Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes

Xing, P.; Robertson, Gilles; Guiver, Michael; Mikhailenko, S.; Wang, K.; Kaliaguine, S.

National Research Council Canada   Conseil national de recherches Canada

Canada

Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes ☆

Peixiang Xing [a,b], Gilles P. Robertson [a], Michael D. Guiver [a,*],
Serguei D. Mikhailenko [b], Keping Wang [b], Serge Kaliaguine [b]

[a] *Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6*
[b] *Chemical Engineering Department, Laval University, Ste-Foy, Que., Canada G1K 7P4*

Abstract

Series of sulfonated poly(ether ether ketone)s (SPEEKs) were prepared by sulfonation of commercial Victrex® and Gatone® PEEK for a comparative study of proton exchange membranes (PEM) intended for fuel cell applications. The degree of sulfonation (DS) of the sulfonated PEEK was determined from deuterated dimethyl sulfoxide (DMSO-d_6) solution of the purified polymers using ^{1}H NMR methods. The second method using a solvent suppression technique, in which DS results were obtained directly from ^{1}H NMR spectra of SPEEK dissolved in sulfuric acid (non-deuterated) reaction medium was evaluated. The variation between the two methods was determined. The room temperature sulfonation of PEEK, monitored directly by second ^{1}H NMR method, proceeded rapidly initially, reaching DS ∼ 0.8 within 1 week, but progressed slowly thereafter. A maximum DS of 1.0 was determined after 1 month at ambient temperature (∼22 °C). The thermal properties of SPEEK were characterized by means of DSC and TGA. The mass averaged molecular weights M_w of both Victrex® and Gatone® PEEK were estimated from intrinsic viscosities measured in sulfuric acid solutions. It was verified that higher temperature (55 °C) did not induce any apparent chain degradation of Victrex® (or Gatone®) PEEK by M_w tests. The water uptake and swelling properties of prepared films were studied and the proton conductivities at different temperatures were measured. The conductivities of the SPEEKs were found to increase with increasing DS and temperatures. The effect of film casting solvents on the conductivities is also discussed.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Poly(ether ether ketone); Sulfonation; Fuel cell; Proton exchange membrane; Ion-exchange membranes

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are among the most promising electrochemical devices for convenient and efficient power generation. The proton exchange membrane (PEM) is a key component in the system, 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, the most commonly used PEM for both hydrogen (H₂-PEMFC) and direct methanol fuel cells (DMFC) are perfluorinated copolymers such as Nafion®, which have high hydrolytic and oxidative stability and excellent proton conductivity. However, the perfluorinated polymers have three major drawbacks: very high cost; loss of conductivity at high temperature (>80 °C); and high methanol permeability, which hinder their further application [1,2].

In view of this, there is widespread effort being spent to develop alternative more economical non-perfluorinated polymer PEMs for high temperature use. Many promising polymers are based on aromatic thermoplastics [1,3–6], such as poly(aryl ether ketone)s (PAEKs) (e.g. PEEK), poly(ether sulfone) (PES), polybenzimidazole (PBI), etc., which have excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost. By attachment of sulfonic groups to the polymers' chains, these sulfonated PEEK [1,3–8], PES [9,10], polyimides [11,12] and PBI [13,14] were applied as PEM materials. Sulfonation of polymers is typically conducted by either directly

introducing the sulfonic acid group onto the polymer backbone by modification [15–17] or by polymerizing sulfonated monomers [9,18]. Many polymers have been sulfonated to improve their membrane properties in terms of better wettability, higher water flux, higher antifouling capacity, better permselectivity, and increased solubility in solvents for processing. In particular, the solubility of certain sulfonated aromatic polymers such as PEEK allows casting from organic solution and offers a more convenient and less expensive process than fabricating perfluorosulfonic acid membranes. Hydrophilic SPEEKs have been used as membrane materials for the separation [19,20] of liquids. However, in a number of studies, SPEEK was reported to be used as a PEM material [1–10,21–25]. In Ref. [24] for instance it was found that a SPEEK-based PEM could have a lifetime of more than 3000 h [24], which indicates that SPEEK may be durable enough under fuel cell operation conditions.

Recently, proton-conducting blend membranes [3,26–29], in which SPEEK was used as a major component, have been explored with the goal to obtain good mechanical properties, high proton conductivity, and optimized membrane properties. SPEEKs were used to prepare blend membranes with PES [3,25,26], and with polyetherimide [27] for PEMFC application and with polysulfone for direct methanol fuel cell (DMFC) [28].

Although several studies on SPEEK were previously conducted, the present paper is a comparative study of the sulfonation of commercial Victrex® and Gatone® PEEK and their membrane properties related to PEM. Although the sulfonation of Victrex PEEK has been studied and Victrex currently has a license agreement with a fuel cell company, there have apparently been no comparative studies of the sulfonation of Gatone PEEK, which is produced by a different polymerization method. In addition, a new technique for directly monitoring the sulfonation reaction of PEEK by NMR was evaluated.

2. Experimental

2.1. Chemicals and materials

Victrex® PEEK grade 450G extruded pellets were kindly provided by Victrex PLC (England). Gatone® PEEK grade 5300P extruded pellets were kindly provided by Gharda Chemicals Ltd. (India). Sulfuric acid (95–98 wt.%), dimethylacetamide (DMAc), dimethylformamide (DMF) and methanol were obtained from Aldrich Chemical Corp. MEMBRA-CEL dialysis tubing was obtained from Helixx Technologies Inc. (Canada).

2.2. Sulfonation of PEEK

PEEK pellets (40 g) were gradually added during 20 min into vigorously mechanically stirred 1.4 l sulfuric acid (95–98 wt.%) in a three-neck flask under argon atmosphere. Usually (unless otherwise specified) the reaction was carried out at room temperature. After a prescribed time, the sulfonated polymer was recovered by precipitating the acid polymer solution into a large excess of ice water. The polymers were washed repeatedly with deionized water until the rinse water was at pH 6–7. For SPEEK with high DS (>0.8), residual acid was difficult to remove from the polymers due to swelling in water. Accordingly, the high DS SPEEKs were washed by placing the polymers in dialysis tubing and dialysing the acid out of the polymers. Typically, several days of dialysis were required to obtain pH values of 6–7. The recovered SPEEKs were dried at room temperature for 2 days, then dried in a vacuum oven at 80 °C for 24 h. The yields for all samples were ∼90–95%.

2.3. Characterization of SPEEK

2.3.1. 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 ^{1}H and 100.579 MHz for ^{13}C. Carbon spectra were acquired using a 10 mm tunable broadband probe. For each analysis, ∼3 wt.% polymer solution was prepared in deuterated dimethyl sulfoxide (DMSO-d$_6$) for ^{1}H NMR and ∼15 wt.% for ^{13}C NMR. The chemical shift of tetramethylsilane was used as the internal standard reference. Most NMR tests were conducted at room temperature (∼22 °C).

