



# Novel sulfonated poly(ether ether ketone)s for direct methanol fuel cells usage: Synthesis, water uptake, methanol diffusion coefficient and proton conductivity

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## ABSTRACT

A novel series of sulfonated poly(ether ether ketone)s (SPEEKs) with different degrees of sulfonation (Ds) were synthesized from 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1,3-SFBB-Na), 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB) and 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) by aromatic nucleophilic polycondensation. The chemical structures of SPEEKs were confirmed by FT-IR spectroscopy and the Ds values of the polymers were calculated by <sup>1</sup>H NMR and titration methods, respectively. The thermal stabilities of the SPEEKs in acid and sodium forms were characterized by thermogravimetric analysis (TGA), which showed that SPEEKs had excellent thermal properties at high temperatures. All the SPEEK polymers were easily solution cast into tough membranes. Water uptakes, proton conductivities and methanol diffusion coefficients of the SPEEK membranes were measured. Water uptake increased with Ds and temperature. Compared to Nafion, the SPEEK-60, -70 and -80 membranes showed higher proton conductivities at 80 °C, while the other SPEEK membranes showed relatively lower proton conductivities. This may be due to the different distribution of ion-conducting domains in membrane. However, these membranes showed lower methanol diffusions in the range of  $8.32 \times 10^{-9}$  to  $1.14 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  compared with that of Nafion ( $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) at the same temperature. The membranes also showed excellent mechanical properties (with a Young's modulus > 1 GPa and a tensile strength > 40 MPa). These results indicate that the SPEEK membranes are promising materials for use in direct methanol fuel cell (DMFC) applications.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), which convert chemical energy efficiently into electrical energy via oxidation and reduction reactions, are receiving considerable attention as transport, stationary, and portable future power sources because of their low emissions and high energy conversion efficiency [1–3]. The proton exchange membrane (PEM), which provides ionic pathways to transfer protons in PEMFCs as well as acting as a separator between the electrodes for the reactant gases, protons, fuel and electrons, is the key component of the PEMFCs. Nafion, one of the perfluorosulfonic acid membranes, is the current state-of-the-art PEM material, due to its good mechanical, thermal and chemical stability, in addition to

high proton conductivity at moderate temperatures (<90 °C) with relatively low ion-exchange capacity (IEC). However, several drawbacks of Nafion, such as high cost, high methanol permeability, low humidity and a major reduction in conductivity at high temperatures, have led researchers to investigate promising alternatives [2,4]. Presently, numerous research efforts are focusing on the sulfonated aromatic polymers because of their low cost, high proton conductivity, and their high thermal, chemical and mechanical stabilities [5–20].

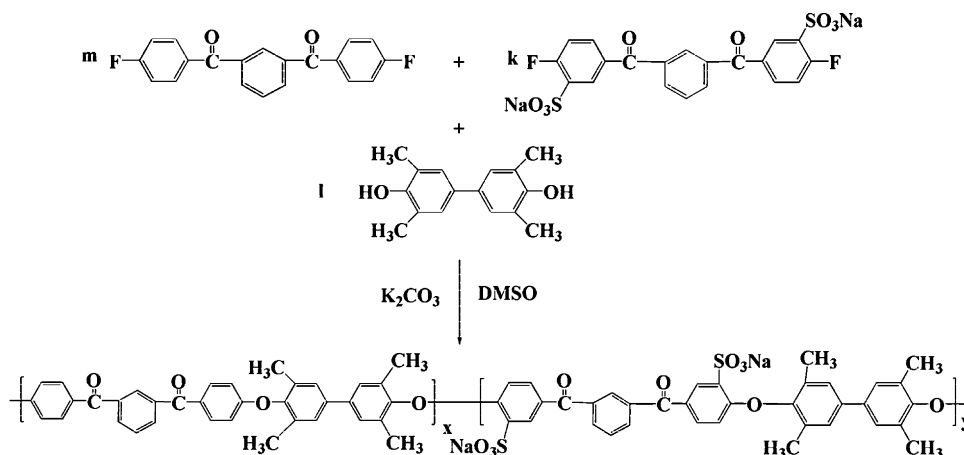
Poly(aryl ether ketone)s, which are important engineering resins, are well known for their excellent high thermal stability, mechanical properties, and oxidation resistance. Two general approaches are available for the synthesis of sulfonated high-performance aromatic polymers: (i) post-sulfonation of existing aromatic polymers usually leading to random functionalization along the polymer main chain and (ii) the direct copolymerization of sulfonated monomers to afford random copolymers [11,21–23].

