



NRC Publications Archive Archives des publications du CNRC

Sulfonated copoly(phthalazinone ether ketone nitrile)s as proton exchange membrane materials

Gao, Yan; Robertson, Gilles P.; Guiver, Michael D.; Wang, Guoqing; Jian, Xigao; Mikhailenko, Serguei D.; Li, Xiang; 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:

<https://doi.org/10.1016/j.memsci.2005.10.041>

Journal of Membrane Science, 278, pp. 26-34, 2006

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

<https://nrc-publications.canada.ca/eng/view/object/?id=8fdaeef4-ddb0-48c3-a260-3235737e4222>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=8fdaeef4-ddb0-48c3-a260-3235737e4222>

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

<https://nrc-publications.canada.ca/eng/copyright>

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

<https://publications-cnrc.canada.ca/fra/droits>

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

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



Sulfonated copoly(phthalazinone ether ketone nitrile)s as proton exchange membrane materials[☆]

Yan Gao^{a,b}, Gilles P. Robertson^a, Michael D. Guiver^{a,*}, Guoqing Wang^b, Xigao Jian^b,
Serguei D. Mikhailenko^c, Xiang Li^c, Serge Kaliaguine^c

^a Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ont. K1A 0R6, Canada

^b Department of Polymer Science and Materials, Dalian University of Technology, Zhongshan Road 158-42#, Dalian 116012, PR China

^c Chemical Engineering Department, Laval University, Que. G1K 7P4, Canada

Received 19 July 2005; received in revised form 26 October 2005; accepted 29 October 2005

Available online 1 December 2005

Abstract

Sulfonated poly(phthalazinone ether ketone nitrile) copolymers (SPPEKN) were prepared by copolymerization of disodium 3,3'-disulfonate-4,4'-difluorobenzophenone (SDFB-Na), 2,6-difluorobenzonitrile (2,6-DFBN), and 4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone (DHPZ) at 160 °C in *N*-methyl-2-pyrrolidone containing anhydrous potassium carbonate. The polymerization reactions proceeded smoothly and in high yield giving high molecular weight SPPEKN copolymers with different sulfonic acid content (SC) values. The polymer structures were defined by ¹H NMR and FT-IR. Membrane films of SPPEKN copolymers in both salt and acid forms, prepared at SDFB-Na to 2,6-DFBN feed ratios up to 60/40 mol/mol, were cast from the *N,N*-dimethylacetamide (DMAc) polymer solutions. The presence of highly polar nitrile groups are expected to increase inter-chain molecular forces, contributing to the observed reduction in water swelling over previously prepared sulfonated poly(phthalazinone ether ketone) (SPPEK) copolymers. Membranes containing nitrile groups are expected to show improved adhesion between polymer and catalyst when utilized in a fuel cell. All SPPEKN copolymers exhibited tensile strength higher than that of Nafion® 117. The proton conductivities of acid form SPPEKN copolymers (SPPEKNH)s, prepared at the sulfonated/unsulfonated monomer feed ratio above 0.35 mol/mol, were around 10⁻¹ S/cm at 80 °C, which is close to or higher than that of Nafion® 117 under same measurement conditions.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Sulfonated poly(phthalazinone ether ketone nitrile); Copolymerization; Proton exchange membrane; Fuel cell; Ionomer; Poly(ether ketone); Poly(ether nitrile)

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising clean power sources for vehicular transportation, residential and institutional, and also for computers, mobile communication equipment, etc. [1]. Numerous investigations have been performed to improve the PEMFCs cost efficiency and performance [2,3]. One of the challenges of the current researches is to develop alternatives to perfluorinated sulfonic acid polymer materials, which are the state-of-the-art polymer electrolyte for PEMFCs. Although perfluorinated sulfonic acid polymers, such as Nafion® developed by DuPont, exhibit good mechanical

properties, extremely high oxidative stability, high proton conductivity and long-term durability under PEMFC operating conditions. However, they suffer from some drawbacks, such as extremely high cost, dehydration at operating temperatures >80 °C causing the conductivity decline, high permeability for liquid fuels and poor environmental safety. To achieve a practical applicability in fuel cells, many new polymer electrolytes have been prepared recently aiming to satisfy several rigorous requirements: high proton conductivity $\geq 10^{-2}$ S/cm, an increased barrier to fuel cross-over compared with Nafion, reasonable hydrophilicity and hydrothermal stability, mechanical strength and low cost.

