



NRC Publications Archive Archives des publications du CNRC

Sulfonated poly(aryl ether ether ketone ketone)s containing fluorinated moieties as proton exchange membrane materials

Liu, Baijun; Robertson, Gilles P.; Guiver, Michael D.; Sun, Yi-Ming; Liu, Yin-Ling; Lai, Juin-Yih; Mikhailenko, Serguei; Kaliaguine, Serge

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<http://dx.doi.org/10.1002/polb.20867>

Journal of Polymer Science: Part B: Polymer Physics, 44, 16, pp. 2299-2310, 2006

NRC Publications Record / Notice d'Archives des publications de CNRC:

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=12339162&lang=en>

<http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/ctrl?action=rtdoc&an=12339162&lang=fr>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=en

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

http://nparc.cisti-icist.nrc-cnrc.gc.ca/npsi/jsp/nparc_cp.jsp?lang=fr

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Contact us / Contactez nous: nparc.cisti@nrc-cnrc.gc.ca.



Sulfonated Poly(aryl ether ether ketone ketone)s Containing Fluorinated Moieties as Proton Exchange Membrane Materials

BAIJUN LIU,¹ GILLES P. ROBERTSON,¹ MICHAEL D. GUIVER,¹ YI-MING SUN,² YIN-LING LIU,³ JUIN-YIH LAI,³ SERGUEI MIKHAILENKO,⁴ SERGE KALIAGUINE⁴

¹Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, K1A 0R6 Ontario, Canada

²Department of Chemical Engineering and Materials Science, Yuan Ze University, Chungli, Taoyuan 32003, Taiwan, Republic of China

³R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan University, Chungli, Taoyuan 32023, Taiwan, Republic of China

⁴Chemical Engineering Department, Laval University, Ste-Foy, Quebec, Canada

Received 28 November 2005; revised 21 March 2006; accepted 6 April 2006

DOI: 10.1002/polb.20867

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of sulfonated poly(aryl ether ether ketone ketone)s statistical copolymers with high molecular weights were synthesized via an aromatic nucleophilic substitution polymerization. The sulfonation content (SC), defined as the number of sulfonic acid groups contained in an average repeat unit, could be controlled by the feed ratios of monomers. Flexible and strong membranes in sodium sulfonate form could be prepared by the solution casting method, and readily transformed to their proton forms by treating them in 2 N sulfuric acid. The polymers showed high T_g s, which increased with an increase in SC. Membranes prepared from the present sulfonated poly(ether ether ketone ketone) copolymers containing the hexafluoroisopropylidene moiety (SPEEKK-6F) and copolymers containing the pendant 3,5-difluoromethylphenyl moiety (SPEEKK-6FP) had lower water uptakes and lower swelling ratios in comparison with previously prepared copolymers containing 6F units. All of the polymers possessed proton conductivities higher than 1×10^{-2} S/cm at room temperature, and proton conductivity values of several polymers were comparable to that of Nafion at high relative humidity. Their thermal stability, oxidative stability, and mechanical properties were also evaluated. ©2006 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 44: 2299–2310, 2006

Keywords: fluoropolymer; fuel cell; poly(ether ether ketone ketone); proton exchange membrane; sulfonation

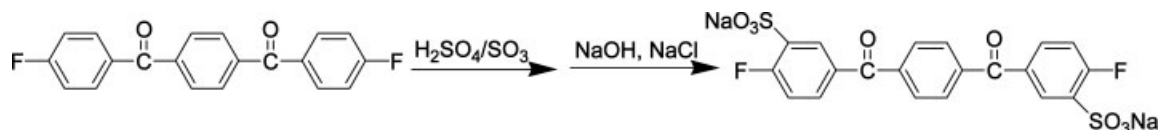
INTRODUCTION

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications.^{1,2} Nafion[®], which is comprised of a perfluorosulfonic acid structure, is the principal material used as the poly-

NRCC Publication No. 47876

Correspondence to: M. D. Guiver (E-mail: michael.guiver@nrc-cnrc.gc.ca)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 44, 2299–2310 (2006)
©2006 Wiley Periodicals, Inc.



Scheme 1. Synthesis of sulfonated BFBB.

meric electrolyte in PEMFC systems because of its excellent chemical and mechanical stabilities, and high proton conductivity. However, high cost, low operation temperature, and high methanol crossover of Nafion and other similar perfluorinated membranes have limited their widespread commercial application in PEMFC and other fuel cells. Currently, there is much research on developing nonperfluorinated polymers with better performance and lower cost as alternative proton exchange membrane (PEM) materials.^{3–7}

Aromatic polymers with sulfonic acid groups are regarded as promising materials for PEMs because of their high thermal and chemical stability. Sulfonated derivatives of poly(ether ether ketone) (SPEEK),^{8–10} poly(ether sulfone),^{11–13} polyimide (SPI),^{14–16} poly(arylene ether),^{17,18} and poly(phenylquinoxaline)¹⁹ are among those being investigated as potential PEMs. There are two generally used methods to attach sulfonic groups onto polymer chains. One is postsulfonation of a polymer, and the other is to incorporate a sulfonated monomer by direct polymerization. For the postsulfonation route, difficulties may occasionally be encountered in the control of the sulfonation position, resulting in a less defined and more diffuse distribution of sulfonic acid groups along the polymer chain. On the other hand, the direct polymerization of sulfonated monomer with other nonsulfonated monomers has the potential for synthesizing statistical copolymers with better control of SC and more defined chain structures.^{20,21}

It is well known that there are two domains in the microstructure of PEMs: the hydrophobic domains formed by nonsulfonated polymer segments provide the PEMs with mechanical strength, whereas the interconnected hydrophilic domains containing sulfonic acid groups provide the proton conductivity.²² To improve the durability of PEMs as fuel cell, several partially fluorinated polymers have been developed.^{15,21,23,24} Recently, our group reported a series of SPAEEK and SPAEEK-co-SPAEEKK copolymers based on 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol 6F) and sodium 5,5'-carbonyl-bis(2-fluorobenzene-sulfonate) in an approach to increase the hydrophobicity and length of nonsulfonated seg-

ments and to improve the mechanical properties and hot water stability of the films, which showed some attractive properties as PEMs.^{21,23} The aim of this study is to make a comparative study of the effect of the length of hydrophobic segments and to investigate the effect of various molecular structures on the properties related to proton conductivity. In this work, sulfonic acid group and fluorinated moieties, hexafluoroisopropylene or 3,5-ditrifluoromethylphenyl groups, were incorporated into poly(ether ether ketone ketone) (PEEKK), by direct copolymerization of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (SBFBB), and 1,4-bis(4-fluorobenzoyl)benzene (BFBB) with bisphenol 6F or (3,5-ditrifluoromethyl)phenylhydroquinone (6F-PH). The structures and some properties, such as thermal stability, water uptake, oxidative stability, mechanical properties, and proton conductivity, are discussed.