Several groups, including our own, use the approach of direct copolymerization of sulfonated monomers, which enables better

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Scheme 1. The preparation of SPEEKK copolymers.

control of morphology and the number of sulfonic acid functions, so as to synthesize a series of sulfonated copoly(aryl ether ketone)s and sulfonated copoly(aryl ether sulfone)s which differ from each other by the structure of the bisphenol monomers [24,25].

In our previous work, new SPEEKK polymer structures with a *para*-substituted chain have been explored for PEMs [26]. These membranes showed better thermal stability and methanol resistance than Nafion while their proton conductivities were relatively lower. It is well known that there are two domain regions in the proton membrane materials: hydrophilic and hydrophobic ones. The hydrophobic domains, which were formed by non-sulfonated polymer segments, provide the hydrated PEMs with mechanical strength, while the hydrophilic domains containing the sulfonate groups supply the proton conductivity with acid groups. The microphase-separated structures developed by the existence of the two regions determine all the properties of PEMs such as water swelling, methanol cross-over and proton conductivity, etc.

In this study, a novel series of SPEEKKs with different degrees of sulfonation ( $D_s$ ) were synthesized from 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1,3-SFBB-Na), 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB) and 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) by aromatic nucleophilic polycondensation. FT-IR spectroscopy was used to confirm the chemical structures of the SPEEKKs.  $D_s$  were calculated by  $^1\text{H}$  NMR and titration methods, respectively. The thermal stabilities of the SPEEKKs in acid and sodium forms were characterized by thermogravimetric analysis (TGA). SPEEKK membranes were easily prepared with solution casting method. Water uptakes, proton conductivities and methanol diffusion coefficients and mechanical properties of the SPEEKK membranes were measured. And the results show the SPEEKK

membranes are promising alternatives to Nafion membranes in DMFCs.

## 2. Experimental

### 2.1. Materials

1,3-Bis(4-fluorobenzoyl)benzene (1,3-FBB) was purchased from Aldrich. 50% fuming sulfuric acid was obtained from Beijing Chemical Works, China. 3,3',5,5'-Tetramethyl-4,4'-biphenol (TMBP) was synthesized by our own group. 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1,3-SFBB-Na) was synthesized following a published procedure [27,28]. DMSO and toluene were purchased and used without further purity.

### 2.2. Synthesis and characterization of sulfonated poly(ether ether ketone ketone)s

As shown in Scheme 1, to a 500-ml completely dried 3-neck flask equipped with a mechanical stirring drive, 1,3-bis(4-fluorobenzoyl)benzene monomer  $k$  ( $k$  mol), 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene monomer  $m$  ( $m$  mol), 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) monomer  $l$  ( $m+k$  mol), and anhydrous potassium carbonate were added together in a DMSO/toluene solvent system. The temperature of round flask was maintained at 140 °C for 3 h in order to remove all the water azeotropically with toluene. Then the system temperature was raised to 180 °C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts and

**Table 1**  
The characterization data of sulfonated polymers.

Polymer	X (mmol) <sup>a</sup>	Y (mmol) <sup>a</sup>	$D_s$ (cal) <sup>b</sup>	$D_s$ (mea) <sup>c</sup>	$D_s$ (nmr) <sup>d</sup>	Yield (%)	$\eta_{sp}$ (dl g <sup>-1</sup> ) <sup>e</sup>
SPEEKK-10	4	36	0.2	0.18	0.18	94	0.85
SPEEKK-20	8	32	0.4	0.36	0.37	95	1.03
SPEEKK-30	12	28	0.6	0.57	0.58	96	1.35
SPEEKK-40	16	24	0.8	0.73	0.72	93	1.57
SPEEKK-50	20	20	1.0	0.89	0.90	96	1.01
SPEEKK-60	24	16	1.2	1.12	1.20	94	1.26
SPEEKK-70	28	12	1.4	1.30	1.38	95	1.48
SPEEKK-80	32	8	1.6	1.43	1.59	93	1.07

<sup>a</sup> The content of monomer  $m$  and monomer  $k$  in the reaction.

<sup>b</sup> Sulfonation degree obtained by calculation.

<sup>c</sup> Sulfonation degree obtained by titration.

<sup>d</sup> Sulfonation degree obtained by  $^1\text{H}$  NMR.

<sup>e</sup> The intrinsic viscosity in DMF at 25 °C.

DMSO were removed by washing in boiling water. Then the pure samples of the polymers were dried under vacuum at 100 °C for 24 h. The Ds values of the polymers were controlled by reacting different amounts of monomers *m* and *k*, as listed in Table 1.