The well-known excellent thermal, mechanical, and dielectric properties, oxidative resistance and other favorable properties of high performance thermoplastic polymers, such as poly(aryl ether sulfone)s, and poly(aryl ether ketone)s are a good basis for their development as proton conducting mate-

[☆] NRCC No. 47863.

* Corresponding author. Tel.: +1 613 993 9753; fax: +1 613 991 2384.
E-mail address: michael.guiver@nrc-cnrc.gc.ca (M.D. Guiver).

rials by the introduction of sulfonic acid or other proto-genic groups. Sulfonated poly(arylene ether ketone)s (SPAEEK) and sulfonated poly(arylene ether sulfone)s (SPAES)s show proton conductivities [4–23] that are adequate for application in fuel cells. For example, biphenyl-based sulfonated poly(arylene ether sulfone)s reported by Wang et al. [8] obtained by direct polymerization reactions of disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS), 4,4'-dichlorodiphenylsulfone and 4,4'-biphenol, show longitudinal proton conductivities of 0.11 and 0.17 S/cm at 30 °C and 100% RH for the 40% and the 60% SDCDPS copolymers, respectively. Wholly aromatic poly(ether ether ketone)s containing pendant sulfonic acid groups (SPAEEKK) prepared by our group via nucleophilic polycondensation of commercially available monomers: 1,3-bis(4-fluorobenzoyl)benzene (BFBB), sodium 6,7-dihydroxy-2-naphthalenesulfonate (DHNS), and 4,4'-biphenol, had transverse proton conductivity of 5.6×10^{-2} S/cm at 100 °C [23].

Poly(phthalazinone ether ketone) (PPEK), poly(phthalazinone ether sulfone) (PPES) and associated copolymers are new engineering thermoplastics currently undergoing commercialization. They have very high T_g 's of 263 and 295 °C, respectively, excellent high-temperature stability, and many other favorable properties. Their sulfonated derivatives: sulfonated poly(phthalazinone ether ketone) (SPPEK) and sulfonated poly(phthalazinone ether sulfone) (SPPEES) have been recently prepared by both post-sulfonation reactions and direct polymerization reactions of phthalazinone monomer and sulfonated dihalo monomers [12–15]. Both methods gave SPPEK and SPPEES copolymers with transverse proton conductivities higher than 10^{-2} S/cm at SC around 1.0. The high proton conductivities indicated their potential as promising proton exchange membranes (PEM)s for fuel cells applications. Compared with post-sulfonation reactions, polymerization reactions allows precise control of the sulfonate content in the polymers and avoid crosslinking or other side reactions that could occur under modification conditions. In addition, polymerized SPPEK copolymers showed less temperature dependence of proton conductivities than post-sulfonated SPPEK copolymers. However, like most SPAEK and SPAES copolymers, they have a tendency to swell in hot water, especially copolymers with high SC. This usually involves a degradation of membrane strength and may impair adhesion of catalyst in membrane electrode assembly (MEA) used in PEMFC.

Recently, it was also reported [24,25] that polar nitrile groups were introduced into sulfonated poly(aryl ether sulfone)s with the aim of decreasing the membrane swelling via enhanced intermolecular interaction, which could potentially promote adhesion of the polymers to heteropolyacid in the composite membrane or MEA study. The introduction of highly polar nitrile groups are expected to increase the inter-chain molecular dipole forces and make the polymers less moisture absorbable than previously prepared sulfonated poly(phthalazinone ether ketone) (SPPEK) copolymers and improve the combination of polymer and catalyst in the possible future usage. We believe that there is a potential for enhanced adhesive ability of SPAEK and SPAES copolymers to inorganic compounds, which would

be beneficial for adhesion of catalyst and carbon black to the membranes in MEA. The present work reports the synthesis of poly(phthalazinone ether ketone nitrile) copolymers containing sulfonic acid groups (SPPEKN) via nucleophilic polycondensation reactions. The properties of SPPEKN membranes, such as thermal stability, tensile properties, water uptake and swelling and proton conductivities are also examined.