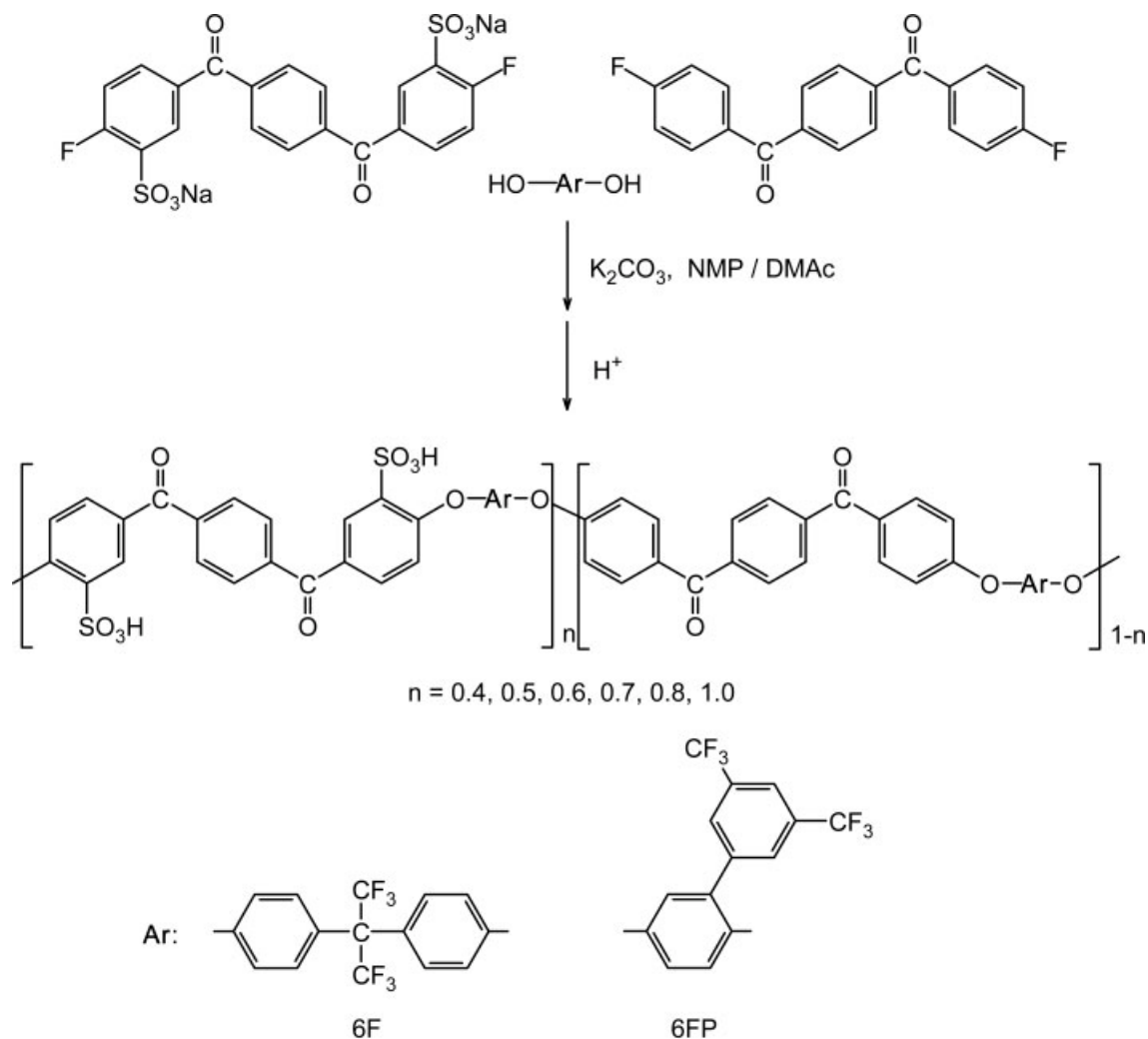
EXPERIMENTAL

Materials

Fuming sulfuric acid (30% SO₃), 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), anhydrous potassium carbonate, and toluene were obtained from Sigma-Aldrich, and used as received. BFBB were received from Jilin University (China) and recrystallized from 1,2-dichlorobenzene before use. Bisphenol 6F was obtained from Sigma-Aldrich, and recrystallized from toluene before use. 6F-PH was synthesized according to a reported synthetic procedure.²⁵ The other solvents were used as received. The synthesis routes for the sulfonated monomer and polymers are illustrated in Scheme 1 and Scheme 2, respectively.

Synthesis of SBFBB

A sulfonated monomer, SBFBB, was synthesized according to a reported procedure.^{26,27} BFBB (32.2 g, 0.1 mol) was dissolved in 60 mL of fuming sulfuric acid (30% SO₃). The mixture was stirred at 100 °C for 24 h. The solution was poured into stirred 250 mL of ice/water after cooling. Sodium hydroxide solution was added to



Scheme 2. Synthesis of SPEEKK-6F and SPEEKK-6FP copolymers.

neutralize the excess sulfuric acid. Sodium chloride (50 g) was added to the mixture to yield a white-yellow precipitate. The precipitate was collected by filtering and recrystallized twice from a mixture of ethanol/water (1:1 volume). The yield of the purified product was about 50%.

FTIR (KBr, cm^{-1}): 1659 (C=O), 1093, 1040 (S=O). ^1H NMR: (DMSO- d_6): 8.15 (dd, $J = 6.8$ Hz, 2.0 Hz, 1H), 7.89 (s, 2H), 7.88–7.84 (m, 1H), 7.39 (t, $J = 8.4$ Hz, 1H). ^{13}C NMR: (DMSO- d_6): 193.83, 161.40 ($J = 257.9$ Hz), 140.07 ($J = 17.6$ Hz), 133.19 ($J = 9.1$ Hz), 131.90, 130.73, 130.08, 116.72 ($J = 23.7$ Hz).

Synthesis of SPEEKK-6F Polymers

Polymerization of SBFBB and BFBB with bisphenol 6F was carried out in the presence of an-

hydrous K_2CO_3 in NMP at 160–170 °C by aromatic nucleophilic polymerization following similar polymerization procedures to those reported previously,^{3,28} as shown in Scheme 2. As a typical example, the synthesis of SPEEKK-6F-50 is given as follows.