FT-IR measurements were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer. The intrinsic viscosities of the polymers were measured at 5.00 gL<sup>-1</sup> in DMF at 25 °C (±1) using an Ubbelodhe viscometer. The <sup>1</sup>H NMR spectra were measured with a BRUKER AVANCZ 500 spectrometer at 298 K with deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as the solvent and tetramethylsilane (TMS) as the standard.

A Pyris-1 (PerkinElmer) TGA was used to study the thermal stability behavior of the SPEKK samples. Before testing, all the polymers were preheated to 150 °C and kept at this temperature for 20 min to remove any residual moisture and solvent. After that, the samples were cooled to 100 °C and then reheated to 650 °C with a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub> flow.

<sup>1</sup>H NMR spectrometry was used to characterize the molecular structure of the sulfonated polymers and to determine Ds (mol.% of sulfonated units). The Ds value was determined from the ratio of a peak in the sulfonated region to one in both the sulfonated and non-sulfonated regions [29]. The Ds value was calculated by the integration of these peaks and with the following formula:

$$\frac{D_s}{16 - D_s} = \frac{AH_1}{\sum AH} \quad (1)$$

where AH<sub>1</sub> is the intensity of H<sub>1</sub> (8.25–8.37 ppm) and  $\sum AH$  is the intensity of the remaining aromatic signals (6.42–8.11 ppm).

### 2.3. Preparation and characterization of SPEKK membranes

#### 2.3.1. Membrane preparation

The SPEKKs were dissolved in DMF to form 10 wt.% solutions. Then the resulting solutions were cast onto clean glass plates and dried at 85 °C for 10 h and then at 100 °C for 48 h in a vacuum oven until most of the solvent was removed. To obtain the membrane in acid form, the membranes were removed from the glass plates and were immersed in 1.0 M HCl solutions overnight, and then rinsed with deionized water to remove any excess acid.

#### 2.3.2. Water uptake and swelling ratio

The water uptake (WU) and swelling ratio were measured by the difference in weight and length between the dry and the swollen membranes in acid form. The membranes were dried at 100 °C for 48 h and measured the weights and lengths as the dry state values. Then the membranes were soaked in distilled water at different temperatures for 48 h. After swelling completely, the samples were taken out and then wiped to quickly remove the excess water that adhered to the surface with a tissue paper. The weights and lengths in the wet state were measured. Water uptake (WU) of the membrane was calculated from the following formula:

$$\text{water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the dry and corresponding water swollen membranes, respectively.

Also, the swelling ratio was calculated from films (5–6 cm) with the following equation:

$$\text{swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

where  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the lengths of the dry and corresponding water swollen membranes, respectively.

#### 2.3.3. Ion-exchange capacity (IEC), proton conductivity and methanol diffusion coefficient

The IEC values were determined by titration. Firstly, the membranes in acid form were immersed in 1 M NaCl solutions for 24 h to exchange all the H<sup>+</sup> ions by Na<sup>+</sup> ions. The H<sup>+</sup> ions in solution were then titrated with 0.01 M NaOH using a phenolphthalein indicator. The ion-exchange capacities of the membrane were calculated from the titration data via the following relationship:

$$\text{IEC} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight of dried membrane}} (\text{mequiv. g}^{-1}) \quad (4)$$

The theoretical IEC that was calculated from the Ds of the polymers was obtained from the following equation:

$$\text{IEC} = \frac{1000 D_s}{520 + 80 D_s} \quad (5)$$

The proton conductivity of the membranes were carried out via AC impedance spectroscopy using an impedance/gainphase analyzer (Solatron 1260, Solatron Analytical, UK) in combination with an electrochemical interface (Solatron 1287), over a frequency range of 10–10<sup>7</sup> Hz with 50–500 mV oscillating voltage. The humidity was kept at 100% during all the conductivity measurements. The proton conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (6)$$

where  $\sigma$  is proton conductivity, *L* is membrane thickness, *R* is membrane resistance and *A* is membrane area.

Methanol diffusion coefficients of the membranes were measured by using a two-chamber liquid permeability cell described in the literature [24,30,31]. This cell consisted of two reservoirs, which were separated by a vertical membrane immersed in DI water for 24 h. Pure methanol (100 ml) was placed on one side of the diffusion cell and water (100 ml) was placed on the other side. The magnetic stirrers were used continuously during the measurement on both sides. Methanol concentrations in the water cell were periodically determined by using a GC-8A gas chromatograph (SHIMADZU, Tokyo, Japan). The methanol diffusion coefficient was calculated with the following equation:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (7)$$

where *A*, *L* and  $V_B$  were the effective area, the thickness of membrane and the volume of the permeated reservoirs, respectively.  $C_A$  and  $C_B$  were the methanol concentration in the methanol chamber and in water chamber, respectively. *DK* was the methanol diffusion coefficient.

