water at 80 °C for 24 h. The proton conductivity of SPAEK membranes with different degrees of sulfonation was measured as a function of temperature. The proton conductivity of the SPAEK films increased with increased DS, and the highest room temperature conductivity (4.2×10^{-2} S/cm) was recorded for a SPAEK membrane with a DS of 1.60, which further increased to 1.1×10^{-1} S/cm at 80 °C. © 2004 Wiley Periodicals, Inc.* J Polym Sci Part A: Polym Chem 42: 2866–2876, 2004

Keywords: poly(ether ketones); ionomers; membrane; polyelectrolytes; polycondensation; proton conductivity; functionalization of polymers

INTRODUCTION

Fuel cells are electrochemical devices that directly convert the chemical energy of a fuel into electrical and thermal energy. For proton exchange membrane fuel cells (PEMFCs), this process involves a PEM, which is sandwiched between two platinum-porous catalytic electrodes (namely, an anode and a cathode) and which functions as an electrolyte for transferring protons from the anode to the cathode as well as providing a barrier to the passage of electrons and gas cross-leaks between the electrodes. Currently, membrane materials typically used for PEM fuel cells are perfluorinated copolymers (such as DuPont™

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Nafion®) because of their excellent mechanical properties and chemical stability and their high proton conductivity. However, very high cost, loss of proton conductivity at temperatures > 80 °C, and high methanol crossover (in direct methanol fuel cells) of the perfluorinated polymer membranes impede their commercial development.[1,2]

Therefore, alternative and more economical nonperfluorinated polymer PEM materials for higher temperature applications are being investigated. Sulfonated derivatives of aromatic polymers,[3] such as poly(ether ether ketone) (PEEK),[1,4–11] poly(ether sulfone) (PES),[12,13] polyimide (PI),[14–16] and poly(benzimidazole) (PBI),[17] have been widely investigated for use as PEM materials because of their excellent chemical stability, high thermo-oxidative stability, good mechanical properties, and lower cost. Enhanced proton conductivity, hydrophilicity, and increased solubility in solvents for processing are useful properties for PEMs to have that can be accomplished by the introduction of sulfonic acid groups into the polymer.

Sulfonated polymers, as can be illustrated by the example of sulfonated poly(aryl ether ketone) (PAEK), may be prepared either by postsulfonation of the polymer backbone[4–11,18–23] or by copolymerizing sulfonated monomers[24–32] with other aromatic monomers. Similarly, the direct synthesis of sulfonated polysulfone copolymers has been reported.[32–38] An advantage of direct polymerization of sulfonated monomers is avoiding polymer degradation and crosslinking, which results from aggressive postsulfonation conditions, such as fuming sulfuric acid, which is often used, with elevated temperatures. Another advantage of the copolymerization technique is having the ability to control the polymer DS by varying the feed ratio of sulfonated to nonsulfonated monomers. When the postsulfonation method is used, the number of sulfonation sites is limited to the most readily activated *ortho* ether linkage position for sulfonic acid groups. By contrast, when sulfonated monomers[24–38] are used, the result is a copolymer containing two sulfonic acid groups per repeat unit at less easily activated *ortho* ether sites on the phenylketone segments.

PAEKs are known as a class of high-performance engineering thermoplastics because of their generally good properties, such as acid- and alkali resistance, heat resistance, mechanical strength, and electrical insulation characteristics.[3] Postsulfonated PEEK (SPEEK) has been studied[1,4–11,39–46] as a material for PEMs.

This article reports a new series of directly copolymerized sulfonated PAEKs containing a naphthalene (NA) moiety. Several nonsulfonated PAEKs containing naphthalene at other linkage sites have been previously reported.[47–50] The rigid planar aromatic NA group was incorporated into the polymers' backbone in order to form long nonsulfonated hydrophobic segments, which could improve the hot water stability of SPAEKs with a high DS and possibly enhance phase separation between the domains of the aromatic polymer backbone and hydrophilic SO_3H groups. Another reason the less symmetric 2,6-disubstituted naphthalene monomer was selected was to attempt the disruption of the polymeric chain packing and to decrease the melting temperature (T_m) and crystallinity of PAEK and to improve its organic solvent solubility. The synthesis, structure, and properties of the polymers were studied as well as PEM-related properties such as proton conductivity and water-induced swelling.

EXPERIMENTAL

Chemicals and Materials

Fuming sulfuric acid (30% SO_3), dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP), potassium carbonate, 4,4′-difluorobenzophenone (DFBP), and 2,6-dihydroxynaphthalene (NA) were obtained from Aldrich Chemical Corp. MEMBRA-CEL™ dialysis tubing (MWCO 3500) was obtained from Serva Electrophoresis (Germany).

Synthesis of Sodium 5,5′-Carbonylbis(2-fluorobenzene-sulfonate)

Sulfonation is an aromatic electrophilic reaction, and because DFBP has two electron-withdrawing groups in each phenyl ring, a powerful sulfonating agent [fuming sulfuric acid (30%)] and elevated temperature (100 °C) were required for the sulfonation reaction. The sulfonic acid group is substituted *ortho* to fluorine atoms because of the *o,p*-orienting effect of the fluorine atom in the phenyl ring. The sulfonation of the monomer DFBP[24–26] as well as 4,4′-dichlorophenyl sulfone[33–35] and 4,4′-difluorodiphenyl sulfone[36,37] was reported previously. Following the procedures of Ueda et al.[33] and Wang et al.,[24] DFBP (21.8 g, 100 mmol) was dissolved in 40 mL of fuming sulfuric acid. The solution was stirred at

100 °C for 12 h, then cooled to room temperature, and poured into 240 mL of ice water. To neutralize the excess fuming sulfuric acid, 40 g of NaOH solid was added. The mixture was cooled again to room temperature, and the subsequent addition of NaCl solid (20 g) resulted in a white precipitate, which was filtered and dried. The recovered monomer was recrystallized from an ethanol:water (1:1) mixture, which was filtered and dried in a vacuum at 100 °C for 24 h. The yield of the white needle-shaped product was 70%. FTIR analyses (cm^{-1}): 1662 (C=O), 1592 (C=C), 1085 (Ar—SO_3Na). ^1H NMR analyses (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.