To a 100-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap were added SBFBB (0.5264 g, 1 mmol), BFBB (0.3223 g, 1 mmol), bisphenol 6F (0.6724 g, 2 mmol), anhydrous K_2CO_3 (0.3594 g, 2.6 mmol), NMP (6 mL), and toluene (12 mL). The system was allowed to reflux for 3 h, and then the toluene was removed. The reaction mixture was heated to 160 °C. After 10 h, another 4–5 mL of NMP was added into the viscous reaction mixture. The polymerization was complete after another 2 h. The viscous solution

was then poured into ethanol. The polymer was thoroughly washed with hot deionized water to remove the salts and solvents, and dried at 100 °C for 48 h.

SPEEKK-6F-100 with high SC was washed by placing it in dialysis tubing (MWCO 3500 obtained from Serva Electrophoresis, Germany) in deionized water. One week of dialysis was required to remove the salts, and the water was changed several times during this period.

Synthesis of SPEEKK-6FP Polymers

DMAc was used as solvent, and bisphenol 6F was replaced by 6F-PH. The polymerization procedure is similar to that of the SPEEKK-6F copolymers.

Measurements

FTIR spectra were measured on a Nicolet 520 Fourier transform spectrometer. The thin and transparent film samples were cast from the polymer solutions in DMAc, and well dried in an oven. ¹H and 2D COSY spectra were recorded on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. Deuterated dimethylsulfoxide (DMSO-*d*₆) was the NMR solvent and the DMSO signal at 2.50 ppm was used as the chemical shift reference.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument 2920 DSC at a heating rate of 20 °C/min under nitrogen. The glass transition temperature (*T*_g) was taken from the DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a TA Hi-Res TGA 2950 thermal analyzer system at a heating rate of 10 °C/min under nitrogen. All the samples were kept in the furnace at 150 °C for 60 min in N₂ atmosphere to remove water before measurement.

Inherent viscosities of the copolymers in sodium form were measured in DMAc (0.5 g/dL) at 30 °C using an Ubbelohde viscometer.

The proton conductivities of the membranes were measured using AC impedance spectroscopy over a frequency range of 1–10⁷ Hz with voltage 50–500 mV, with a Solartron 1260 gain phase analyzer. To ensure *in situ* equilibration of the specimens with the environment, a frame cell similar to the one proposed in ref. ²⁹ has been used in the work. The conductivity was measured in the longitudinal direction along mem-

brane faces, exposed to the cell atmosphere. The membrane strips (~20 × 10 mm²) were clamped between two pairs of electrodes and placed in a temperature-controlled chamber with some liquid water inside ensuring ~100% relative humidity at all temperatures up to 100 °C. The cell was open to the air with a pinhole to release excessive pressure built up upon heating. Film samples were previously hydrated by boiling in water for 5 min and then kept immersed in water for several days, or kept in water at room temperature for at least one week prior to the test. The measurements were carried out after sample conditioning in the closed cell overnight or longer. The conductivity (σ) of the samples was calculated, using the relationship $\sigma = L/RdW$ where *L* is the distance between the electrodes, *d* and *W* are the thickness and width of the sample stripe, respectively. *R* was derived from the diameter of semicircle or its fit on a complex impedance plane (intersection with the Re (*Z*) axis).

Mechanical properties of wet films were evaluated at room temperature on an Instron 5565 instrument at a strain rate of 10 mm/min, and a 500 N load cell was used. The test samples were prepared by stamping out dumbbell shaped strips on a press die (50 × 4 mm²) according to DIN-53504-S3A standard. The samples in the wet state were obtained by immersing the samples in water for 48 h.

Membrane Preparation

The films of the copolymers in sodium form were prepared by casting their DMAc solution (0.5 g/12 mL) onto glass plates and dried at 50 °C for 72 h. The membranes in proton form were obtained by soaking the above films in 2 N H₂SO₄ at room temperature for 24 h. The films were thoroughly washed with water over 24 h to remove excess acid, and then dried at 120 °C for 12 h. The thickness of the films was in the range of 30–60 μm.

Oxidative Stability, Water Uptake, and Swelling Ratios

Oxidative stability of the SPFEEKK membranes was evaluated by immersing the films into Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C. The water uptake and swelling ratios of the polymers were measured by immersion of the dry polymer films (~50 μm × 4 mm × 20 mm) in deionized water at 23 °C and 80 °C for 24 h,

Table 1. Inherent Viscosity and Sulfonation Content of PEEKK Copolymers

Polymer	Feed Ratio of Sulfonated Monomer ^a (mol %)	SC ^b	η_{inh}^c (dL/g)
SPEEKK-6F-40	40	0.8	1.34
SPEEKK-6F-50	50	1.0	1.08
SPEEKK-6F-60	60	1.2	1.34
SPEEKK-6F-70	70	1.4	1.38
SPEEKK-6F-80	80	1.6	1.45
SPEEKK-6F-100	100	2.0	–
SPEEKK-6FP-40	40	0.8	2.40
SPEEKK-6FP-50	50	1.0	2.09
SPEEKK-6FP-60	60	1.2	2.79
SPEEKK-6FP-70	70	1.4	1.70
SPEEKK-6FP-80	80	1.6	2.20
SPEEKK-6FP-100	100	2.0	–

^a Calculated by the feed ratio of the monomers.

^b Sulfonation content by $-\text{SO}_3\text{Na}$ or $-\text{SO}_3\text{H}$ groups.

^c Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

followed by wiping with tissue paper for removal of any water on the surface.

The water uptake content was calculated by

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

where ω_{dry} and ω_{wet} are the weights of dry and wet samples, respectively.

The swelling ratio was calculated from films 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.

RESULTS AND DISCUSSION

The sulfonated monomer, SBFBB, was synthesized via an electrophilic reaction²⁶ using fuming sulfuric acid (30%) as the sulfonation agent. The substitution reaction occurred on the ortho position of fluorine atoms. A long reaction period (~24 h) was required to obtain fully disulfonated monomer. The FTIR and NMR spectra were in good agreement with the expected structure. It was noted that sulfonation of the benzene ring connected with two carbonyl groups did not occur even at an extended reaction time of 48 h at 100 °C.