The DS was determined by ^{1}H NMR using the following two methods. The first method normally used was to measure the intensity of the appropriate signal [8] from recovered and washed SPEEK samples dissolved in deuterated DMSO (DMSO-d$_6$) solvent. The limitation of this method is that PEEK and SPEEK with low DS (≤0.4) do not dissolve in common organic solvents. However, SPEEK with DS ≥ 0.5 can be dissolved in common solvents such as DMSO, DMAc, DMF, and 1-methyl-2-pyrrolidinone (NMP) [5]. Hence, a secondary method was developed for measuring the DS value of SPEEK directly from the sulfuric acid reaction mixture solution. This technique requires that the proton spectrum of H$_2$SO$_4$ solvent does not overlap with the polymer signals. In this experiment, presaturation of the intense sulfuric acid peak was performed, resulting in a reasonably good hydrogen spectrum of the aromatic region. Using this solvent suppression technique, the DS of SPEEK could be determined directly from the sulfonation reaction mixture from the relative integration intensities of the signals.

2.3.2. FTIR

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

2.3.3. Thermal properties of SPEEK

A TA DSC 2920 differential scanning calorimetry (DSC) was employed to study the thermal transition behavior of SPEEK samples. The samples ($\sim$10 mg) were preheated under nitrogen from room temperature to 160 °C at 10 °C/min to remove moisture, then cooled to 90 °C, and reheated from that temperature to 250 °C at 10 °C/min.

A DuPont Instruments 951 and a TA Hi-Res TGA 2950 thermogravimetric analyzer (TGA) were employed to study the thermal stability behavior of SPEEK samples. The samples ($\sim$10 mg) were preheated under air from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to 90 °C, then reheated from that temperature to 800 °C at 10 °C/min in air.

2.3.4. Viscosity measurements

The solution viscosities were measured in sulfuric acid (95–98 wt.%) at 25 °C using an Ubbelohde viscometer. The intrinsic viscosity was taken as the arithmetical mean of reduced and inherent viscosities extrapolated to zero concentration.

2.4. Membrane preparation

Dried SPEEK powder was dissolved either in DMAc or DMF (15 wt.%), then the solution was filtered using a fine glass frit filter funnel. Solutions were cast onto glass plates, then dried at ambient condition for 1 day in an oven under argon gas flow for reducing humidity, at 60 °C for 2 days and at 120 °C under vacuum for 24 h. The thickness of the resulting membranes was in the range of $\sim$70–120 μm.

2.5. Water uptake and swelling

Before measurement, the membranes were dried in a vacuum oven at 120 °C for 24 h. Weighed films with area 10 mm × 50 mm were immersed in deionized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The liquid water on the surface of wetted membranes was removed using tissue paper before weighing. The weight and the dimensional length gain of films were recorded. The percentage weight gain with respect to the original membrane weight was taken as water uptake. The percentage of length gain to original length was taken as the swelling ratio. Each sample was tested with three specimens, and the results were the average of three test results.

2.6. Proton conductivity measurements

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

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

3. Results and discussion

3.1. Sulfonation and NMR study

Sulfonation of PEEK in sulfuric acid is an electrophilic substitution reaction, in which the sulfonic groups are introduced into the hydroquinone segment of the polymer chain activated for electrophilic substitution by the ether linkage. Table 1 shows the comparison of the DS of both Victrex® and Gatone® PEEK sulfonated at room temperature. Several

Table 1
DS and T_g of Victrex® and Gatone® PEEK sulfonated at 22 °C

Polymer designation	Reaction time (h)	Color of polymer	DS (from ^{1}H NMR in DMSO-d$_6$)	T_g (°C)
Victrex PEEK	–	Gray	–	150
V-SPEEK48	60	Yellow	0.48	–
V-SPEEK64	110	Yellow	0.64	217.8
V-SPEEK66	140	Yellow	0.66	221.0
V-SPEEK67	160	Yellow	0.67	214.6
V-SPEEK79	190	Yellow	0.79	223.9
V-SPEEK78	240	Yellow	0.78	–
V-SPEEK99(55)	10 (55 °C)	Yellow	0.99	–
Gatone PEEK	–	Brown	–	156.0
G-SPEEK59	140	Brown	0.59	217
G-SPEEK77	190	Brown	0.77	220.2
G-SPEEK79	240	Brown	0.79	–
G-SPEEK97(55)	10 (55 °C)	Brown	0.97	–
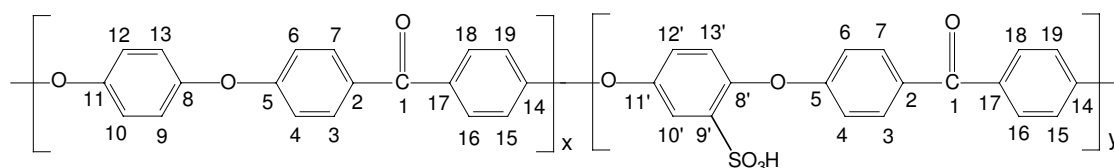
Fig. 1. Structure and atom numbering of SPEEK, $x + y = n$, $y/(x + y) = $ DS.
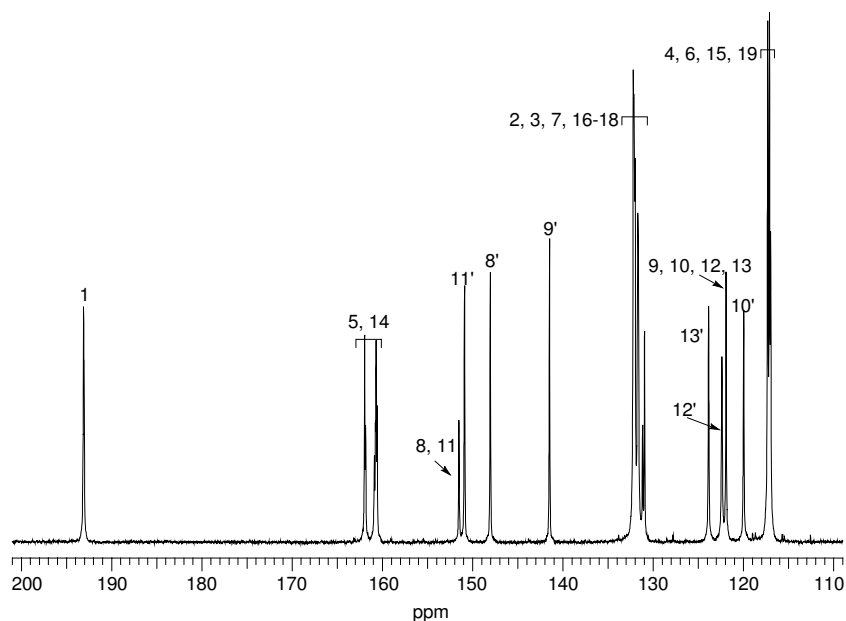
Fig. 2. ^{13}C NMR spectrum of sulfonated Victrex PEEK in DMSO-d$_6$.