Synthesis of Poly(aryl ether ketone)s

The monomers DFBP, SDFBP-Na (combined total 1 mmol) and 2,6-dihydroxynaphthalene (1 mmol), and potassium carbonate (1.1 mmol) were added to a 100-mL three-necked flask equipped with a Dean–Stark trap and an argon inlet. NMP (20 mL) and toluene (15 mL) were used as solvents. The mixture was refluxed for 3 h at 130 °C until water was removed from the reaction mixture by azeotropic distillation, and then the excess toluene was distilled off. The temperature of the reaction mixture was slowly raised to 160 °C and maintained at that temperature for 10 h. After ~10 h of copolymerization at 160 °C, the solutions became highly viscous, and NMP was added to dilute the reaction solution and allow the copolymerization to continue for another 4 h. After a prescribed time, the polymer was cooled and recovered by precipitating into ethanol, then washed with acetone. Polymers with a DS ≤ 1.6 were washed repeatedly with deionized water until the pH reached 6–7. Polymers with a high DS (2.0) were washed by placing the polymers in 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 higher than 90%.

Membrane Preparation

Dried sulfonated poly(aryl ether ketone) (SPAEK) that was in a sodium salt form (powder) was dissolved in DMAc (15 wt %), and then the solutions were filtered using a fine glass frit filter funnel. Solutions were cast onto glass plates and then dried at 50 °C for 2 days and at 120 °C under vacuum for 24 h. The SPAEK membranes in acid form were obtained by immersing the sodium salt SPAEK membranes in a dilute HCl solution for 24 h, followed by washing with deionized water.

Characterization of SPAEKs

NMR

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 400 NMR spectrometer operating at a resonance frequency of 399.95 MHz for ^1H NMR and at 100.579 MHz for ^{13}C NMR. The 1D and 2D hydrogen NMR spectra were recorded using a 5-mm indirect detection probe, whereas the 1D and 2D carbon spectra were acquired using a 10-mm broadband probe. For each analysis, about 5–15 wt % polymer solutions were prepared in deuterated dimethyl sulfoxide (DMSO-d_6). The chemical shift of tetramethylsilane was used as the internal standard reference.

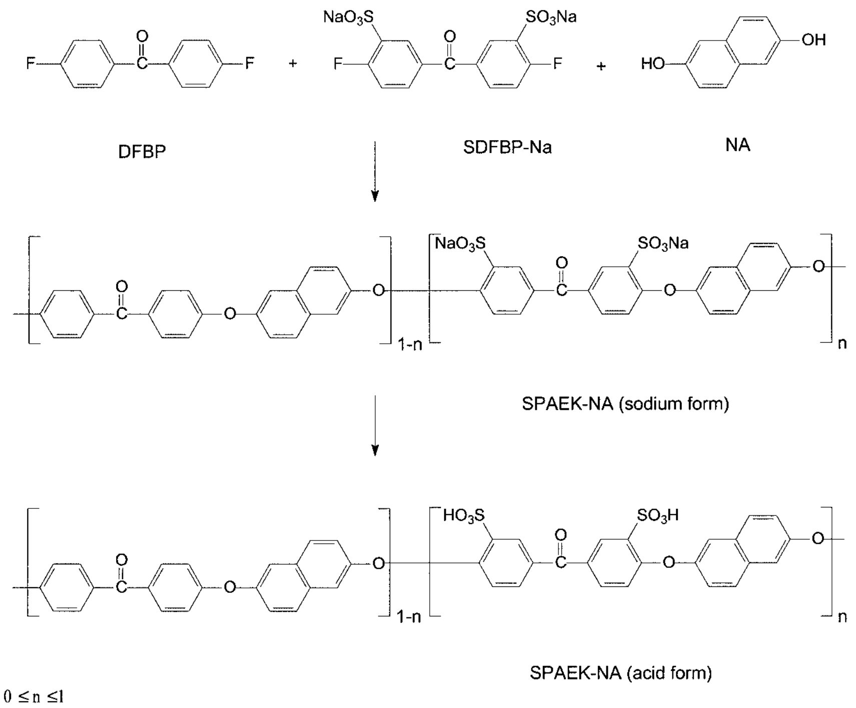
FTIR

FTIR spectra were recorded on a Nicolet 520 Fourier transform spectrometer, using either powder samples inside a diamond cell or KBr pellets composed of 50 mg of IR spectroscopic–grade KBr and 1 mg of polymer sample.

Thermal Properties of SPAEKs

A DuPont Instruments 951 and TA Hi-Res TGA 2950 thermogravimetric analyzers were employed to study the thermal stability behaviors of SPAEK samples. The samples were preheated under a 50 cc/min air flow from room temperature to 150 °C at 10 °C/min and maintained at 150 °C for 10 min to remove moisture, cooled to 90 °C, and then reheated from that temperature to 800 °C at 10 °C/min.

A TA DSC 2920 differential scanning calorimeter was employed to study the thermal transition behavior of SPAEK samples. The samples were preheated under 50 cc/min nitrogen from room temperature to 160 °C at 10 °C/min to remove moisture and avoid the effects of thermal history, cooled to 90 °C, and then reheated from that temperature to 250 °C at 10 °C/min.



Scheme 1. Synthesis of sulfonated poly(aryl ether ketone) containing a naphthalene moiety.

Water Uptake and Swelling

Before measurement, the membranes were dried in a vacuum oven at 120 °C for 24 h. Weighed films 5 mm × 50 mm in area were immersed in deionized water at various temperatures for 24 h. The gains in weight and length of the films were recorded. The percentage weight gain relative to the original membrane weight was considered water uptake; the percentage of length gain to original length, the swelling ratio.