#### 2.3.4. Mechanical properties

The tensile strength of the membranes was measured using SHIMADZU AG-1 1KN at a test speed of 2 mm min<sup>-1</sup>, and the size of specimen was 15 mm × 4 mm. For each testing reported, at least three measurements were taken and an average value was calculated.

## 3. Results and discussion

### 3.1. Preparation and characterization of the polymers

As shown in Scheme 1, the sulfonated poly(ether ether ketone)s with different Ds were prepared by an aromatic nucleophilic substitution polycondensation in high yields (>93%). In this system, the content of monomer I was kept at 40 mmol, which is equal to the combined amount of monomer *m* and monomer *k*. The Ds values were controlled by adjusting the ratio of monomer *m* to monomer *k*. The polymerization results and analytical data are displayed in Table 1. The Ds values were measured by both titration

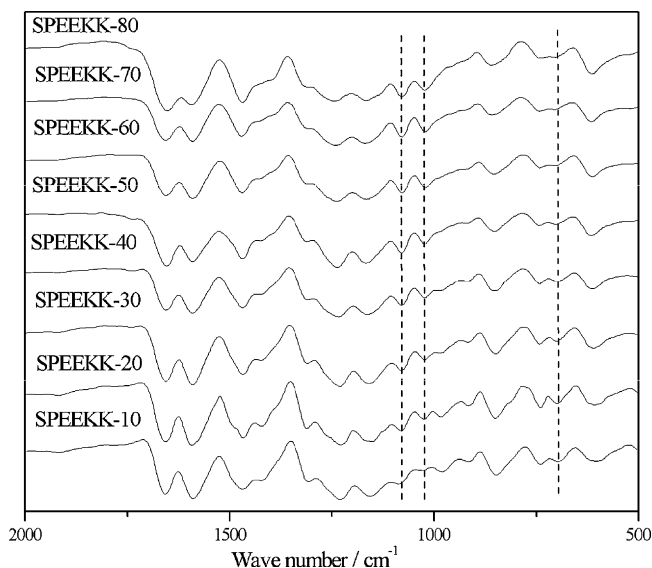


Fig. 1. FT-IR spectra of SPEKKs.

and  $^1\text{H}$  NMR data and the results agree with the calculated ones. The high intrinsic viscosities of the polymers mean that the polymers have high molecular weights. This reaction proceeds by a classical nucleophilic aromatic substitution.

The chemical structures of the polymers were confirmed by FT-IR spectroscopy. Fig. 1 shows the FT-IR spectra of SPEKK polymers. The absorption bands at  $1080$  and  $1024\text{ cm}^{-1}$  can be assigned to asymmetric and symmetric  $\text{O}=\text{S}=\text{O}$  stretching vibrations of sodium sulfonate groups. The absorption band at  $699\text{ cm}^{-1}$  can be assigned to the  $\text{S}-\text{O}$  stretching of sodium sulfonate groups. No peaks attributed to the aromatic sulfone group in the range of  $1140\text{--}1110\text{ cm}^{-1}$  were found, which indicates that no cross-linking occurred during copolymerization.

$^1\text{H}$  NMR spectroscopy was used as the principal method for characterization of polymers in the  $\text{Na}^+$  form.  $^1\text{H}$  NMR spectra obtained

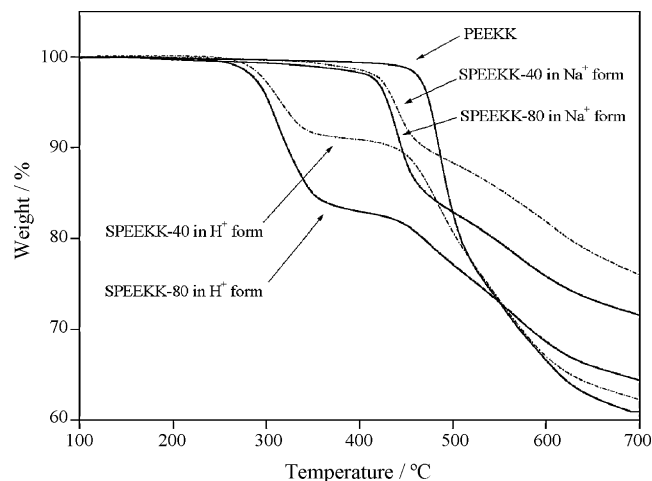


Fig. 3. TGA curves of PEEKK and SPEKK-40, SPEKK-80 in acid and sodium forms.