2. Experimental

2.1. Materials

DHPZ was provided by Dalian Polymer New Material Co. Ltd., PR China and the preparation procedure was reported previously [26–29]. SDFB-Na was prepared according to the procedures described in literature [10] and elsewhere [12]. *N*-Methyl-2-pyrrolidone (NMP) was vacuum distilled before use. All other chemicals (obtained from Aldrich) were reagent grade and used as received.

MEMBRA-CELTM dialysis tubing (MWCO 3500) was obtained from Serva Electrophoresis (Germany).

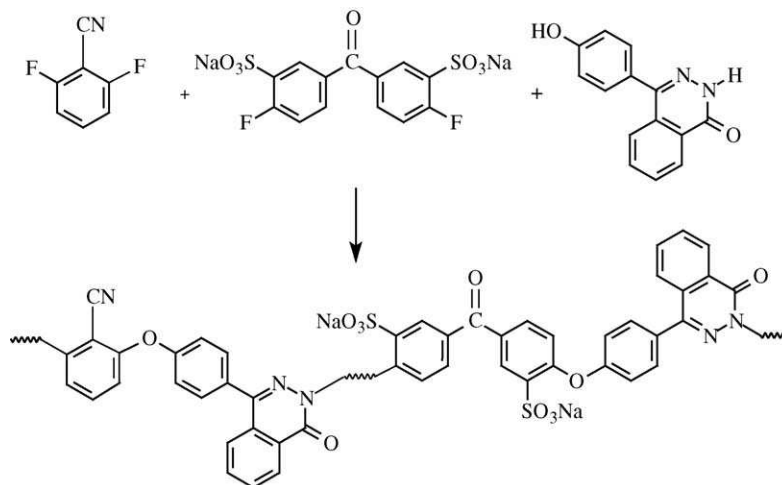
2.2. Copolymerization reaction

As depicted in Scheme 1, the SPPEKN copolymers were synthesized via nucleophilic polycondensation reaction. The synthesis of SPPEKN-40 is used as a typical example, where *n* (40) denotes the SDFB-Na monomer feed ratio to total amount of difluoro monomers (mol/mol). Into a three-neck flask equipped with a magnetic stirrer and furnished with a Dean-Stark trap, condenser and an argon inlet, 0.8605 g 2,6-DFBN (4.04 mmol), 1.706 g SDFB-Na (6 mmol), 2.383 g DHPZ (10 mmol), and 1.8 g potassium carbonate (13 mmol) were added. Then 12 mL of NMP and 20 mL chlorobenzene were charged into the reaction flask under argon atmosphere. The reaction mixture was heated to 140 °C. After dehydration and removal of chlorobenzene (~3–4 h), the reaction temperature was increased to about 165 °C. After 5–7 h, when the solution viscosity apparently increased, several mL of NMP was added to dilute the solution and the reaction was continued for a further 3–5 h. Then, the mixture was cooled to 100 °C and coagulated in a large excess of ethanol under vigorous stirring. After recovering the product, SPPEKN-40 was washed with deionized water to remove residual solvent and salt.

2.3. Copolymer analysis and measurement

¹H NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. Deuterated dimethylsulfoxide (DMSO-*d*₆) was the most convenient NMR solvent for SPPEK; the TMS signal at 0 ppm was used as the chemical shift reference. IR spectra were recorded on a Nicolet 520 Fourier transform spectrometer on the membrane film samples in air.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for measuring the degradation (weight loss) temperatures (T_d) and a TA Instruments differen-



Scheme 1. Synthesis of SPPEKN copolymers.

tial scanning calorimeter (DSC) model 2920 calibrated with tin at 231.93 °C was used for measuring the glass transition temperatures (T_g 's). Copolymer samples for TGA analysis were preheated to 120 °C at 10 °C/min in air and held isothermally for 60 min for moisture removal. Samples were then heated from 90 to 750 °C at 10 °C/min for T_d measurement. Samples in sodium form for DSC analysis were initially heated rapidly at a rate of 20 °C/min under nitrogen atmosphere to 450 °C, followed by quenching in liquid nitrogen. When the DSC cell had cooled to around 50 °C, the samples were replaced in the cell and heated at a rate of 10 °C/min to 400 °C. The procedure for the samples in acid form was similar except that the initial heating rate was 10 °C/min and the end point was below the polymer T_d point.