Proton Conductivity Measurements

The transverse proton conductivities of the acid SPAEK membranes were measured by AC impedance spectroscopy over a frequency range of 1–10^7 Hz, with a 50–500 mV oscillating voltage, using a Solatron 1260 gain phase analyzer. Films 13 mm in diameter sandwiched between two stainless-steel block electrodes with ~3 kg/cm^2 pressure were placed in an open, temperature-controlled cell. The films had previously been hydrated by immersion in deionized water for 24 h at room temperature.

The proton conductivities (σ) of samples in the transverse direction were calculated from the impedance data using the relationship $\delta = d/RS$, where d and S are the thickness and face area of the membrane sample, respectively, and R is derived from the low intersection of the high frequency semicircle with the $Re(Z)$ axis on a complex impedance plane. The impedance data were corrected for the contribution from empty and short-circuited cells.

RESULTS AND DISCUSSION

Syntheses of SPAEKs

As shown in Scheme 1, the sulfonated PAEKs were synthesized by the aromatic nucleophilic substitution polycondensation of activated aromatic halides (DFBP and SDFBP) with 2,6-dihydroxynaphthalene. The DS of the SPAEKs was controlled by varying the feed ratio of SDFBP to DFBP. NMP was used as the reaction solvent, and toluene was used to remove the water during copolymerization. After a reaction time of ~10 h at 160 °C, the solutions became highly viscous, and NMP was added to dilute the reaction solution and allow the copolymerization to continue for another 4 h. Table 1 shows the nomenclature used for the prepared copolymers in sodium salt

Table 1. Sulfonated PAEK-NA and their Thermal Properties

Polymer	Percentage of Sulfonated Monomer (%)[a]	DS Theoretical	DS Experimental from ^{1}H NMR	η_{inh}^{b} (dL/g)	T_g (°C)	T_m[c] (°C)	T_d (°C) Acid	T_d (°C) Sodium
PAEK-NA	0	0	—	—	247	310	382	
SPAEK-NA-30	30	0.6	—	—	—	—	—	—
SPAEK-NA-40	40	0.8	0.72	0.94	263	NC	250	377
SPAEK-NA-50	50	1.0	0.96	1.83	286	NC	236	376
SPAEK-NA-60	60	1.2	1.21	1.29	320	NC	241	390
SPAEK-NA-70	70	1.4	1.37	1.54	—	NC	255	370
SPAEK-NA-80	80	1.6	1.60	0.87	333	NC	236	401
SPAEK-NA-100	100	2.0	—	—	—	—	229	431

[a] Percentage of sulfonated monomer = SDFBP-Na/(DFBP + SDFBP-Na) × 100, as shown in Scheme 1. PAEK-NA indicates polymers containing the naphthalene moiety.

[b] η_{inh} was measured at a concentration of 0.6 g/dL in DMAc for the sodium form of SPAEK-NA at 30 °C.

[c] NC indicates no crystallinity was observed.

form. In all cases the yields were > 90%, and high molecular weights were obtained, as shown by inherent viscosity (η_{inh}) values > 0.8 in DMAc. These results can be attributed to the good solubility of the polymer in the reaction solvent, which enabled a polymer with a high M_w to be obtained. In fact, the incorporation of the 2,6-naphthalene segment into the PAEK resulted in higher polymer chain rigidity that led to reduced solubility in solvents. However, introducing sulfonic acid (or salt) functions into the polymer chain produced a counteracting effect that improved the solubility of the polymer in polar aprotic solvents. Thus, the SPAEK-NA series with DS ≥ 0.8 were readily soluble in DMAc, NMP, and DMSO.

FTIR Study

The comparative FTIR spectra of PAEK-NA and SPAEK-NA in sodium salt form with different nominal DS values are shown in Figure 1. All the polymers showed a characteristic absorption band at 1652 cm^{-1} because of C═O stretching and an absorption band corresponding to aromatic C═C stretching at 1590 cm^{-1}. The aromatic C═C band at 1500 cm^{-1}, corresponding to disubstitution on aromatic phenyl for PAEK-NA, was split into two bands at 1506 and 1480 cm^{-1} for the SPAEK-NA samples because of sulfonation in the phenyl ring. The intensity of the 1480 cm^{-1} band, corresponding to trisubstituted phenyl rings, increased with an increasing sulfonated monomer ratio. New absorption bands at 1029 and 1085 cm^{-1} in SPAEK-NA were assigned to symmetric and asymmetric stretching vibration O═S═O because of the incorporation of the sodium sulfonate group.[18,25] Their intensities relative to the backbone carbonyl band at 1652 cm^{-1} increased with DS. This dual stretching mode was absent in the nonsubstituted PAEK-NA polymer.

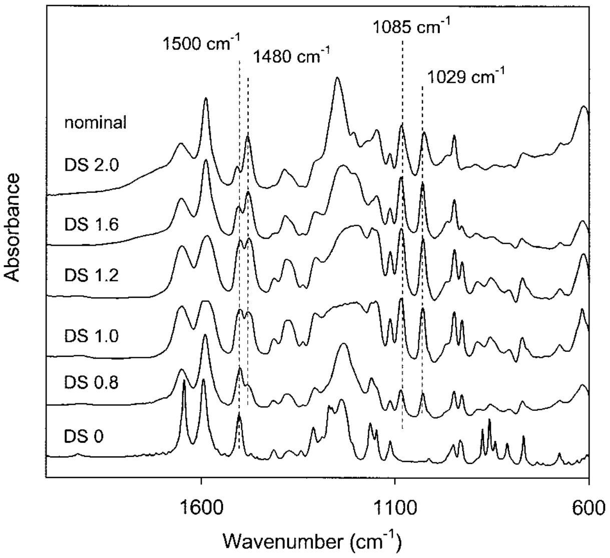


Figure 1. Comparative FTIR spectra of SPAEK-NAs.