studies on the sulfonation reaction kinetics and characterization of SPEEK were reported [7,8,14–17,29–35]. Jin et al. [15] investigated the sulfonation of PEEK using concentrated sulfuric acid at room temperature and reported that sulfonation is limited to DS 1.0 and occurs only on the four chemically equivalent positions of hydroquinone segment [29] (Fig. 1). In the present study, the ^{13}C NMR spectra of Victrex® and Gatone® SPEEK sulfonated at room temperature were assigned. They confirmed (Figs. 1 and 2, Table 2) that sulfonation occurred exclusively on the hydroquinone segment, which is consistent with the results of Jin et al. [15]. Further, sulfonation on this ring does not exceed DS 1.0 under the ambient condition, due to the electron-withdrawing deactivating effect

of the –SO$_3$H group once it is introduced in that ring. The other two phenyl rings connected through the ether linkages are therefore deactivated for electrophilic sulfonation by the electron-withdrawing effect of the carbonyl group. In related PAEKs, oxy-phenylene-carbonyl units of poly(ether ketone) (PEK) and poly(ether ketone ether ketone ketone) (PEKEKK) were substituted by sulfonic groups [7] when strong sulfonation conditions were employed. The substitution position in hydroxyquinone for model compounds of PEEK was evaluated by ^{13}C NMR [32,33]. It is noted in the present study that the structures of the two commercial PEEK products are identical by ^{13}C and ^{1}H NMR spectral analysis of Victrex® and Gatone® SPEEK.

The chemical shift assignments of ^{13}C NMR (Fig. 2) and ^{1}H NMR spectra (Fig. 3) are listed in Tables 2 and 3, respectively. The DS of SPEEK can be calculated from the

Table 2
^{13}C NMR data for V-SPEEK79 in DMSO-d$_6$

δ (ppm)	Carbon[a]	δ (ppm)	Carbon[a]
116.50–117.70	4, 6, 15, 19	148.05	8'
119.98	10'	150.90	11'
121.93	9, 10, 12, 13	151.53	8, 11
122.39	12'	160.71	5 or 14
123.87	13'	161.97	14 or 5
130.90–132.30	2, 3, 7, 16–18	193.11	1
141.49	9'		

[a] Refer to Fig. 1 for carbon designation.

Table 3
^{1}H NMR of G-SPEEK77 in DMSO-d$_6$

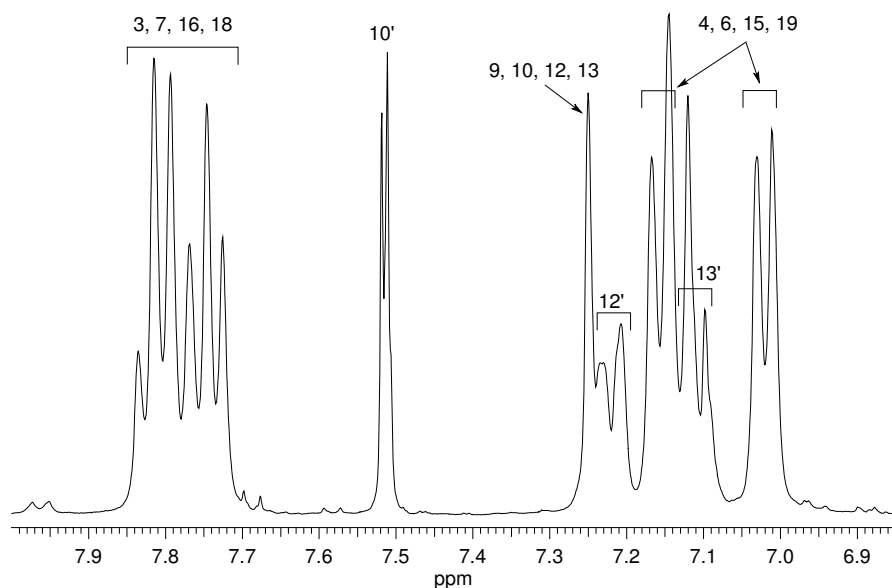| δ (ppm)	Proton designation	δ (ppm)	Proton designation
7.01, 7.17	4, 6, 15, 19	7.25	9, 10, 12, 13
7.10	13'	7.51	10'
7.22	12'	7.70–7.86	3, 7, 16, 18

Fig. 3. ^{1}H NMR spectra of G-SPEEK77 in DMSO-d$_6$.

relative integration of the H10′ peak from ^{1}H NMR [8,36] (see Figs. 1 and 3).

Due to the insolubility of SPEEK with low DS (≤ 0.4) in common deuterated organic solvents, it is difficult to obtain their ^{1}H or ^{13}C NMR spectra in organic solvent. In the present study, a new technique to acquire NMR spectra directly from the sulfuric acid reaction solution was evaluated.

Although well-resolved spectra are normally difficult to obtain in non-deuterated solvents, a solvent suppression technique for ^{1}H NMR enabled us to extract usable DS data for SPEEK solution directly in sulfuric acid. A typical ^{1}H NMR spectrum is shown in Fig. 4. To evaluate the accuracy of this method, a comparative analysis of purified SPEEK dissolved in DMSO-d$_6$ and SPEEK dissolved in sulfuric acid reaction mixture was performed. A portion of sulfuric acid reaction mixture was withdrawn from reaction flask

and used to measure the DS directly by NMR using solvent (H$_2$SO$_4$) suppression method. Another portion was poured into water, and the resulting precipitated SPEEK was purified using dialysis tubing. The dried purified SPEEK sample was dissolved in DMSO-d$_6$ and its ^{1}H NMR spectrum was recorded. Three pairs of results obtained from the above two methods are listed in Table 4. The DS obtained from H$_2$SO$_4$ solutions are greater by ~ 0.1–0.2 than those obtained from DMSO-d$_6$. This may be explained by factors inherent in this technique such as incomplete suppression of the intense sulfuric acid peak, lower resolution and lower signal to noise ratio. Another possible reason is that the ^{1}H NMR test in H$_2$SO$_4$ reaction mixture was run at 30 °C, which may induce some further sulfonation. The samples were run at 30 °C to reduce the reaction solution viscosity and obtain better signal resolution. For the above reasons,
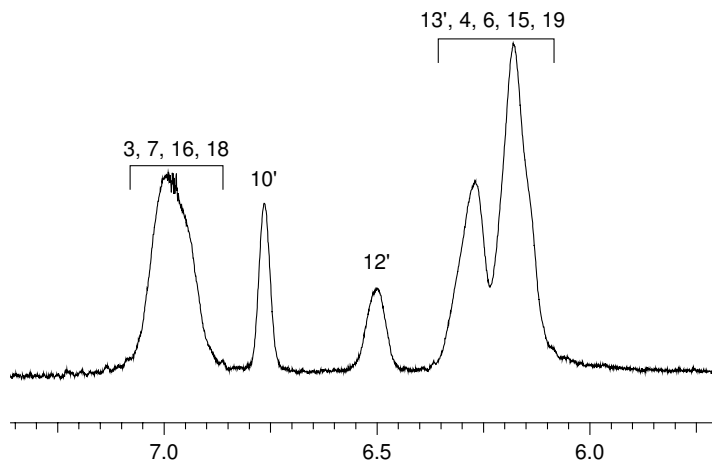

Fig. 4. ^{1}H NMR spectrum of V-SPEEK in H$_2$SO$_4$ (non-deuterated).