in  $\text{DMSO-}d_6$  provided unambiguous structure elucidation. Fig. 2 shows the aromatic region of a  $^1\text{H}$  NMR spectrum of SPEKK-80 polymer sample. Each signal was assigned to a single proton or to a group of aromatic protons. The Ds can be derived from the ratio between the peak area of the  $^1\text{H}$  signal, and the integrated peak area of the signals of other protons. The Ds that calculated from  $^1\text{H}$  NMR spectrometry and summarized in Table 1 was well consistent with monomer feed ratio values, which clearly suggest that Ds can be readily manipulated by controlling the amount of sulfonated monomer added.

### 3.2. Thermal stabilities of polymers

The thermogravimetric analysis (TGA) curves of the SPEKK polymers both in acid and sodium forms are shown in Fig. 3. The TGA experiments were performed at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . All the polymers in the sodium form have better thermal stability than those of the acid form. For SPEKK-80, the tempera-

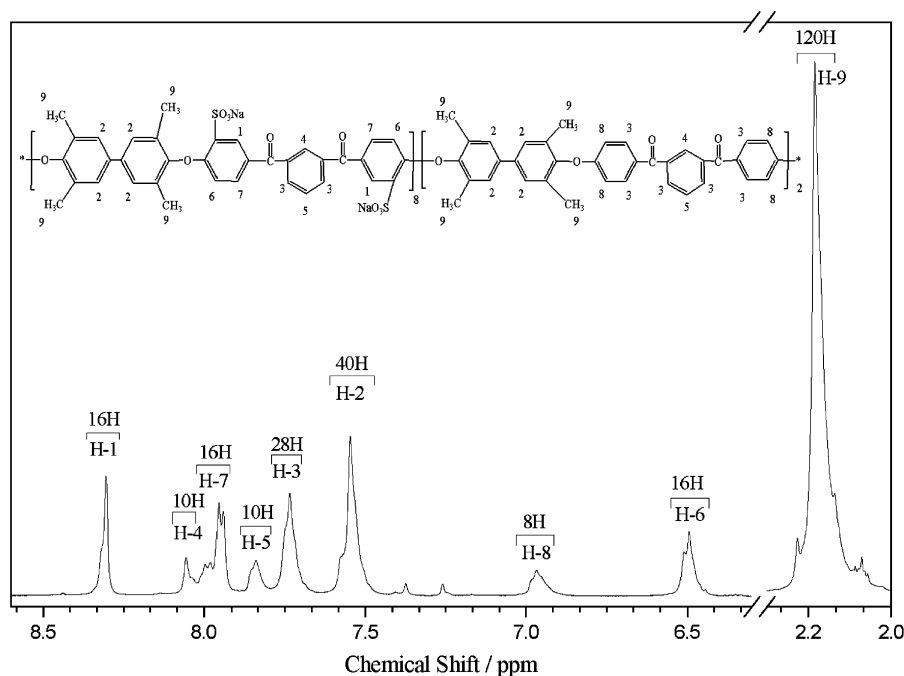


Fig. 2.  $^1\text{H}$  NMR spectrum of SPEKK-80 polymer in  $\text{DMSO-}d_6$ .

tures at 10% weight loss ( $T_{d10\%}$ ) are 445 and 323 °C in the sodium and the acid form, respectively.  $T_{d10\%}$  decreased with an increase in the concentration of the sodium sulfonate groups in the polymer chain. This may be due to the thermal decomposition temperature of the sulfonic acid groups was lower than that of the backbone of the polymers [32]. As observed previously, there are two distinct weight loss steps in the TGA curves of SPEEKK polymers [11,23,24]. The second thermal degradation in both the sodium and the acid forms around 450 °C are assigned to the degradation of the polymer main chain, indicating that the incorporation of 3,3',5,5'-tetramethyl-4,4'-biphenol did not decrease the thermal stability due to the strong  $-CH_3$  bonds. Compared with SPEEK [24], no obvious difference in the thermal stability of SPEEKK polymers was observed and because all of their 10% weight loss temperatures and the extrapolated onset temperatures are higher than 300 °C, the SPEEKK polymers in acid form have high thermal stability.