Copolymerization of bisphenol 6F/6F-PH with activated difluorinated aromatic ketones, SBFBB/

BFBB, was carried out in the presence of K_2CO_3 in NMP/DMAc as the solvent at 160–170 °C after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in Scheme 2. The SC of the polymers were controlled by the monomer feed ratios of SBFBB/BFBB. It is well known that the polymerization of commercial PEEKTM (Vicatex[®]) and PEEKKTM (Hostatec[®]) must be conducted under vigorous reaction condition including high temperature (>300 °C), due to their tendency for crystallization that leads to precipitation at the initial stage of polymerization. In contrast, improved solubility brought about by the introduction of bulky moieties into the polymer backbone maintains the growing polymer chain in solution during polymerization. High molecular weight polymers were readily obtained in 12 h under relatively mild polymerization conditions. The inherent viscosities of the resulting polymers were above 1.08 dL/g in DMAc at 30 °C (Table 1).

A typical FTIR spectral comparison of the polymers with different SC is given in Figure 1. Absorption bands around 1029 and 1085 cm^{-1} arise from symmetric and asymmetric stretching vibrations of sodium sulfonate groups, that around 1478 cm^{-1} arises from trisubstitution of benzene rings caused by the introduction of sodium sulfonate groups, and a characteristic band at around 1660 cm^{-1} is due to aryl carbonyl groups. Absorptions at 1029, 1085, and 1478 cm^{-1} increased obviously with the increase of SC.

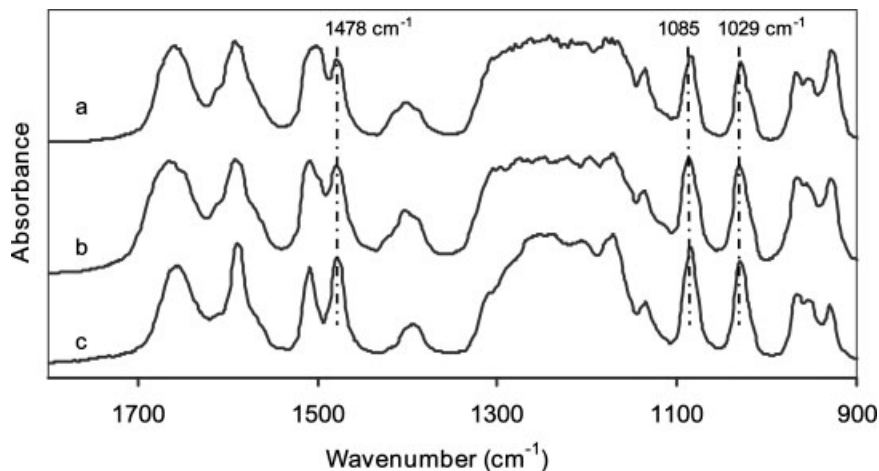


Figure 1. FTIR spectra of SPEEKK-6F-50 (a), SPEEKK-6F-70 (b), and SPEEKK-6F-100 (c) copolymers and homopolymer in sodium form.

^1H NMR (1D and 2D COSY) spectroscopy was used to confirm the structure of the sulfonated polymers. Figure 2 shows the aromatic region of SPEEKK-6F-Na with sulfonation contents (SCs) of 100, 80, and 50%. All three samples were measured using polar $\text{DMSO-}d_6$ as the solvent, which gave improved solubility for the polymers containing higher SC. The improved solubility resulted in better resolved spectra and less broad signals for SPEEKK-6F-100-Na and -80-Na compared with the less soluble SPEEKK-6F-50-Na with lower SC. Signal assignment is displayed for the repeat unit (R.U.) of the homopolymer (top spectrum) as well as the copolymers with SCs of 80 and 50%. The stacked spectra show variations in signal intensities of protons H-3,4,5 and H-7,8 of sulfonated and unsulfonated R.U. respectively; these variations are in accordance with the different feed ratios of the monomers used in the preparation of the polymers with different SCs. Figure 3 shows a spectrum and signal assignment of the aromatic region of SPEEKK-6FP-100-Na in $\text{DMSO-}d_6$. The bulky pendant phenyl group makes the R.U. nonsymmetrical resulting in 50% of the polymer chains as displayed in Figure 3 and 50% with the pendant group at the 3 position. As a result of this, the sulfonated ring protons H-6,7,8 appear as two signals of equal intensity. The complexity of the spectra increases dramatically as nonsulfonated R.U. are introduced into the polymer chains and therefore only the spectrum of SPEEKK-6FP-100-Na is shown in Figure 3.

The thermal properties of the polymers in acid form (—H) and sodium form (—Na) were evaluated by DSC and TGA, as summarized in Table 2.

The T_g s of SPEEKK-6F and SPEEKK-6FP polymers in acid form were above 196 °C and 212 °C, respectively. All the sulfonated polymers had higher T_g values than PEEK (~ 143 °C), PEEKK based on bisphenol 6F (~ 176 °C), and PEEKK based on 6F-PH (~ 163 °C). The polymers with higher SC showed higher T_g values, which is a result of an increased interactions and rigidity of the polymer chains brought about by the sulfonic acid group. No melting endotherms were observed in the DSC traces, which suggest that the nature of the polymers is amorphous. Despite the fact that the T_g value of nonsulfonated PEEKK based on bisphenol 6F is higher than the PEEKK based on 6F-PH, the SPEEKK-6FP series had higher T_g values than corresponding SPEEKK-6F series.

A distinct two-stage decomposition was observed from the TGA curves of SPEEKK-6F-H and SPEEKK-6FP-H (Fig. 4). The first decomposition was associated with the loss of the sulfonic acid groups in the range of 224–332 °C, and the other loss was caused by the decomposition of the main chains of the polymers in the range of 485–513 °C. Compared with the SPEEKK copolymers in acid form, those in the sodium form had high thermal stabilities. The temperatures at a 5% weight loss (T_{d5}) were all greater than 378 °C and the decomposition temperatures were above 407 °C in N_2 . SPEEKK-6F-40, -50, -60, -70 and SPEEKK-6FP-40, -50, -60, -70 polymers showed high thermal stability because of aromatic chains and strong C—F bonds their molecular structures.