Table 4
DS of V-SPEEK in DMSO-d_6 and in H_2SO_4 obtained from ^{1}H NMR

Reaction time (h)	DS (^{1}H NMR from H_2SO_4)	DS (^{1}H NMR from DMSO-d_6)
60	0.68	0.48
86	0.79	0.70
206	1.03[a]	0.90

[a] This value cannot be larger than 1.00.

the relative integrations of signals are not precise, leading to a small DS overestimation (average ∼ 0.15). Therefore, the DS derived by this method must be adjusted by deducting this variation. However, DS obtained directly from sulfuric acid is a convenient method to follow the real-time sulfonation reaction and readily monitor the sulfonation of PEEK to achieve the desired DS. The direct method is also especially valuable in the case of SPEEK with low DS (≤0.4), since there is no common deuterated organic solvent to dissolve this SPEEK for running the ^{1}H NMR test. In our previous studies, lower DS SPEEKs were used in the preparation of mixed-matrix PEMs containing inorganic proton conductors.

This technique can also be used to study kinetics of sulfonation. The sulfonation was conducted at room temperature (20 °C). The start-time for the sulfonation reaction in previous studies was ∼90 and 60 min, respectively [17,32], since it was inferred that PEEK was almost completely dissolved in concentrated H_2SO_4 at that time. In the present paper, the reaction start-time was not set at the exact time of complete dissolution, since complete dissolution of SPEEK in concentrated sulfuric acid (95–98%) took several hours due to the nature of the commercial extruded pellets. The starting time was set at 1 h after adding the PEEK to the sulfuric acid, since the sulfonation reaction and dissolution of PEEK occur simultaneously. It is noted in the present study that Gatone PEEK dissolves much more rapidly than Victrex PEEK in concentrated H_2SO_4.

The DS as a function of reaction time has been studied previously by different methods [8,17,29–35]. In the present study, the DS values acquired for Victrex[®] PEEK (V-PEEK) at ambient temperature directly in sulfuric acid solution, after deducting a variation of 0.15, are plotted versus sulfonation reaction time (Fig. 5). The values in Fig. 5 represent a single reaction whereas the values in Table 1 are derived from individual batch reaction. The results show that the sulfonation of PEEK proceeded rapidly initially, reaching DS ∼ 0.8 within 1 week, but progressed slowly thereafter, which is consistent with other reported work [8,23,32,34,35].

3.2. FTIR study

The comparative FTIR spectra of V-PEEK and V-SPEEK samples with different DS are shown in Fig. 6. The broad-band in SPEEK samples appearing at $3460 \, cm^{-1}$ was assigned to O–H vibration from sulfonic acid groups in-
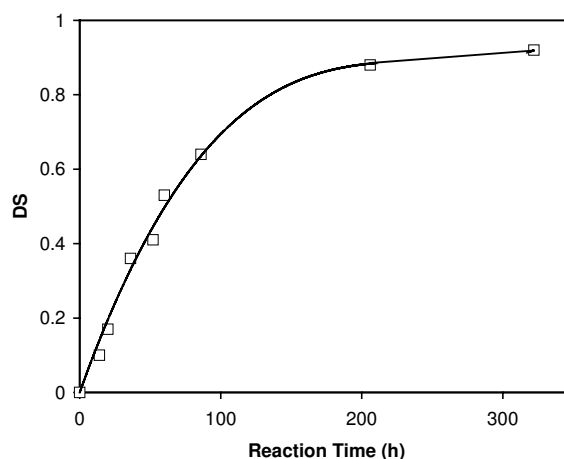

Fig. 5. DS measured by ^{1}H NMR in H_2SO_4 reaction mixture, after deducting a DS value of 0.15.

teracting with molecular water. The aromatic C–C band at $1489 \, cm^{-1}$ for PEEK was observed to split due to new substitution upon sulfonation. A new absorption band at $1080 \, cm^{-1}$ in SPEEK was assigned to sulfur–oxygen symmetric vibration O=S=O. The new absorptions at 1255, 1080, and $1020 \, cm^{-1}$ which appeared upon sulfonation were assigned to the sulfonic acid group in SPEEK [31], as their intensities with respect to the backbone carbonyl band at $1651 \, cm^{-1}$ increased with DS. There is no change in the carbonyl band at $1651 \, cm^{-1}$ for SPEEK compared with PEEK.

During the course of this study, efforts were made to thermally crosslink SPEEK for PEMs. A patent [21] reported that two sulfonic acid groups of SPEEK form a sulfone group upon treatment at 120 °C under vacuum. FTIR spectra were recorded for SPEEK samples after annealing at 160 °C in vacuum for 24 h, however no apparent new absorptions for the sulfone group were observed in the spectra. The thermally treated SPEEKs (initially with high DS) could still be dissolved in hot water, indicating contrary to what was claimed in [21], that an insignificant amount of crosslinking, if any, occurred through this mechanism at temperatures up to at least 160 °C.

3.3. Molecular weight (M_w) of PEEK

Due to the poor solubility of PEEK, it was difficult to measure its molecular weight directly. GPC has been successfully applied to measure M_w of pure PEEK using phenol/1,2,4-trichlorobenzene 50/50 mixture at 115 °C [31]. Other successful methods to determine the M_w of PEEK have been based on the study of SPEEK properties, such as dynamic light scattering [16,31] viscosity (using H_2SO_4 as solvent) and ultracentrifugation (using DMF/LiCl as solvent) [7]. Devaux et al. [31] measured M_w of PEEK, fully sulfonated with sulfonic acid, by both dynamic light scattering and intrinsic viscosity. Using the experimental
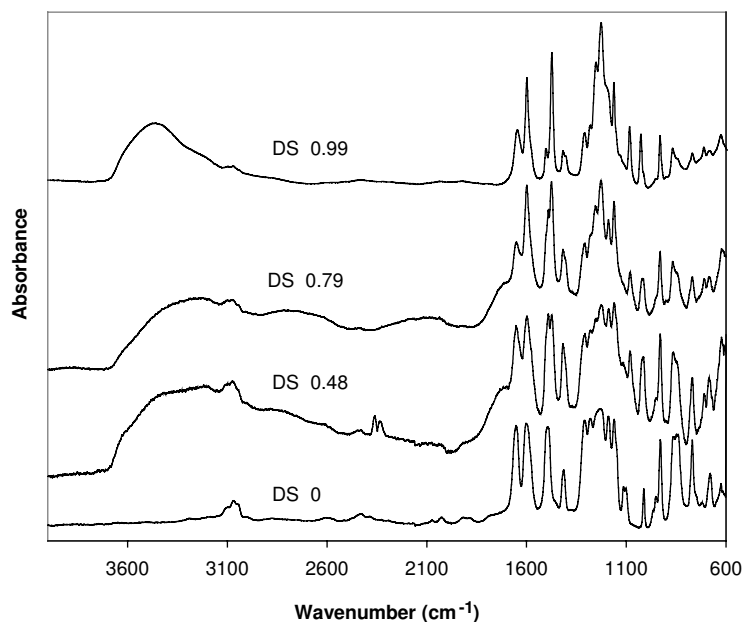
Fig. 6. Comparative FTIR spectra of V-PEEK and sulfonated V-SPEEK.