### 3.3. The properties of membrane

#### 3.3.1. Water uptake, swelling ratio and water desorption

Water uptake and swelling ratio of membranes play a very important role in the properties of the PEMs. First of all, the proton transport in SPEEKK membranes is largely influenced by the water content in the membranes. Since proton conduction requires a significant amount of water to coordinate with a proton as it moves through the membrane, the proton conductivity increases when the water uptake increases. Ionic membranes are not good proton conductors in the dry state, but they become conductive and functioning when hydrated. At the same time, the ionized sulfonic acid groups provide counter ions to the protons for transport in the PEMs. So, it is very important to select membranes with appropriate levels of sulfonic acid groups and water uptake. The sulfonic acid groups form hydrophilic hydrated domains contributing to the proton conductivity and the non-sulfonated backbone forms a well-networked hydrophobic domain providing mechanical strength. Most of the sulfonated copoly(aryl ether ketone)s, such as SPEEK, exhibit hydrophobic/hydrophilic nanophase separation in the presence of water [3,24]. Figs. 4 and 5 and Table 2 present the water uptake (wt.%) and linear swelling (%) of SPEEKK membranes in the acid form at different temperatures. They show the swelling and water uptake as a function of temperature. Because only the hydrophilic domains of the nanostructure are hydrated in the presence of water, Fig. 4 clearly shows that the water uptake continues to increase with Ds and temperature, and is especially high for SPEEKK-80, which was about 300%. Also, the sulfonate groups in SPEEKKs are dispersed throughout the aromatic matrix, and the membrane with the lower Ds is less hydrophilic than the higher Ds ones. All these characteristics lead to the increased water uptakes of SPEEKK membranes with increasing Ds. Table 2 shows the linear swelling of SPEEKK membranes at 25 and 80 °C. The results show that the linear swelling increased with the increasing Ds. Fig. 5 shows that the linear swelling at 80 °C increased from

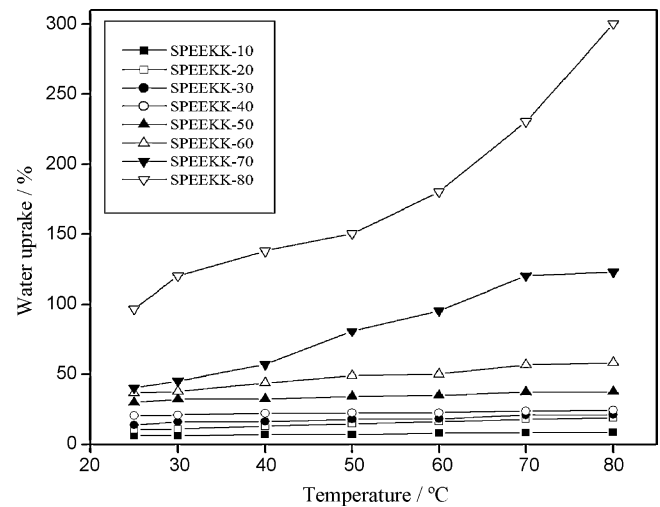


Fig. 4. Water uptake of SPEEKK membranes.

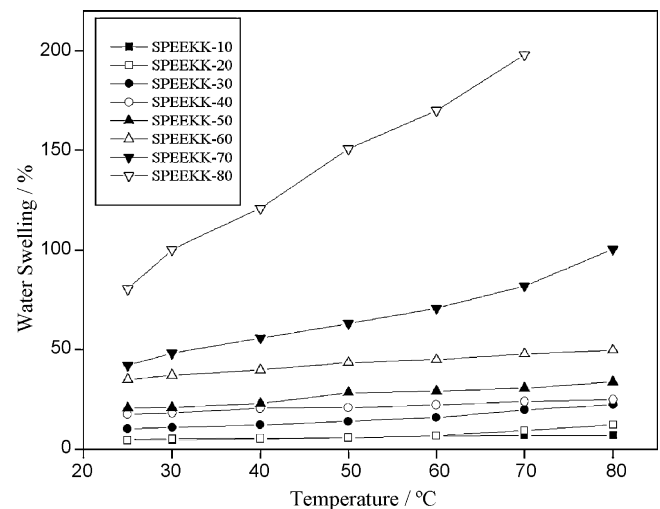


Fig. 5. Water swelling of SPEEKK membranes.

71.1 to 100.6%. However, the swelling data of the SPEEKK-80 was not obtained at 80 °C because the membrane was unable to maintain a smooth morphology after several hours in water at 80 °C, although the water uptake data could still be obtained at this moment.