NMR Analysis

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 SPAEK-NA polymers in the sodium salt form. Polymer samples were dissolved in DMSO-d_6 for spectroscopic

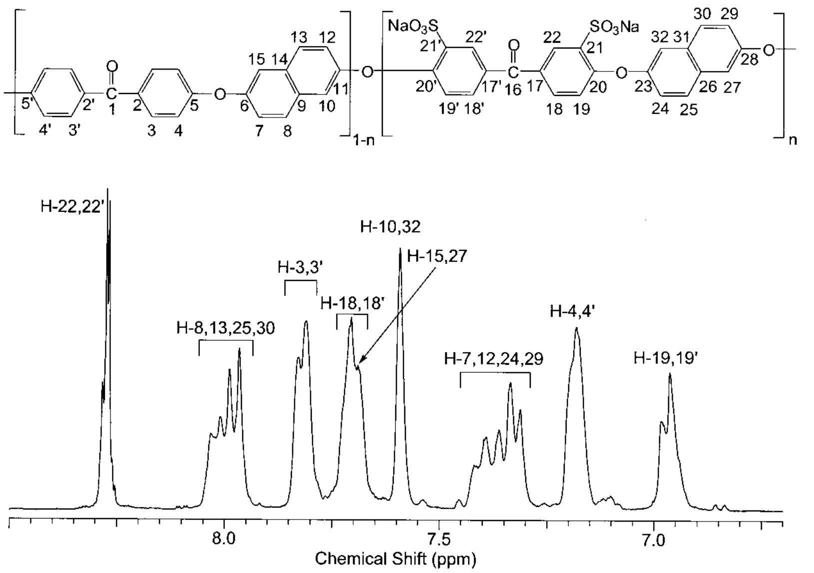


Figure 2. ^{1}H NMR spectrum of SPAEK-NA-60 (DS 1.21) in DMSO-d_6.

measurements. ^{1}H NMR spectra provided unambiguous structure elucidation and were also used for DS determination. DS ($0 < \mathrm{DS} \leq 2$) is defined as the average number of —SO_3Na groups per polymer repeat unit (R.U.) and was derived from the signal intensities of the different aromatic protons.

Figure 2 shows the aromatic region of a ^{1}H NMR spectrum of a typical SPAEK-NA polymer sample dissolved in DMSO-d_6. Each signal was assigned to a single or to a group of aromatic protons of sulfonated or nonsulfonated R.U. The DS was measured by comparing the intensities of the well-resolved, nonoverlapping aromatic signals H-19,19′ or H-22,22′ with the intensities of the remaining aromatic signals. The following equation explains how the DS is derived from these signal intensities:

$$\frac{i_{22}}{i_{\mathrm{R}}} = \frac{\mathrm{DS}}{14 - \mathrm{DS}} \quad \therefore \quad \mathrm{DS} = \frac{14 i_{22}}{i_{\mathrm{R}} + i_{22}}$$

or

$$\frac{\mathrm{i}_{19}}{i_{\mathrm{R}'}} = \frac{\mathrm{DS}}{14 - \mathrm{DS}} \quad \therefore \quad \mathrm{DS} = \frac{14 i_{19}}{i_{\mathrm{R}'} + i_{19}}$$

where i_{22} is the intensity of H-22,22′ (8.15–8.40 ppm), i_{19} is the intensity of H-19,19′ (6.90–7.05 ppm), i_{R} is the intensity of the remaining aromatic signals (6.80–8.15 ppm), $i_{\mathrm{R}'}$ is the intensity of 7.05–8.40 ppm, and DS is the number of —SO_3Na per R.U.

As an example, the DS calculation of SPAEK-NA-60 in Figure 2 is described here. The signal intensity value of sulfonated R.U. protons H-22,22′ (i_{22}) was first set to 1.00H, and the resulting total signal intensity for the remaining aromatic signals (i_{R}) was 10.64H, hence, an actual calculated DS of 1.20. The same calculation was performed using i_{19} and $i_{\mathrm{R}'}$, and the resulting DS was found to be 1.22; therefore, in Table 1 the average DS value for SPAEK-NA-60 is reported as 1.21. The DS values measured by NMR for all tested samples also are listed in Table 1, which shows values in very close agreement with the monomer feed ratio during copolymerization. However, three experimental DS values were a few percentage points lower than the feed ratio. As pointed out by Harrison et al.,[36] this may be within a reasonable experimental error resulting from weighing the hygroscopic (sulfonated) monomer. Figure 3 shows three stacked ^{1}H NMR spectra of SPAEK-NA with DS values ranging from 0.72 to 1.60. Variations in signal intensity and shape were observed with increasing DS, as nonsulfonated R.U. was replaced by sulfonated R.U.

A ^{13}C NMR spectrum of SPAEK-NA polymer (DS 1.21) is shown as an example in Figure 4, and the chemical shifts are listed in Table 2. Assignment of most of the carbon signals was carried out

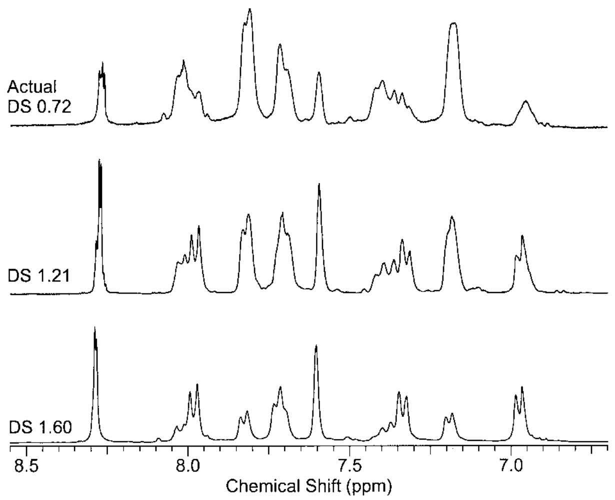


Figure 3. ^{1}H NMR spectra of three SPAEK-NA polymers in DMSO-d_6 with increasing DS.