Water uptake and swelling ratios of PEMs are closely related to SC, proton conductivity,

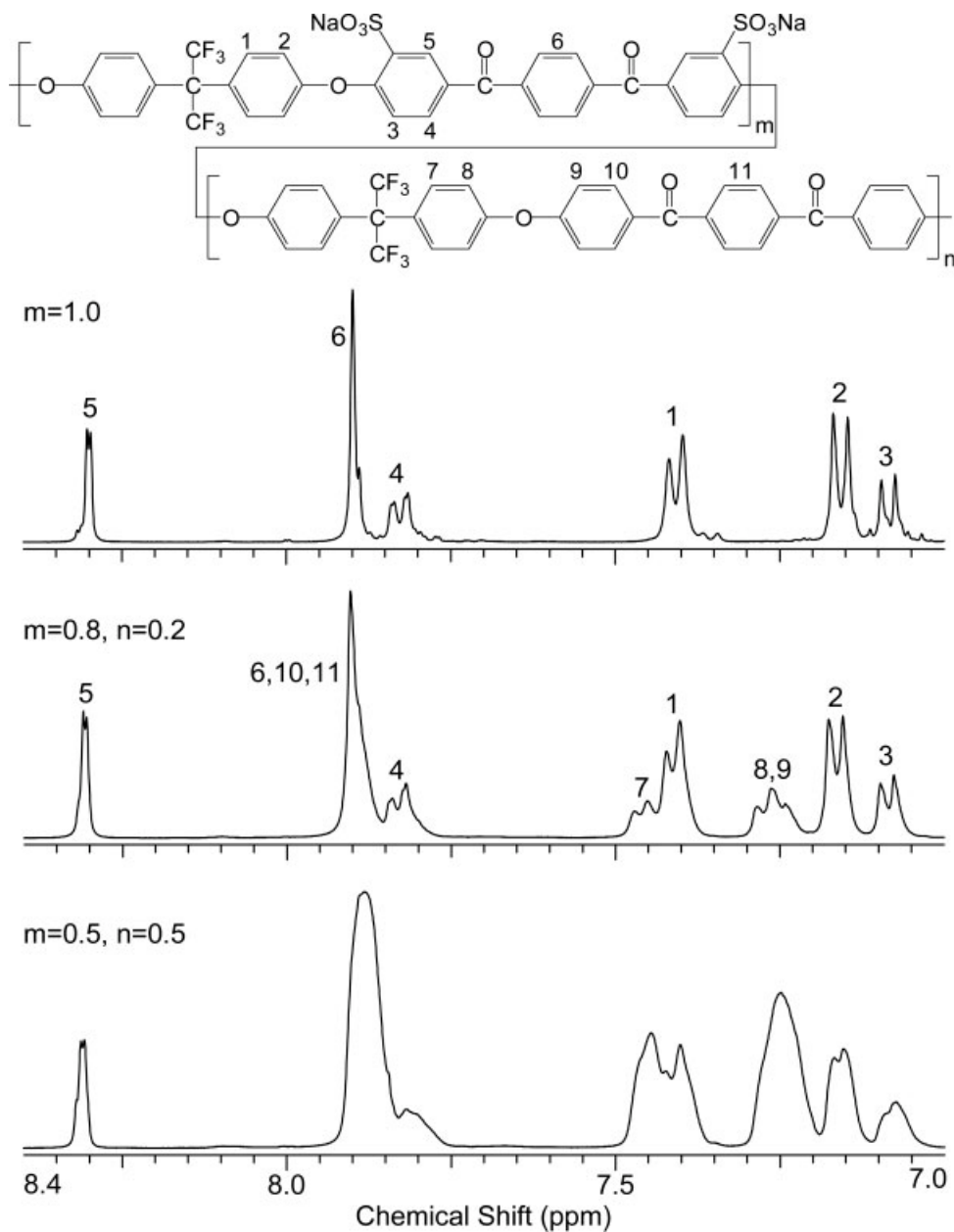


Figure 2. ^1H NMR spectra of SPEKK-6F-100-Na (top), SPEKK-6F-80-Na (middle), and SPEKK-6F-50-Na (bottom) in $\text{DMSO-}d_6$.

and mechanical strength. Fluorine-containing moieties impart a higher degree of hydrophobicity than nonfluorinated groups, which improves dimensional stability of the sulfonated polymer in water. The water uptake and swelling ratios of SPEKK-6F and SPEKK-6FP membranes were tested at 23 °C and 80 °C, and the results are listed in Table 3. The films were immersed in water at 23 °C for 24 h, after which time all the polymers had swelling ratios below 24%, and water uptakes less than 55%. At 80 °C,

SPEKK-6F-40, 50, 60, 70 and SPEKK-6FP-40, 50, 60 maintained their dimensional shapes. However, water uptakes and swelling ratios of SPEKK-6F-80 SPEKK-6FP-70 with high SC values increased dramatically, implying that these samples were above the percolation threshold. SPEKK-6FP-80 membrane dissolved in water at 80 °C after 24 h.

The proton conductivities of the membranes in SO_3H form as a function of the temperature are given in Figure 5. The conductivities of all

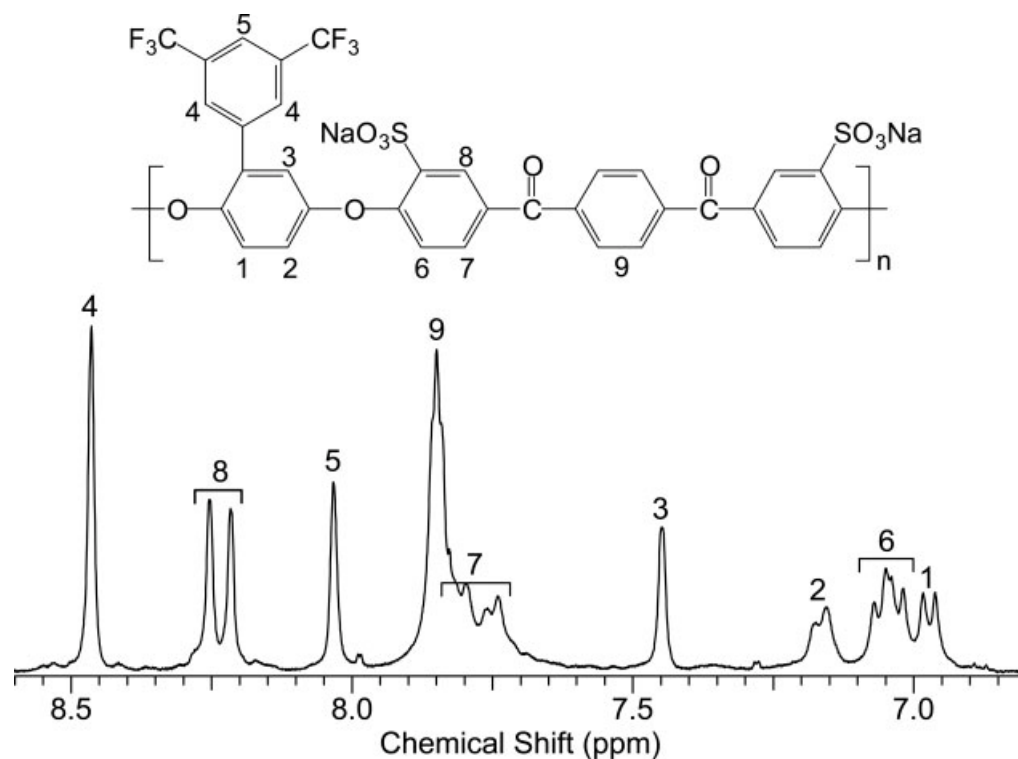


Figure 3. ^1H NMR spectrum of SPEEKK-6FP-100-Na homopolymer in $\text{DMSO-}d_6$.