data for fully substituted SPEEK (DS 1.00) obtained by both methods, Devaux et al. [31] established an empirical Mark–Houwink equation (Eqs. (1) and (2)) relating viscosity and molecular weight was obtained:

$$[\eta_s]_{25\,^\circ C} = 3.849 \times 10^{-5} (\bar{M}_w)_s^{0.94} \; (dl/g) \tag{1}$$

where $(\bar{M}_w)_s$ is the molecular weight of the sulfonated PEEK. The molecular weight of unsulfonated PEEK could be estimated from the intrinsic viscosity of SPEEK by removing the contribution of SO_3H group in Eq. (1). The following empirical Mark–Houwink equation was obtained:

$$[\eta_a]_{25\,^\circ C} = 6.195 \times 10^{-5} (\bar{M}_w)_u^{0.94} \; (dl/g) \tag{2}$$

where $(\bar{M}_w)_u$ is the molecular weight of the unsulfonated PEEK.

Two series of three different SPEEK samples obtained from both Victrex® and Gatone® SPEEK and having DS ∼1.0 and ∼0.8, were tested and the results are presented in Table 5. The samples include the Victrex® and Gatone® SPEEK with DS ∼ 1 (as determined by ^{1}H NMR in DMSO-d$_6$). They were obtained by sulfonating PEEK either at room temperature for 1 month or at 55 °C for 10 h.

It has been previously reported [15,16,29] that no chemical degradation and no sulfone crosslinking were observed when concentrated sulfuric acid (concentration below 100%) was used for sulfonation at ambient temperature. Therefore the M_w values of both Victrex® and Gatone® PEEK extrapolated from SPEEK with DS 1.0 sulfonated at room temperature should be regarded as a credible approximation of the M_w of initial PEEK samples. From Table 5 it can be seen that the M_w values for Victrex® and Gatone® PEEKs are similar. Following this, the $(M_w)_s$ of both Victrex® and Gatone® PEEK sulfonated at 55 °C (V-SPEEK99(55),

G-SPEEK97(55)) were measured. The obtained $(M_w)_s$ for Victrex® and Gatone® PEEKs sulfonated at 22 °C room temperature (V-SPEEK99, G-SPEEK100) and at 55 °C are almost the same (Table 5). Hence, it is deduced that no chemical degradation of either Victrex® or Gatone® PEEK occurs when they are sulfonated at 55 °C, confirming another report [15]. This suggests that sulfonation of PEEK can be conducted for short times at elevated temperature (55 °C) without degradation.

For Eq. (1) to be valid, the DS value should be close to 1.0. To verify this, SPEEK with DS 0.8 was dissolved in concentrated sulfuric acid and the M_w was measured. It should be noted that the process of sulfonation of PEEK in concentrated sulfuric acid is very slow after the DS reaches 0.8. The M_w found for these samples (V-SPEEK79, G-SPEEK77) are overestimated by 30% (Table 5), compared with SPEEK DS ∼ 1.0. Thus, it is necessary to use SPEEK with DS ∼ 1.0 to determine a realistic M_w value from viscosity tests.

Table 5
Intrinsic viscosity and molecular weights for Victrex® and Gatone® SPEEK

	Sample	DS	η_s	$(M_w)_s$[a]	M_w[b]
Victrex SPEEK	V-SPEEK99(55)	0.99	0.673	32600	25500
	V-SPEEK99	0.99	0.663	32100	25100
	V-SPEEK79[c]	0.79	0.883	43600	34100
Gatone SPEEK	G-SPEEK97(55)	0.97	0.647	31300	24500
	G-SPEEK100	1.00	0.631	30500	23800
	G-SPEEK77[c]	0.77	0.796	39000	30500

[a] Molecular weight of SPEEK.
[b] Molecular weight for unsulfonated PEEK, $M_w = (M_w)_s/1.278$.
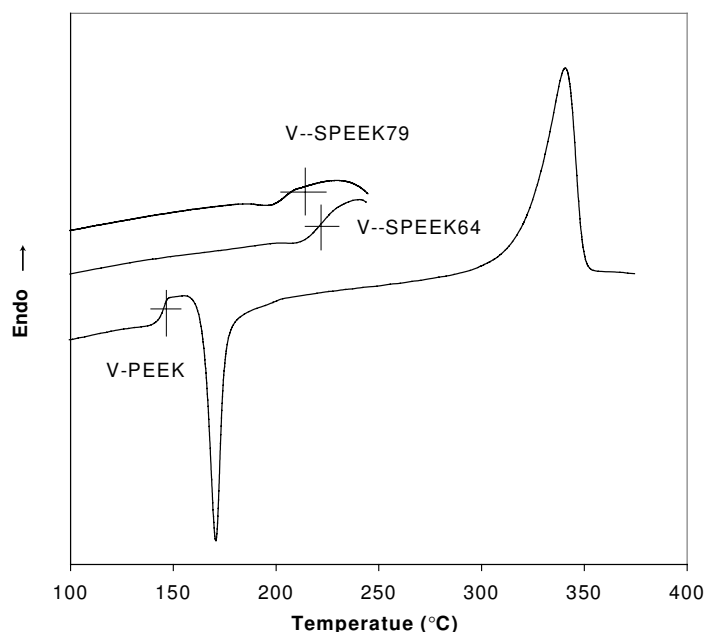[c] M_w is overestimated due to incomplete sulfonation of PEEK.

Fig. 7. Typical DSC curves of PEEK and SPEEKs.

3.4. Thermal properties

PEEK is a highly thermostable polymer with a T_g of $\sim 150\,^{\circ}$C. TGA tests were run under air flow, in similarity with real fuel cell conditions. TGA results showed there was no oxidation of SPEEK in the presence of air during pre-treatment of the samples under air (running to $160\,^{\circ}$C). DSC results show the T_gs of SPEEK occur in the range of 200–$220\,^{\circ}$C depending on the DS (Table 1, Fig. 7), in similarity with results previously reported [8,15]. This increase of T_g values is typically observed in ionomeric polymers, due to strong interaction between sulfonic groups.

The narrow dispersion of T_g values ($20\,^{\circ}$C range, Table 1) may however be due to the effective ionic interaction (physical crosslinking) which could become saturated at a certain DS. T_g is a parameter reflecting the polymer chain mobility in a ~ 100 nm segment. The effective physical crosslinking may not increase with increasing DS above a certain DS value, which would make the chain mobility and therefore T_g invariant under these conditions. For example, the effective ionic interaction (physical crosslinking) may attain almost the same level in both SPEEK with DS 0.6 and 1.0.