Table 2. ^{13}C NMR Chemical Shifts of SPAEK-NA-60 (DS 1.21) in DMSO-d_6

Carbon Number	Chemical Shift (δ) (ppm)
C-1,16	193.0
C-5,5′,6,11,20,20′,23,28	151.8–161.0
C-21,21′	137.4–138.3
C-3,3′,18,18′	132.0
C-2,2′,9,14,17,17′,26,31	128.0–131.5
C-22,22′	130.5–131.1
C-8,13,25,30	129.0–130.0
C-7,12,24,29	120.7–121.5
C-19,19′	118.3–118.8
C-4,4′	117.4
C-10,15,27,32	115.5–116.1

using ^{1}H–^{13}C correlation. Carbon atoms linked to oxygen and sulfur atoms (C═O, C—O, C—S) were discerned by their well-known and expected high-frequency shifts. Only a few carbon atoms grouped in 128.0–131.5 ppm remained unassigned.

Thermal Properties

Unsulfonated PAEK-NA is a semicrystalline polymer with a T_m of 310 °C and a T_g of 247 °C, as determined by differential scanning calorimetry. PAEK-NA exhibited a significantly higher T_g compared with the T_g (~150 °C) of PEEK, which can be attributed to the increased stiffness of the polymer chain from the incorporation of a rigid naphthalene moiety into the polymer backbone. In contrast, the T_m of PAEK-NA (310 °C) was lower than that of PEEK (~340 °C), evidently because of the introduction of the less symmetric 2,6-disubstituted naphthalene into the polymer backbone. The ΔH_m of PAEK-NA was 48.9 J/g, which is quite low, indicating the low crystallinity of the polymer.

The thermal stabilities of the PAEK polymers were studied by thermogravimetric analysis

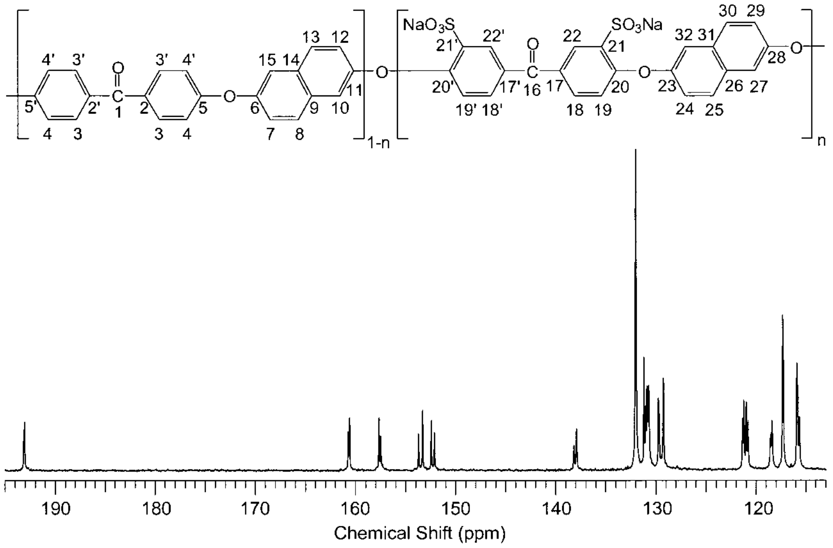


Figure 4. ^{13}C NMR spectrum (^{1}H noise decoupled) of SPAEK-NA-60 (DS 1.21) in DMSO-d_6.

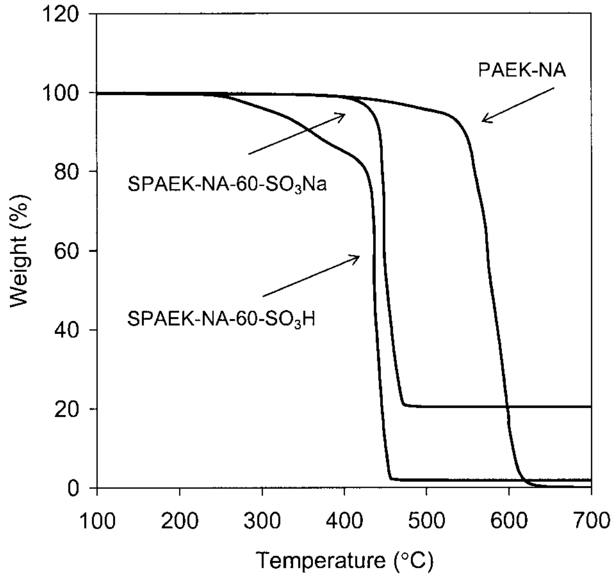


Figure 5. Typical TGA curves of SPAEK-NA.

(TGA; Table 1 and Fig. 5). The TGA experiments were performed in air at a heating rate of 10 °C/min. As can be seen from Figure 5, PAEK-NA showed single-step thermal degradation starting at ~400 °C. Unlike PAEK-NA, SPAEK-NA exhibited two distinct thermal degradation steps. In a manner similar to SPEEK,[10,18,51] the acid-form SPAEK-NA polymer showed a first weight-loss step in the range of 250–300 °C, which is believed to be associated mainly with loss of sulfonic groups. The second weight-loss step, starting at about 400 °C, can be attributed to decomposition of the main chain of PAEK-NA. However, the main-chain degradation temperature of SPAEK-NA was lower than that of PAEK-NA (Fig. 5) as a result of the catalytic effect of SO_3H,[10,51] increasing the rate of polymer decomposition.