the samples increased with increasing temperature. At the same temperature, high SC samples had higher conductivities. All of the samples exhibited proton conductivities higher than 1

$\times 10^{-2}$ at room temperature, which is regarded as the lowest value for PEM to use in fuel cells. Some of the copolymers showed higher proton conductivities than that of Nafion 112, and com-

Table 2. Thermal Properties of PEEKK Copolymers

Polymer	T_g^a ($^{\circ}\text{C}$)		T_{d5}^b ($^{\circ}\text{C}$)		T_d^c ($^{\circ}\text{C}$)		RW d (%)	
	–H e	–Na f	–H	–Na	–H	–Na	–H	
SPEEKK-6F-40	196	492	340	490	330/503	59.48	56.69	
SPEEKK-6F-50	203	492	338	488	323/512	60.30	56.33	
SPEEKK-6F-60	229	492	349	486	332/507	59.58	57.01	
SPEEKK-6F-70	236	486	326	484	308/513	60.57	46.89	
SPEEKK-6F-80	–	462	320	482	231/505	58.81	60.89	
SPEEKK-6F-100	–	465	255	479	224/504	59.76	48.46	
SPEEKK-6FP-40	212	487	341	487	270/485	58.48	57.34	
SPEEKK-6FP-50	219	478	358	473	279/489	60.16	57.78	
SPEEKK-6FP-60	235	479	358	481	279/489	58.48	57.78	
SPEEKK-6FP-70	239	477	324	470	261/489	59.81	55.77	
SPEEKK-6FP-80	271	479	311	467	265/485	59.93	55.75	
SPEEKK-6FP-100	–	378	–	407	–/–	55.47	–	

^a Glass transition temperature from the second heating cycle of DSC.

^b 5% Weight loss temperature measured by TGA.

^c Onset temperature of decomposition.

^d Residue weight at 700 $^{\circ}\text{C}$ in N_2 .

^e In acid form.

^f In sodium form.

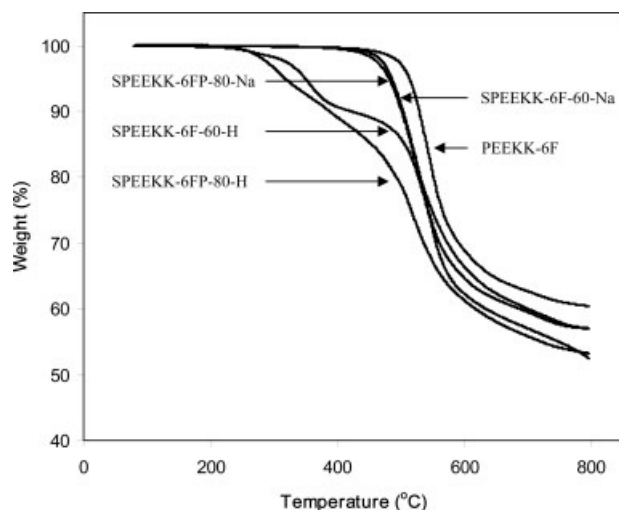


Figure 4. Typical TGA curves of the copolymers and PEEKK-6F.

parable proton conductivities to Nafion 117. At around 80 °C, proton conductivity values of SPEEKK-6FP-50 and SPEEKK-6FP-60 were 1.0×10^{-1} and 1.6×10^{-1} S/cm, which were higher than that of Nafion 117.

It was noted that the present SPEEKK-6F series had relatively low water uptake and swelling ratios while still maintaining comparable

proton conductivity in comparison with previously prepared SPAEEK²³ and SPAEEK-co-SPAEEKK²¹ copolymers having similar equivalent weight (EW) values. For example, the present SPEEKK-6F-50 (EW = 699) showed a higher proton conductivity (7.1×10^{-2} S/cm at 80 °C) and lower water uptake (10% at 80 °C) and swelling ratio (8% at 80 °C) than that of SPAEEK-40 (EW = 723, $\sigma = 3.0 \times 10^{-2}$ S/cm, water uptake 25%, swelling ratio 9% at 80 °C).

Based on similar EW, the present SPEEKK-6FP series containing bulky pendant groups exhibited higher water uptake and swelling ratios than those of the SPEEKK-6F series, which have comparatively regular molecular chains. It is likely that bulky pendant 3,5-ditrifluoromethyl-phenyl pendant groups led to large free volume between polymer chains, in which water molecules could be confined, as has been suggested in refs. 30 and 31. This supposition corroborates well with the observation of a higher conductivity exhibited by the SPEEKK-6FP series, particularly at 80 °C. For example, SPEEKK-6FP-50 and SPEEKK-6FP-60 have proton conductivities of 3.2×10^{-2} and 4.6×10^{-2} S/cm at 25 °C and 1.0×10^{-1} and 1.6×10^{-1} S/cm at 80 °C, respectively. Compared with SPEEKK-6FP-50 and SPEEKK-6FP-60, SPEEKK-6F-50 and SPEEKK-6F-60

Table 3. Water Uptake, Swelling Ratios, and Proton Conductivities of PEEKK Copolymers (SO₃H form) at Different Temperatures

Polymer	EW (g/mol SO ₃)/ IEC ^a (Mequiv g ⁻¹)	Water Uptake (%)		Swelling Ratio (%)		σ^b (S/cm)	
		23 °C	80 °C	23 °C	80 °C	25 °C	80 °C
SPEEKK-6F-40	853/1.17	2	7	2	5	3.1×10^{-2}	6.5×10^{-2}
SPEEKK-6F-50	699/1.43	5	10	3	8	3.4×10^{-2}	7.1×10^{-2}
SPEEKK-6F-60	595/1.68	9	20	5	16	4.4×10^{-2}	8.3×10^{-2}
SPEEKK-6F-70	522/1.92	21	81	10	60	5.0×10^{-2}	8.5×10^{-2}
SPEEKK-6F-80	467/2.14	30	SW ^c	19	SW	5.3×10^{-2}	9.6×10^{-2}
SPEEKK-6FP-40	836/1.20	8	16	3	6	1.3×10^{-2}	5.4×10^{-2}
SPEEKK-6FP-50	685/1.46	13	29	6	12	3.2×10^{-2}	1.0×10^{-1}
SPEEKK-6FP-60	584/1.71	15	54	8	33	4.6×10^{-2}	1.6×10^{-1}
SPEEKK-6FP-70	512/1.95	28	SW	15	SW	6.3×10^{-2}	–
SPEEKK-6FP-80	458/2.18	55	S ^d	24	S	1.1×10^{-1}	–
Nafion 112 ^e	1100/–	12	23	4.3	9.6	3.3×10^{-2}	5.6×10^{-2}
Nafion 117 ^f	1100/–	19	30	13	20	7.5×10^{-2}	9.6×10^{-2}

^a Calculated equivalent molecular weight (EW) and ionic exchange capability (IEC).