Victrex® PEEK has a starting temperature of thermal degradation (T_{d1}) at $550\,^{\circ}$C. However, Gatone® PEEK shows a considerably lower T_{d1} of $467\,^{\circ}$C. This is possibly due to different residual reaction reagents present in the extruded pellets of Victrex® and Gatone® PEEK. The sulfonated PEEKs show a progressive deterioration of thermal stability with increasing DS (Fig. 8). In comparison with pure PEEK, which exhibits a single step thermal degradation, SPEEK has two distinct steps [8,36]. The first thermal degradation temperature T_{d1} of SPEEK decreased and the

signal broadened with DS. The first weight loss step is mainly associated with loss of the sulfonic groups in the range of 250–$280\,^{\circ}$C. The second weight loss step (at T_{d2}) is related to the decomposition of the main chain of PEEK in the range of 400–$580\,^{\circ}$C. The main chain degradation temperature of SPEEK is lower than that of PEEK because of the catalytic degradation of the polymer chain caused by SO_3H.

TGA analysis has been used to estimate the DS of SPEEK [8]. The method is based on the assumption that the first weight loss step at temperatures ranging between T_{d1} and T_{d2} (the starting point of second step) is entirely caused by SO_3 release. The results in Table 6 show that the DS values obtained from TGA are comparable with those from NMR spectroscopy. The DS values obtained from TGA are slightly overestimated (about 0.05 higher) [8], probably because the TGA test is carried out under non-equilibrium conditions ($10\,^{\circ}$C/min) and small amounts of chain scission at the sulfonated ether and carbonyl linkages may be involved in the first step degradation [36].

3.5. Water uptake and proton conductivity

It has been reported that the proton conductivity of SPEEK depends on the DS, pre-treatment of the membrane, hydration state, ambient relative humidity and temperature [21,22]. In general, for ionomeric membranes, the proton conductivity depends on the number of available acid groups and their dissociation capability in water, which is accompanied by generation of protons. Water molecules dissociate acid functionality and facilitate proton transport, so the water uptake is an important parameter in studying PEMs. Swelling is also a key factor for the mechanical integrity of
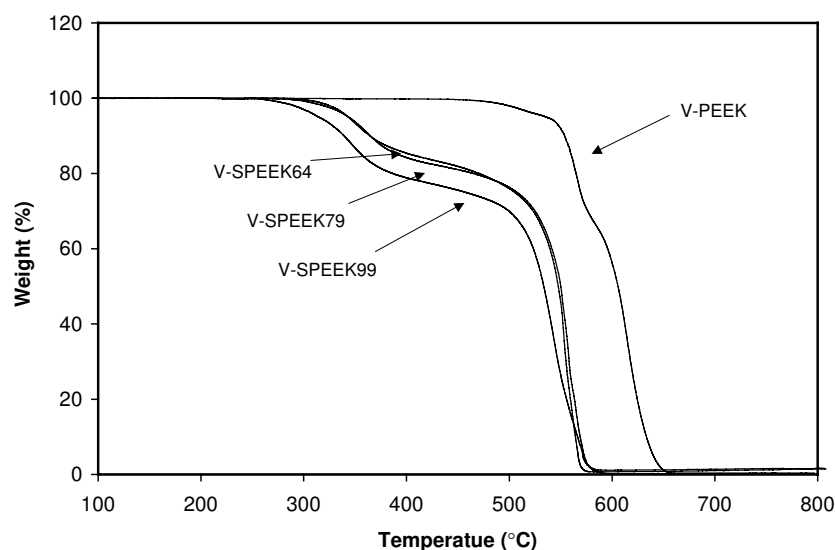
Fig. 8. Typical TGA curves of PEEK and SPEEKs.

membranes. Excessively high levels of water uptake can result in membrane fragility and dimensional change leading to failures in mechanical properties, and in extreme cases, solubility in water at elevated temperatures. Therefore, it is important to know the relationship between the DS and water uptake for SPEEK PEMs.

In a fuel cell, PEMs are typically exposed to an operating environment of humidified gases at elevated temperatures. In the present work, membranes were submersed in water for treatment, which can be considered to be a harsher condition than the PEM operating environment. From Table 7 it follows that the equilibrium water contents of SPEEK increased with DS, as expected. SPEEK film with DS 1.0 could be dissolved over time in water when immersed at room temperature. The room temperature water uptake of SPEEK films with DSs of 0.66 and 0.79 corresponded to 4.5 and 8 water molecules per sulfonic acid group of SPEEK, respectively. Accordingly, the dimensions of the film changed when the film absorbed water. The swelling of both Victrex® and Gatone® SPEEK films are shown in Table 7. Gener-

ally, the swelling of films should not be excessive in order to maintain adequate mechanical properties.

In the present study, membranes were initially hydrated by immersion in water for 24 h at room temperature, then the conductivity was measured. As shown in Fig. 9a, the conductivity increased as a function of DS. In similarity with conductivity, the water uptake also increased with DS as shown in Table 7.

It was also found that the conductivity increases with temperature. The conductivity of SPEEK with DS 0.8 reaches $\sim 10^{-1}$ S/cm at 90 °C, which is considered to be high. It was also reported that the conductivity of SPEEK is close to that of Nafion 117 at high temperature [13]. However, the water uptake for Nafion 117 has the same value of about 20% at room temperature and at 50 °C, while SPEEK with high DS (0.8) shows a $\sim 23\%$ uptake at room temperature and a higher uptake of 58% at 50 °C.

Recently, it was also observed that the proton conductivity of membranes cast from DMF and DMAc is significantly different [38]. Films of identical SPEEK cast from DMF and

Table 6
DS obtained from TGA and NMR data

| Polymer designation	DS (from ^{1}H NMR)	DS (from weight loss)	First weight loss (%)	Decomposition temperature, T_{d1} (°C)	Decomposition temperature, T_{d2} (°C)
V-SPEEK48	0.48	0.62	14.7	262	407
V-SPEEK69	0.69	0.74	17.1	249	429
V-SPEEK66	0.66	0.73	16.8	263	426
V-SPEEK67	0.67	0.72	16.7	260	434
V-SPEEK78	0.78	0.80	18.1	262	433
V-SPEEK79	0.79	0.83	18.7	258	435
V-SPEEK99(55)	0.99	0.95	20.9	251	420
G-SPEEK59	0.59	0.72	16.7	259	431
G-SPEEK77	0.77	0.88	19.7	243	434
G-SPEEK79	0.79	0.90	20.0	246	432
G-SPEEK97(55)	0.97	0.96	21.0	239	422