#### 3.3.2. IEC, proton conductivity and methanol diffusion coefficient

The IEC of a sulfonated polymer is usually defined as the mmoles of attached  $SO_3^-$  sites per gram of polymer. The IEC values play a definitive role in determining the proton conductivity of membranes in the fuel cells. Table 3 shows that the IEC values of the

**Table 2**  
Thermal stabilities and water properties of SPEEKK copolymers.

Polymer	$T_{d10\%}$ (°C) <sup>a</sup>		Water uptake (%)		Swelling ratio (%)	
	Sodium form	Acid form	25 °C	80 °C	25 °C	80 °C
SPEEKK-10	492	486	5.9	8.5	4.5	7.1
SPEEKK-20	487	473	10.6	18.9	4.7	12.3
SPEEKK-30	473	445	13.9	21.2	10.3	22.5
SPEEKK-40	470	436	20.7	24.4	17.6	25.0
SPEEKK-50	468	387	29.9	37.7	20.7	33.9
SPEEKK-60	456	350	36.8	58.2	35.0	49.8
SPEEKK-70	442	335	40.5	123.1	42.2	100.6
SPEEKK-80	445	323	96.9	300.2	80.5	–

<sup>a</sup> Temperature at 10% weight loss.



**Table 3**  
The properties of membranes.

Polymer	$d^a$ ( $\mu\text{m}$ )	IEC (mequiv. $\text{g}^{-1}$ )			Methanol diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )	Proton conductivity ( $\text{S cm}^{-1}$ )	
		Calculated	Measured <sup>b</sup>	NMR <sup>c</sup>		25 °C <sup>d</sup>	80 °C <sup>d</sup>
SPEEKK-10	53	0.37	0.04	0.34	$8.32 \times 10^{-9}$	0.005	0.022
SPEEKK-20	100	0.72	0.45	0.67	$6.28 \times 10^{-8}$	0.007	0.032
SPEEKK-30	97	1.05	0.93	1.02	$1.72 \times 10^{-7}$	0.014	0.035
SPEEKK-40	96	1.36	1.09	1.24	$3.65 \times 10^{-7}$	0.019	0.062
SPEEKK-50	87	1.66	1.30	1.52	$3.24 \times 10^{-7}$	0.027	0.072
SPEEKK-60	121	1.94	1.46	1.94	$1.02 \times 10^{-7}$	0.052	0.139
SPEEKK-70	79	2.20	1.69	2.18	$2.45 \times 10^{-7}$	0.073	0.161
SPEEKK-80	90	2.45	1.97	2.43	$1.14 \times 10^{-7}$	0.098	0.201

<sup>a</sup> Thickness of membranes.

<sup>b</sup> IEC obtained by titration.

<sup>c</sup> IEC obtained by calculation from  $^1\text{H}$  NMR.

<sup>d</sup> The proton conductivity measured at different temperatures with 100% relative humidity.

SPEEKK membranes as determined by titration and from Ds calculations, increased with the Ds, and the titrated values are in good agreement with the calculated IEC values. The IEC values of the membranes were controlled during synthesis by adjusting the various ratios of sulfonated to unsulfonated monomers. This indicates that the sulfonate groups were successfully incorporated into the polymer backbones via sulfonated monomer copolymerization without any side reactions.

Proton conductivities of the membranes at different temperatures were calculated from resistance measurements and are summarized in Table 3. As reported in Fig. 6, the proton conductivity of membranes increased when Ds (or IEC) and temperature increased. SPEEKK-60, -70 and -80 membranes showed higher proton conductivities than  $10^{-2} \text{ S cm}^{-1}$  at 80 °C and 100% relative humidity, which is the lowest value of practical interest for use as proton exchange membranes in fuel cells. The values are higher than that of Nafion, which may be an indication that percolation in the hydrophilic domains of these three polymers is possibly similar to that of Nafion 117 [3]. Compared to Nafion, all the other SPEEKK membranes showed relatively lower proton conductivity, and this is possibly due to the different distribution of ion-conducting domains in membrane [33]. Because of the more ion-rich domains that Nafion has, the ions move more easily than those in the SPEEKK. This is attributed to the lower hydrophobicity of SPEEKK polymer backbone compared with the perfluorinated backbone of Nafion, as well as to the relatively strong interactions between the water molecules and sulfonic acid groups [2], which

**Table 4**  
The mechanical properties of SPEEKK membranes.

Membrane	Tensile strength (MPa)	Maximum elongation (%)	Tensile modulus (GPa)
SPEEKK-10	56.31	14.49	1.37
SPEEKK-20	43.88	8.89	1.21
SPEEKK-30	55.43	12.70	1.35
SPEEKK-40	52.68	8.50	1.23
SPEEKK-50	41.72	4.06	1.6
SPEEKK-60	49.82	10.41	1.32
SPEEKK-70	44.31	15.01	1.21
SPEEKK-80	45.20	8.64	1.15

results in improving water retention and increasing proton conductivity at elevated temperature.