^b Proton conductivities of the membranes.

^c Sharply swollen in water at 80 °C.

^d Soluble in water at 80 °C.

^e The data were given in ref. 20.

^f The data were given in ref. 23.

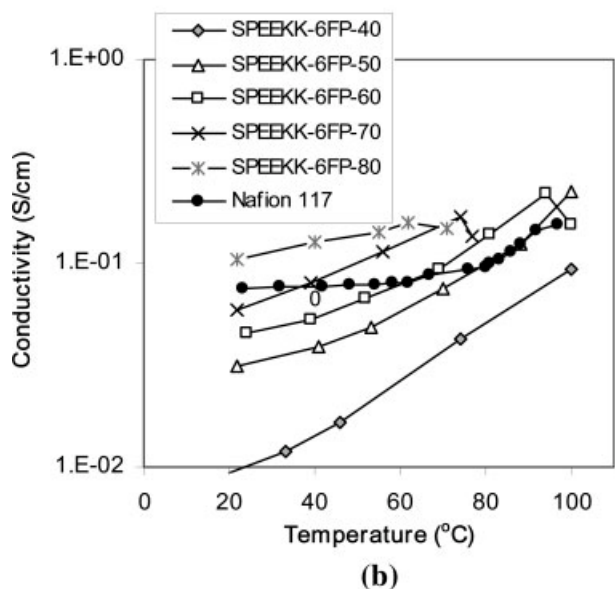
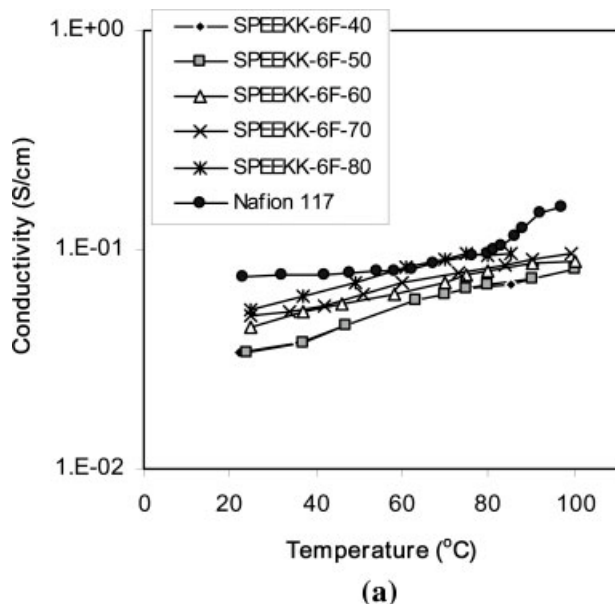


Figure 5. Proton conductivities of SPEEKK-6F (a) and SPEEKK-6FP (b) copolymers.

showed comparative proton conductivities at 25 °C (3.4×10^{-2} and 4.4×10^{-2} S/cm) but lower proton conductivities at 80 °C (7.1×10^{-2} and 8.3×10^{-2} S/cm).

The difference in the structures of these two polymers results in very different behavior when their conductivities are compared as IEC functions (Fig. 6). The less regular structure of the SPEEKK-6FP copolymer series provoke a lower conductivity at low SO_3H group concentration, but at higher SC provide a better pass for the protons than more ordered SPEEKK-6F.

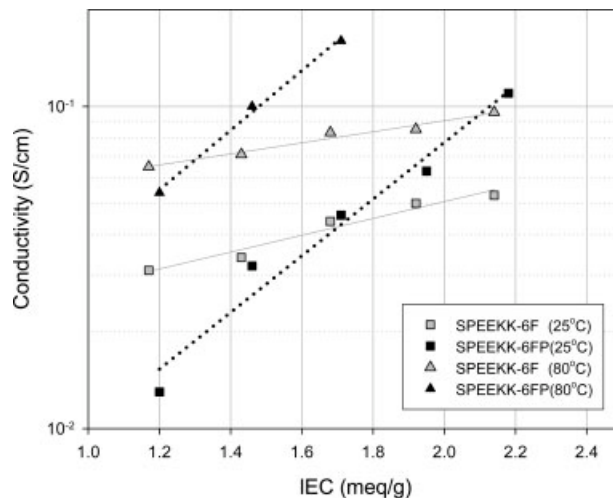


Figure 6. Conductivity of SPEEKK-6F and SPEEKK-6FP membranes as a function of the IEC at 25 and 80 °C.

The oxidative stability of the polymers was evaluated in Fenton's reagent at 80 °C. As expected, the polymers with the higher SC had the lower oxidative stability. SPEEKK-6FP-70 and SPEEKK-6F-70 membranes with high IEC value were dissolved into the Fenton reagent after about 30 min. The membranes of SPEEKK-6FP-60 and SPEEKK-6F-60 were dissolved after 1.5 and 2 h of treatment, respectively. SPEEKK-6FP-40, -50 and SPEEKK-6F-40, -50 maintained dimensional shapes after 6 h. They could not be dissolved in the reagent even after 12 h, indicating their relatively higher oxidative resistance.