The thermal stabilities of the sodium salt forms of SPAEK-NA were also analyzed by TGA. In contrast to what was observed for the acid SPAEK-NA, no initial degradation step was observed for the sodium salt form of the SPAEK-NA samples between 250 and 300 °C. All sodium from the SPAEK-NA samples showed much higher thermal stability, and single-step thermal degradation started at a temperature of about 380 °C (Table 1).

Water Uptake and Proton Conductivity

To be suitable for PEMFC application, the sulfonated polymer membranes require adequate mechanical integrity after hydration. Membranes with excessively large water uptake or swelling lead to low mechanical strength, which is incompatible with FC working conditions. Thus, these parameters are essential for PEM characterization, which make it necessary to determine the temperature and the DS dependence of the degree of swelling and water uptake of the studied membranes. Because the acid form of SPAEKs is more suitable for PEM application, it was chosen for the tests. From the results, presented in Table 3 and in Figure 6(a,b), it can be seen that SPAEK-NA membranes with a higher DS exhibited greater water uptake and swelling. Figure 6(a) shows that the water uptake of SPAEK-NA-70 (DS 1.37) and of SPAEK-NA-80 (DS 1.60) increase sharply with temperature and to a much greater degree than samples with a lower DS. It was observed that most of the SPAEK-NA membranes before and after the swelling tests at room temperature had good mechanical properties. SPAEK-NA polymers with a DS $\leq$ 1.4 maintained mechanical integrity after the swelling tests at higher temperatures. For example, the SPAEK-NA-60 (DS 1.21) membrane did not show excessive water uptake and maintained adequate mechanical strength after immersion in boiling water for 24 h. The SPAEK-NA-70 (DS 1.37) membrane underwent considerable swelling, especially at higher temperatures, but retained its mechanical strength. However, the SPAEK-NA-80 (DS 1.60) polymer membrane had excessive water uptake and lost its mechanical properties after boiling in water for 24 h as a result of its high DS (1.60). The observed excellent mechanical strength and hydrothermal properties of the SPAEK-NA membranes with a DS $\leq$ 1.4 are clearly related to the structure of the copolymerized SPAEKs, which contained phase domains of hydrophilic and hydrophobic regions, in which the hydrophilic segments had two sulfonic groups on neighboring phenyl rings and the hydrophobic segments formed by one or more of the rigid aromatic NA moieties connected with nonsulfonated DFBP. Thus, the incorporation of naphthalene into the polymer backbone improved the mechanical properties of the membrane both in the dry and the hydrated states through the formation of long nonsulfonated segments.

The water uptake at 25 °C by SPAEK-NA films with a DS of 0.8–1.6 corresponded to absorption of, respectively, 11–19 water molecules per sulfonic acid group of SPAEK. This is in the same range as Nafion®, which absorbs 11 water mole-

Table 3. Water Uptake, Swelling, and Proton Conductivities of Sulfonated PAEK-NAs at Different Temperatures

Polymer	DS Measured by NMR	Meq. Calc.	Water Uptake (%) 25 °C	Swelling (%) 25 °C	Water Uptake (%) 80 °C	Swelling (%) 80 °C	Water Uptake (%) 100 °C	Swelling (%) 100 °C	H_2O/SO_3H 25 °C	H_2O/SO_3H 80 °C	σ (S/cm) 25 °C	σ (S/cm) 80 °C
SPAEK-NA-40	0.72	549	36	10	57	12	76	15	11	17	6.7×10^{-3}	1.1×10^{-2}
SPAEK-NA-50	0.96	432	50	16	81	25	97	27	12	19	7.1×10^{-3}	2.5×10^{-2}
SPAEK-NA-60	1.21	359	74	21	137	38	196	50	15	27	1.5×10^{-2}	3.6×10^{-2}
SPAEK-NA-70	1.37	327	87	27	361	72	666	117	16	66	2.4×10^{-2}	4.9×10^{-2}
SPAEK-NA-80	1.60	291	115	35	1200	150	—	—	19	194	4.2×10^{-2}	1.1×10^{-1}
SPAEK-NA-100	2.00	249	—	—	—	—	—	—	—	—	—	—
Nafion 112	—	1100[a]	12	4.3	23	9.6	23	9.6	7[b]	14[b]	3.3×10^{-2}	5.6×10^{-2}

[a] Meq. of 1100 for Nafion 112 is based on theoretical value, whereas the measured value in ref. 52 was 890.

[b] Authors' measured value.