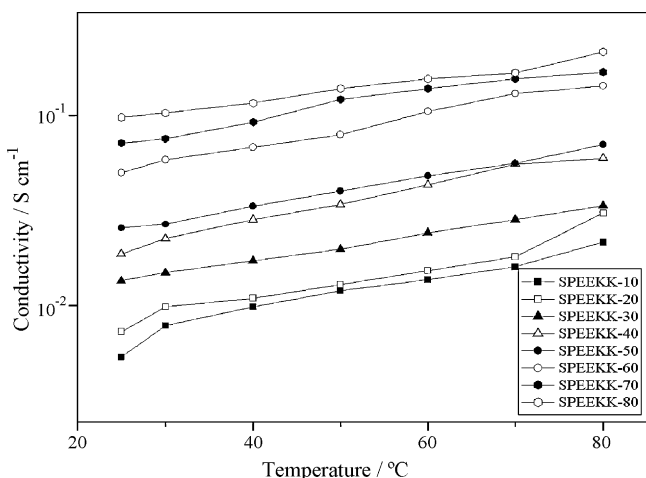
For DMFCs performance, methanol permeability and proton conductivity are the two key properties. What a real DMFC environment needs is low methanol permeability and high proton conductivity. Table 3 shows that the SPEEKK membranes exhibit increased methanol diffusion coefficients at 25 °C depending on the Ds. These membranes show low methanol diffusion in the range of  $8.32 \times 10^{-9}$  to  $1.14 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which is much lower than that of Nafion ( $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) at the same temperature. The results suggest the influence of the position of sulfonate group in polymer on the hydrodynamic solvent transport (water and methanol) properties of membranes. In the SPEEKK membranes, sulfonate groups are dispersed throughout the polymer matrix and are not easily phase separated. However, the sulfonate groups in Nafion are on the side chains of polymers which may lead to phase separation [34]. All these characteristics lead to a much lower methanol diffusion coefficient for SPEEKK membranes than for Nafion.

### 3.3.3. Mechanical properties of SPEEKK membranes

The mechanical properties of SPEEKK membranes are shown in Table 4. The initial Young's modulus for the SPEEKK membranes is 1.37, 1.21, 1.35, 1.23, 1.6, 1.32, 1.21 and 1.15 GPa, respectively, which are higher than that of Nafion 117 (249 MPa). All the SPEEKK membranes show an elongation at break from 8.50 to 15.01%, and tensile strength ranging from 41 to 56 MPa. These data indicate that the SPEEKK membranes are strong and tough enough for use in PEMs. Compared to Nafion, SPEEKK membranes show relatively better mechanical stability at ambient condition, which shows the excellent properties derives from none sulfonated PEEKK.

## 4. Conclusions

A novel series of sulfonated poly(ether ether ketone ketone)s (SPEEKKs) with different degrees of sulfonation (Ds) were suc-



**Fig. 6.** The proton conductivities of SPEEKK membranes as a function of temperature at 100% relative humidity.

cessfully synthesized by direct copolymerization of sulfonated monomers. The chemical structures of the SPEEKs were confirmed by FT-IR spectroscopy, and  $D_s$  values were measured by  $^1\text{H}$  NMR spectrometry and titration, respectively. TGA show that SPEEKs have excellent thermal stability at high temperatures. All the SPEEK polymers can be solution cast into tough membranes. Water uptake increased with  $D_s$  and temperature. SPEEK-60, -70 and -80 membranes show higher proton conductivities than that of Nafion at  $80^\circ\text{C}$ , whereas the other SPEEK membranes showed relatively lower proton conductivities in comparison to Nafion. This may be due to the different distribution of ion-conducting domains in membrane. However, these membranes showed low methanol diffusion in the range of  $8.32 \times 10^{-9}$  to  $1.14 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  compared with Nafion ( $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) at the same temperature. The membranes also showed the excellent mechanical properties (Young's modulus  $> 1 \text{ GPa}$ , Tensile strengths  $> 40 \text{ MPa}$ ). All results indicated that the SPEEK membranes can be candidates for DMFC applications.

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