The tensile properties of the films in the wet state were run to evaluate the quality of membranes under humidified conditions, as listed in Table 4. The samples in the wet state had tensile stress at maximum load of 36.5–60.7 MPa,

Table 4. Mechanical Properties of PEEKK Wet Films

Polymer	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
SPEEKK-6F-40	52.8	1.61	110
SPEEKK-6F-50	60.7	1.20	91
SPEEKK-6F-60	47.0	1.41	79
SPEEKK-6F-70	36.5	0.90	84
SPEEKK-6FP-40	52.7	1.21	141
SPEEKK-6FP-50	57.7	1.41	117
SPEEKK-6FP-60	59.2	0.61	116
Nafion 117	28.4	0.10	329

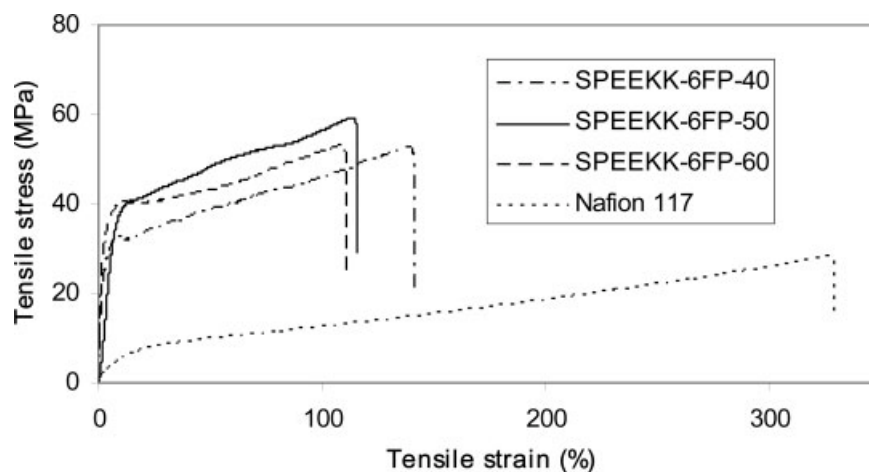


Figure 7. Tensile stress–strain properties of SPEEKK-6FP-40, -50, -60 and Nafion 117 wet films.

Young's moduli of 0.61–1.61 GPa, and elongations at break up to 79–141%. As shown in Figure 7, these materials showed higher tensile strengths and lower elongations than Nafion 117. The overall mechanical properties indicate that they are strong and flexible membrane materials.

CONCLUSIONS

Novel aromatic PEEKKs, SPEEKK-6F, and SPEEKK-6FP copolymer series, were synthesized using a nucleophilic substitution polycondensation derived from SBFBB and two fluorinated bisphenols. Flexible films in sodium form were obtained via solution casting, and then transformed to their acid forms by immersion in 2 N H₂SO₄ aqueous solution for 24 h. The resulting polymers in acid form showed high T_g values above 196 °C. The first-stage decomposition temperatures associated with the loss of sulfuric acid groups of polymers in acid form were in the range of 224–332 °C. The polymers in sodium form had high thermal stability up to 400 °C in N₂. SPEEKK-6F series had relatively low water uptake and swelling ratios while still maintaining comparable proton conductivity in comparison to SPAEEK and SPAEEK-co-SPAEEKK copolymers. All of the polymers possessed proton conductivities higher than 1×10^{-2} S/cm at room temperature, and proton conductivity values of several polymers were comparable to that of Nafion. SPEEKK-6FP-50 and SPEEKK-6FP-60 have proton conductivities up to 1.0×10^{-1} and 1.6×10^{-1} S/cm at 80 °C. Some of them exhibited excellent

tensile strength and good oxidative stability. Considering the combined properties of proton conductivities and dimensional stability in hydrated state, SPEEKK-6F-60, -70 and SPEEKK-6FP-50, -60 may be promising PEM materials for fabricating into membrane electrode assemblies for fuel cells.

Financial support for this project, provided by the joint research cooperation program between the National Science Council of Taiwan (Republic of China) and the National Research Council of Canada, is gratefully acknowledged.

REFERENCES AND NOTES

- Rikukawa, M.; Sanui, K. *Prog Polym Sci* 2000, 25, 1463.
- Stelle, B. C. H.; Heinzl, A. *Nature* 2001, 414, 345.
- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
- Roziere, J.; Jones, D. J. *Annu Rev Mater Res* 2003, 33, 503.
- Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membr Sci* 2002, 197, 231.
- Xiao, G. Y.; Sun, G. M.; Yan, D. Y.; Zhu, P. F.; Tao, P. *Polymer* 2002, 43, 5335.
- Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J Polym Sci Part A: Polym Chem* 1993, 31, 853.
- Gao, Y.; Robertson, G. P.; Guiver, M. D.; Jian, X. G.; Mikhailenko, S. D.; Wang, K. P.; Kaliaguine, S. *J Polym Sci Part A: Polym Chem* 2003, 41, 2731.
- Gao, Y.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Macromolecules* 2004, 37, 6748.

10. Wang, F.; Chen, T. L.; Xu, J. P. *Macromol Rapid Commun* 1998, 19, 135.
11. Kerres, J. A. *J Membr Sci* 2001, 185, 3.
12. Nolte, R.; Ledjeff, K.; Bauer, M.; Mülhaupt, R. *J Membr Sci* 1993, 83, 211.
13. Miyatake, K.; Chikashige, Y.; Watanabe, M. *Macromolecules* 2003, 36, 9691.
14. Fang, J. H.; Guo, X. X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* 2002, 35, 9022.
15. Miyatake, K.; Asano, N.; Watanabe, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 3901.
16. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* 2001, 42, 359.
17. Wang, L.; Meng, Y. Z.; Wang, S. J.; Shang, X. Y.; Li, L.; Hay, A. S. *Macromolecules* 2004, 37, 3151.
18. Miyatake, K.; Oyaizu, K.; Tsuchida, E.; Hay, A. S. *Macromolecules* 2001, 34, 2065.
19. Jones, D. J.; Rozière, J. *J Membr Sci* 2001, 185, 41.
20. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *J Polym Sci Part A: Polym Chem* 2004, 42, 2866.
21. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Polymer* 2005, 46, 3257.
22. Kreuer, K. *J Membr Sci* 2001, 185, 29.
23. Xing, P.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Macromolecules* 2004, 37, 7960.
24. Tchatchoua, C.; Harrison, W.; Einsla, B.; Sankir, M.; Kim, Y. S.; Pivovar, B.; McGrath, J. E. *Prepr Symp—Am Chem Soc Div Fuel Chem* 2004, 49, 601.
25. Liu, B. J.; Hu, W.; Chen, C. H.; Jiang, Z. H.; Zhang, W. J.; Wu, Z. W.; Matsumoto, T. *Polymer* 2004, 45, 3241.
26. Li, X. F.; Na, H.; Lu, H. *J Appl Polym Sci* 2004, 94, 1569.
27. Wang, F.; Chen, T. L.; Xu, J. P. *Macromol Chem Phys* 1998, 199, 1421.
28. Cotter, R. J. *Engineering Plastics: Handbook of Polyarylethers*; Gordon & Breach: Switzerland, 1995.
29. Zawodzinski, T. A.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J Phys Chem* 1991, 95, 6040.
30. Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem Commun* 2003, 368.
31. Miyatake, K.; Zhou, H.; Matsuo, T.; Uchida, H.; Watanabe, M.; *Macromolecules* 2004, 37, 4961.