Table 7
Water uptake and conductivity of SPEEK

| Polymer designation	DS (from ^{1}H NMR)	Transverse proton conductivity at 25 °C (S/cm)	Water uptake (wt.%)	Swelling in water (%)[a]	H$_2$O/SO$_3$H
V-SPEEK48	0.48	2.0×10^{-3}[b]	5	2	1.9
V-SPEEK64	0.64	5.6×10^{-3}[c]	12	6	3.3
V-SPEEK66	0.66	0.9×10^{-2}[c]	19	6	4.6
		2.2×10^{-3}[b]	16	7	
V-SPEEK67	0.67	2.2×10^{-2}[c]	19	6	4.5
		2.7×10^{-3}[b]	16	4.4	
V-SPEEK79	0.79	3.9×10^{-2}[c]	23	6.6	4.9
	0.79	4.5×10^{-3}[b]	20	6	
V-SPEEK99	0.99		Soluble or gel		
G-SPEEK59	0.59	1.8×10^{-2}[c]	10	4.4	3.16
G-SPEEK77	0.77	1.7×10^{-2}[c]	30	8	7.57
G-SPEEK79	0.79	1.6×10^{-2}[c]	32	9.2	7.90
G-SPEEK97	0.97		Soluble or gel		

[a] Dimension length change.
[b] Film cast from DMF.
[c] Film cast from DMAc.
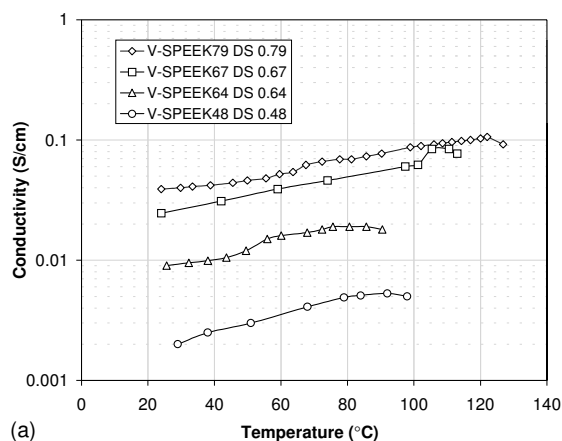
(a)
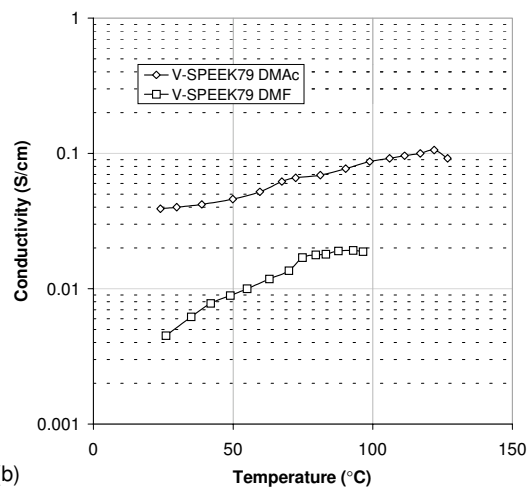
(b)

Fig. 9. (a) Proton conductivities of V-SPEEK films cast from DMAc at different temperatures, (b) proton conductivities of V-SPEEK79 (DS 0.79) films cast from DMAc and DMF.

DMAc were first dried at 60 °C, then dried at 120 °C under vacuum for 24 h. The room temperature conductivity of the films cast from DMAc is much higher (approximately half an order of magnitude) than those cast from DMF (Fig. 9b). A combination of factors has been found to be responsible for this behavior. Detailed NMR studies [37,38] explain the possible processes occurring during PEM fabrication that leads to differences in proton conductivity. The room temperature water uptakes of the two SPEEK samples cast from DMAc and DMF shown in Fig. 9b were almost the same. This discounts water uptake as a sole or primary reason for the difference in proton conductivity. It is reported that the proton conductivity mechanism of hydrated materials is due to the transportation of H$_3$O$^+$ or H$_5$O$_2$$^+$. Therefore, the lower conductivity of the hydrated film cast from DMF compared with DMAc may be due to its lesser number of available acid groups.

TGA data showed that both T_d of V-SPEEK79 film cast from DMF and DMAc are about 184 °C, which is 70 °C lower than the T_d (258 °C) of virgin V-SPEEK79 directly recovered from water. This indicates that some residues (or solvent-derived compounds) still exist in the film, and that they form complexes with SPEEK even when the films were dried in vacuum at 120 °C. It appears clear that casting solvents represent an important factor leading to significant differences in proton conductivity. As indicated in Refs. [37,38], one of the most important reasons for such behavior is that during PEM fabrication, DMF undergoes acid-catalyzed decomposition at relatively low temperatures (much more easily than DMAc) to produce dimethylamine and the volatile compounds: formic acid for DMF or acetic acid for DMAc [37,38]. The acid-catalyzed decomposition takes place in the presence of sulfonic acid groups of SPEEK or residual sulfuric acid in SPEEK from the sulfonation process (particularly at high DS, because of the greater difficulty in washing acid out of the swellable samples). The decomposed product dimethylamine of DMF forms a strong

complex with sulfonic group, which reduces the amount of available free sulfonic group as compared with DMAc. This leads to less protonated water and results in lower proton conductivity. It is clear from NMR that the resulting degradation byproduct dimethylamine can form a strong acid–base complex with sulfonic acid groups. Hence, although DMF may appear to be a better choice of solvent for PEM fabrication due to its lower boiling point compared with DMAc, a combination of factors result in DMF giving lower proton conductivity than DMAc and other solvents.

4. Conclusion

A comparative study of sulfonation and product characterization of both commercial Victrex® and Gatone® PEEK was conducted. Both PEEKs show identical chain structure according to NMR spectroscopy and have similar molecular weights. It is verified that higher temperature sulfonation (55 °C) did not induce any apparent chain degradation of PEEK as shown by M_w tests. A new method for determining the DS of SPEEK directly in the sulfuric acid (non-deuterated) reaction solution was accomplished by ^{1}H NMR using a solvent suppression technique. A ^{1}H NMR method, using a solvent suppression technique, gives DS values higher than those obtained by what might be considered the more accurate method of ^{1}H NMR analysis of a recovered samples in DMSO-d_6 solution. The new method is useful to evaluate the sulfonation kinetics and to obtain a desired target DS for SPEEK. From TGA tests, both Victrex® and Gatone® derived SPEEKs show a high first thermal degradation temperature (~250 °C). As follows from comparison with NMR results, TGA is also be a practical method to determine the DS of SPEEKs. The conductivities of the SPEEKs were found to increase with increasing DS. Films cast from DMAc show higher proton conductivity than those of SPEEK membranes cast from DMF. The effect of casting solvents on the proton conductivity of SPEEK was recently explained by the formation of strong complexes between the decomposed product of the solvent and sulfonic acid groups [38].

Acknowledgements

References

[1] O. Savadogo, Emerging membranes for electrochemical system. I. Solid polymer membranes for fuel cell systems, J. New Mater. Electr. Syst. 1 (1998) 47.

[2] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, Electron and proton conducting polymers: recent developments and prospects, Electrochim. Acta 45 (2000) 2403.