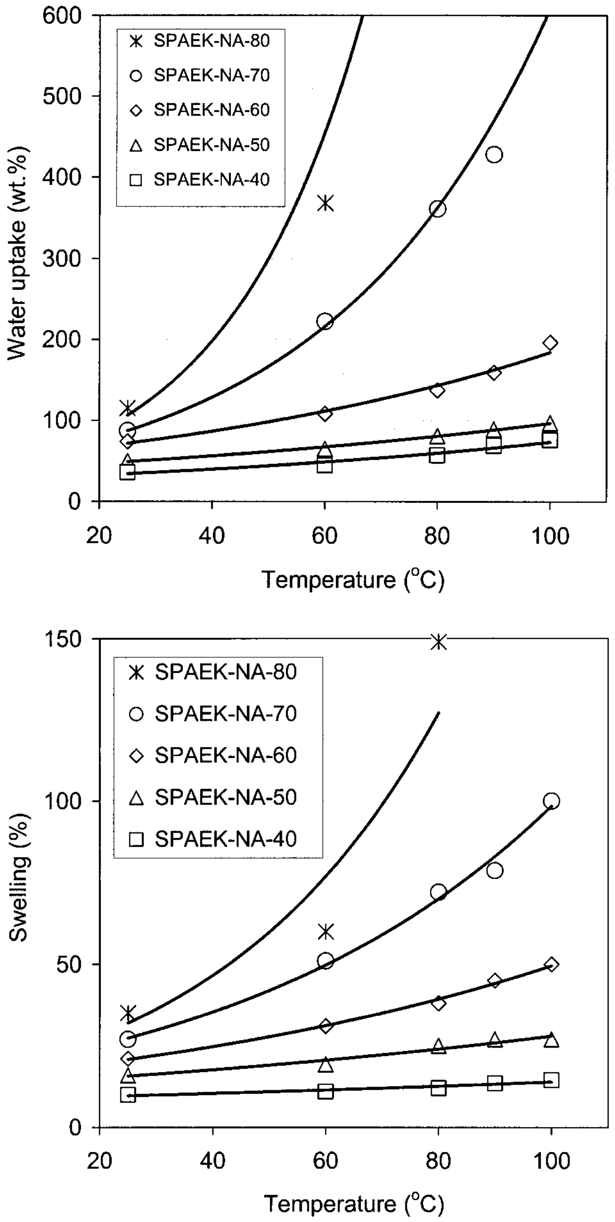


Figure 6. (a) Water uptake and (b) swelling of SPAEK-NA films at different temperatures.

cules per sulfonic acid group at room temperature and 90% relative humidity (RH).[6] At higher temperatures (80 °C) the SPAEK-NA water uptake surpassed that of Nafion®. Proton conductivity is a fundamental property of sulfonated polymer PEM materials and depends on such characteristics as the DS, pretreatment of the membrane, hydration state, and temperature.[40,41] In the present study membranes were initially hydrated by immersion in water for 24 h at room temperature, and then the transverse proton conductiv-

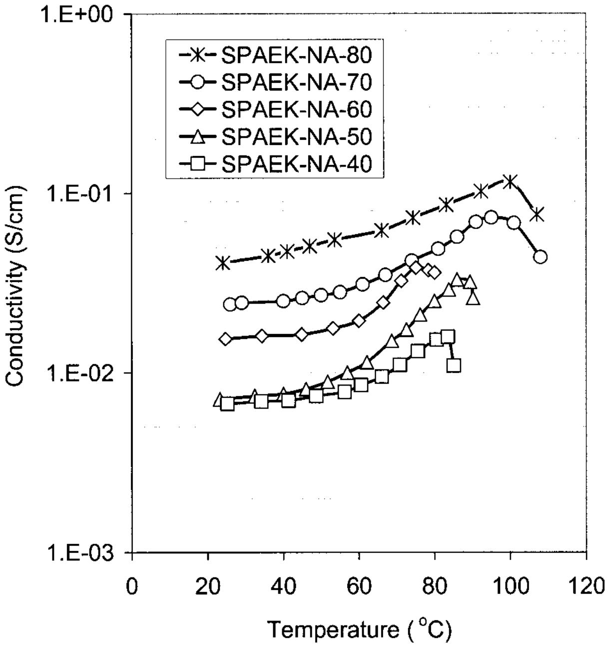


Figure 7. Proton conductivities of SPAEK-NA films at different temperatures.

ity was measured. As can be seen in Figure 7, the conductivities of SPAEK-NA membranes in the acid form increased with DS. For example, the proton conductivity increased from 6.7 $\times 10^{-3}$ S/cm for SPAEK-NA-40 (DS 0.72) to 4.2 $\times$ 10^{-2} S/cm for SPAEK-NA-80 (DS 1.60) at 25 °C (Table 3). In common with the results found in many other studies, the proton conductivity increased with temperature and at 80 °C (Table 3) exceeded 10^{-2} S/cm for all five SPAEK-NA samples. The conductivities of SPAEK-NA-60 (DS 1.21) and SPAEK-NA-80 (DS 1.60) were 3.6 $\times$ 10^{-2} and 1.1 $\times$ 10^{-1} S/cm at 80 °C, which is considered high enough for PEM operation in a fuel cell. It is worth noting that SPAEK-NA has a much higher acid capacity than Nafion®. The equivalent weight of SPAEK-NA-60 is 376 Meq, whereas DuPont™ Nafion® membranes N-112, N-115, and N-117 have a measured value of 890 Meq[52] and a calculated value of 1100 Meq. The similarity of the PEM properties of these two polymers, despite the lower acid loading in Nafion®, can be explained by more effective phase separation in the perfluorinated material, where pendant sulfonic acid groups form hydroclusters, providing proton channeling passages through the polymer bulk, as well as by the higher acidity of fluorosulfonic acids in perfluorinated material compared with that in aromatic sulfonic acids in SPAEK.

CONCLUSIONS

A series of sulfonated poly(aryl ether ketone)s (SPAEK)s were prepared directly by aromatic nucleophilic copolycondensation of 2,6-dihydroxynaphthalene with 5,5′-carbonyl-bis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone in various ratios. The structure and degree of sulfonation (DS) of the SPAEKs were determined using ^{1}H NMR spectroscopy. The experimentally measured DS values were close to the theoretical values expected from the monomer ratio. The thermal stabilities of the polymers were characterized by TGA, which showed that the SPAEKs were thermally stable up to ~240 °C in air. The water uptake and swelling properties of the prepared films also were studied, and the proton conductivities at different temperatures were measured. The SPAEK-NA-hydrated membranes (up to DS 1.37) exhibited better mechanical properties compared with SPEEK membranes, even when hydrated at elevated temperatures of 80 and 100 °C for 24 h. The proton conductivities of SPAEK-NA membranes with a DS from 0.72 to 1.60 ranged from 6.7 $\times$ 10^{-3} to 4.2 $\times$ 10^{-2} S/cm at 25 °C and from 1.1 $\times$ 10^{-2} to 1.1 $\times$ 10^{-1} S/cm at 80 °C.