[3] J. Kerres, Development of ionomer membranes for fuel cells, J. Membr. Sci. 185 (2001) 3.

[4] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cell, J. Membr. Sci. 185 (2001) 29.

[5] M. Rikukawa, K. Sanui, Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, Prog. Polym. Sci. 25 (2000) 1463.

[6] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, Polymeric proton conducting membranes for medium temperature fuel cell (110–160 °C), J. Membr. Sci. 185 (2001) 73.

[7] H.H. Ulrich, G. Rafler, Sulfonated poly(aryl ether ketone)s, Die Angew. Makromol. Chem. 263 (1998) 71.

[8] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, Proton conducting composite membranes from poly(ether ether ketone) and heteropolyacids for fuel cell application, J. Membr. Sci. 173 (2000) 17.

[9] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes, J. Membr. Sci. 197 (2002) 231.

[10] J. Kerres, A. Ullrich, F. Meier, Th. Haring, Synthesis and characterization of novel acid–base polymer blends for the application in membrane fuel cells, Solid State Ionics 125 (1999) 243.

[11] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes, Polymer 42 (2001) 359.

[12] X. Guo, J. Fang, T. Watari, K. Tanaka, H. Kita, K. Okamoto, Novel sulfonated polyimides as polyelectrolytes for fuel cell application. 2. Synthesis and proton conductivity of polyimides from 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid, Macromolecules 35 (2002) 6707.

[13] D.J. Jones, J. Roziere, Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications, J. Membr. Sci. 185 (2001) 41.

[14] J.A. Asensio, S. Borros, P. Gomz-Remero, Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles, J. Polym. Sci. A 40 (2002) 3703.

[15] X. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, A sulphonated poly(aryl ether ether ketone), Br. Polym. J. 17 (1985) 4.

[16] M.T. Bishop, F.E. Karasz, P.S. Russo, K.H. Langle, Solubility properties of a poly(aryl ether ether ketone) in strong acids, Macromolecules 18 (1985) 86.

[17] C. Bailly, D.J. Williams, F.E. Karasz, W.J. MacKnight, The sodium salts of sulphonated poly(aryl-ether-ether-ketone) (PEEK): preparation characterization, Polymer 28 (1987) 1009.

[18] F. Wang, J. Li, T. Chen, J. Xu, Synthesis of poly(ether ether ketone) with high content of sodium sulfonate groups and its membrane characteristics, Polymer 40 (1999) 795.

[19] M.C. Wijers, M. Jin, M. Wessling, H. Strathmann, Support liquid membranes modification with sulphonated poly(ether ether ketone): permeability, selectivity and stability, J. Membr. Sci. 147 (1998) 117.

[20] F.G. Wilhelm, I.G.M. Punt, N.F. van der Vegt, H. Strathmann, M. Wessling, Cation permeable membranes from blends of sulfonated poly(ether ether ketone) and poly(ether sulfone), J. Membr. Sci. 199 (2002) 167.

[21] F. Helmer-Metamann, F. Osan, A. Schneller, H. Ritter, K. Ledjeff, R. Nolte, R. Thorwirth, US Patent 5 438 082 (1995).

[22] B. Bauer, D.J. Jones, J. Roziere, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, A. Peraio, S. Besse, E. Ramunni, Electrochemical characterization of sulfonated polyetherketone membranes, J. New Mater. Electr. Syst. 3 (2000) 93.

[23] T. Kobayashi, M. Rikukawa, K. Sanuui, N. Ogata, Proton-conducting polymers derived from poly(ether-etherketone) and

poly(4-phenoxybenzoyl-1,4-phenylene), Solid State Ionics 106 (1998) 219.

[24] T. Soczka-Guth, J. Baurmeister, G. Frank, R. Knauf, Method for producing a membrane used to operate fuel cells and electrolysers, International Patent WO99/29763 (1999).

[25] K.D. Kreuer, T. Dippel, J. Maier, Membrane materials for PEM fuel cells: a microstructural approach, Proc. Electrochem. Soc. 95 (23) (1995) 241.

[26] S.P.S. Yen, S.R. Narayanan, G. Halpert, E. Graham, A. Yavrouian, Polymer material for electrolytic membranes in fuel cells, US 5 795 496 (1998).

[27] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, Electrical properties of sulfonated polyether ether ketone/polyetherimide blend membranes doped with inorganic acids, J. Polym. Sci. B 38 (2000) 1386.

[28] C. Manea, M. Mulder, Characterization of polymer blends of polyethersulfone/sulfonated polysulfone and polyethersulfone/sulfonated polyetheretherketone for direct methanol fuel cell applications, J. Membr. Sci. 206 (2002) 443.

[29] D. Daoust, J. Devaux, P. Godard, A. Jonas, R. Legras, in: H. Kausch (Ed.), Advanced Thermoplastic Composites—Characterization and Processing, Carl Hanser, Munich, 1992, Chapter 1.

[30] T. Ogawa, C.S. Marvel, Polyaromatic ether-ketones ether-ketone-sulfones having various hydrophilic groups, J. Polym. Sci. A 23 (1985) 1231.

[31] J. Devaux, D. Delimoy, D. Daoust, R. Legras, J.P. Mercier, C. Strazielle, E. Nield, On the molecular weight determination of a poly(aryl ether ether ketone) (PEEK), Polymer 26 (1985).

[32] D. Daoust, J. Devaux, P. Godard, Mechanism kinetics of poly(ether ether ketone) (PEEK) sulfonation in concentrated sulfuric acid at room temperature. Part 1. Qualitative comparison between polymer and monomer model compound sulfonation, Polym. Int. 50 (2001) 917.

[33] D. Daoust, J. Devaux, P. Godard, Mechanism kinetics of poly(ether ether ketone) (PEEK) sulfonation in concentrated sulfuric acid at room temperature. Part 2. Qualitative interpretation of model compound sulfonation, Polym. Int. 50 (2001) 925.

[34] N. Shibuya, R.S. Porter, A kinetic study of PEEK sulfonation in concentrated sulfuric acid by ultraviolet-visible spectroscopy, Polymer 35 (1994) 3237.

[35] R.Y.M. Huang, P. Shao, C.M. Burns, X. Feng, Sulfonation of poly(ether ether ketone) (PEEK): kinetic study characterization, J. Appl. Polym. Sci. 82 (2001) 2651.

[36] Y. Luo, R. Huo, X. Jin, F.E. Karasz, Thermal degradation of sulfonated poly(aryl ether ether ketone), J. Anal. Appl. Pyrol. 34 (1995) 229.

[37] S. Kaliaguine, S.D. Mikhailenko, K. Wang, P. Xing, G.P. Robertson, M.D. Guiver, Properties of SPEEK based PEMs for fuel cell application, Catal. Today 82 (2003) 213.

[38] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, Casting solvent interactions with sulfonated poly(ether ether ketone) during proton exchange membrane fabrication, J. Membr. Sci. 219 (2003) 113.