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REFERENCES AND NOTES

1. Savadogo, O. J New Mat Electr Syst 1998, 1, 47–66.
2. Inzelt, G.; Pineri, M.; Schultz, J. W.; Vorotyntsev, M. A. Electrochim Acta 2000, 45, 2403–2421.
3. Cotter, R. J. Engineering Plastics: Handbook of Polyarylethers; Gordon & Breach: Switzerland, 1995.
4. Kerres, J. A. J Membr Sci 2001, 185, 3–27.
5. Kreuer, K. D. J Membr Sci 2001, 185, 29–39.
6. Rikukawa, M.; Sanui, K. Prog Polym Sci 2000, 25, 1463–1502.
7. Ulrich, H. H.; Rafler, G. Die Angew Makromol Chem 1998, 263, 71–78.
8. Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. J Membr Sci 2001, 185, 73–81.
9. Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2000, 173, 17–34.

10. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K.; Kaliaguine, S. J Membr Sci 2004, 229, 95–106.
11. Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. Solid State Ionics 1998, 106, 219–225.
12. Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. J Membr Sci 1993, 83, 211–220.
13. Kerres, J.; Ullrich, A.; Meier, F.; Haring, T. Solid State Ionics 1999, 125, 243–249.
14. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359–373.
15. Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Macromolecules 2002, 35, 6707–6713.
16. Miyatake, K.; Asano, N.; Watanabe, M. J Polym Sci Polym Chem Ed 2003, 41, 3901–3907.
17. Jones, D. J.; Roziere, J. J Membr Sci 2001, 185, 41–58.
18. Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. Br Polym J 1985, 17, 4–10.
19. Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langle, K. H. Macromolecules, 1985, 18, 86–93.
20. Bailly, C.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. Polymer 1987, 28, 1009–1016.
21. Daoust, D.; Devaux, J.; Godard, P. Polym Int 2001, 50, 917–924.
22. Shibuya, N.; Porter, R. S. Polymer 1994, 35, 3237–3242.
23. Huang, R. Y. M.; Shao, P.; Burns, C. M.; Feng, X. J Appl Polym Sci 2001, 82, 2651–2660.
24. Wang, F.; Chen, T.; Xu, J. Macromol Chem Phys 1998, 199, 1421–1426.
25. Wang, F.; Li, J.; Chen, T.; Xu, J. Polymer 1999, 40, 795–799.
26. Wang, F.; Chen, T.; Xu, J. Macromol Rapid Commun 2001, 19, 135–137.
27. Liu, S.; Wang, F.; Chen, T. Macromol Rapid Commun 2001, 22, 579–582.
28. Liu, S.; Chen, T. Polymer 2001, 42, 3293–3296.
29. Xiao, G.; Sun, G.; Yan, D. Macromol Rapid Commun 2002, 23, 488–492.
30. Xiao, G.; Sun, G.; Yan, D. Polym Bull 2002, 48, 309–315.
31. Gan, D.; Lu, S.; Wang, Z. Polym Int 2001, 50, 812–816.
32. Gao, Y.; Robertson, G. P.; Guiver, M. D.; Jian, X.; Mikhailenko, S. D.; Wang, K.; Kaliaguine, S. J Polym Sci Polym Chem Ed 2003, 41, 2731–2742.
33. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. J Polym Sci Polym Chem Ed 1993, 31, 853–858.
34. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J Membr Sci 2002, 197, 231–242.
35. Wang, F.; Hickner, M.; Ji, Q.; Zawodzinski, T. A.; McGrath, J. E. Macromol Symp 2001, 175, 387–396.
36. Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. J Polym Sci Polym Chem Ed 2003, 41, 2264–2276.
37. Xiao, G.; Sun, G.; Yan, D.; Zhu, P.; Tao, P. Polymer 2002, 43, 5335–5339.
38. Kang, M.; Choi, Y.; Choi, I.; Yoon, T.; Moon, S. J Membr Sci 2003, 216, 39–53.
39. Helmer-Metamann, F.; Osan, F.; Schneller, A.; Ritter, H.; Ledjeff, K.; Nolte, R.; Thorwirth, R. U.S. Patent 5,438,082, 1995.
40. Bauer, B.; Jones, D. J.; Roziere, J.; Tchicaya, L.; Alberti, G.; Casciola, M.; Massinelli, L.; Peraio, A.; Besse, S.; Ramunni, E. J New Mat Electr Syst 2000, 3, 93–98.
41. Soczka-Guth, T.; Baurmeister, J.; Frank, G.; Knauf, R. International Patent WO99/29763, 1999.
42. Kreuer, K. D.; Dippel, T.; Maier, J. Proc Electrochem Soc 1995, 95–23, 241–246.
43. Yen, S. P. S.; Narayanan, S. R.; Halpert, G.; Graham, E.; Yavrouian, A. U.S. Patent 5,795,496, 1998.
44. Kaliaguine, S.; Mikhailenko, S. D.; Wang, K.; Xing, P.; Robertson, G. P.; Guiver, M. D. Catal Today 2003, 82, 213–222.
45. Robertson, G. P.; Mikhailenko, S. D.; Wang, K.; Xing, P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2003, 219, 113–121.
46. Li, L.; Zhang, Z.; Wang, Y. J Membr Sci 2003, 226, 159–167.
47. Ohno, M.; Takada, T.; Endo, T. J Polym Sci Polym Chem Ed 1995, 33, 2647.
48. Douglas, J. E.; Wang, Z. Y. Can J Chem 1997, 75, 1340–1345.
49. Ruan, R.; Jiang, Z.; Xu, W.; Li, G. Wu, Z.; Shibata, M.; Yosomiya, R. Die Angew Makromol Chem 1999, 270, 33–37.
50. Colquhoun, H. M.; Aldred, P. L.; Zhu, Z.; Williams, D. J. Macromolecules 2003, 36, 6416–6421.
51. Luo, Y.; Huo, R; Huo; Jin, X.; Karasz, F. E. J Anal Appl Pyrol 1995, 34, 229–242.
52. DuPont™ Nafion® PFSA Membranes Product Information; Bulletin NAE101, DuPont Fluoroproducts, NC, November 2002.