Intrinsic viscosities were determined using an Ubbelohde viscometer for *N,N*-dimethylacetamide (DMAc) solutions of polymer at 25 °C.

2.4. Preparation of membrane films

An amount of 1 g sulfonated polymer in sodium form (SPPEKN) was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at 40 °C for about 2 days. The acid form (SPPEKNH) membrane films were obtained by immersing sodium form films in 2N H_2SO_4 for 24 h at room temperature, followed by deionized water for 24 h during which period deionized water was changed several times in order to remove excess of acid, and dried in the air for several hours.

2.5. Water uptake and swelling ratio measurement

The sample films were soaked in deionized water for 24 h. The membrane films were then dried at 80 °C for 24 h. Weights of dry and hydrated membranes were measured. The water uptake 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 masses of dried and wet samples, respectively. The swelling ratio was calculated from films

(5–10 cm long) 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.

2.6. Tensile test

Tensile tests were performed on an Instron tensile tester (model 1123) at a strain speed of 50 mm/min at room temperature. Membrane films with a typical size of 40 mm × 4 mm × 0.05 mm were used for testing.

2.7. Proton conductivity

The proton conductivity measurements were performed on SPPEKNH membrane films by AC impedance spectroscopy over a frequency range of 1–10⁷ Hz with oscillating voltage (50–500 mV), using a system based on a Solatron 1260 gain phase analyzer. A 20 mm × 10 mm membrane sample was clamped by the edges between stainless steel electrodes and placed in a temperature controlled cell open to the air by a pinhole where the sample was equilibrated at 100% RH at ambient atmospheric pressure. Specimens were soaked in deionized water for 24–48 h prior to the test. The conductivity (σ) of the samples in the longitudinal direction was calculated from the impedance data, using the relationship $\sigma = l/R \times d \times w$, where l is a distance between the electrodes, d the thickness, w the width of the sample and R was derived from the low intersect 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. Copolymerization

In order to obtain polymers with target proton conductivities of $\geq 10^{-2}$ S/cm, a specific range of monomer compositions

Table 1
Viscosity data for SPPEKN copolymers

Polymer	SDFB-Na (mmol)	2,6-DFBN (mmol)	DHPZ (mmol)	$[\eta]^a$ (dL/g)	EW (IEC) expected (g/mol SO ₃ (milliequiv. g ⁻¹))	SC expected
SPPEKN-30	3.0	7.07	10	2.32	702 (1.42)	0.6
SPPEKN-35	3.5	6.56	10	1.71	631 (1.58)	0.7
SPPEKN-40	4.0	6.06	10	1.39	562 (1.78)	0.8
SPPEKN-45	4.5	5.56	10	1.20	515 (1.94)	0.9
SPPEKN-50	5.0	5.05	10	1.45	478 (2.09)	1.0
SPPEKN-55	5.5	4.55	10	0.684	447 (2.24)	1.1
SPPEKN-60	6.0	4.04	10	1.02	422 (2.37)	1.2

^a Measured at 25 °C in DMAc.

was designed for SPPEKN copolymers. The series of SPPEKN copolymers were prepared by nucleophilic substitution reactions with DHPZ as the diphenol, SDFB-Na and 2,6-DFBN as activated dihalides and K₂CO₃ as a weak base. All SPPEKN copolymers were obtained under the same polymerization conditions previously used for the syntheses of SPPEK and SPPEK copolymers [12]: argon atmosphere, NMP used as solvent, chlorobenzene used to remove the water generated by the reaction of diphenol with K₂CO₃ at 130–140 °C. When an obvious increase in the viscosity of reaction solution was observed at 170 °C, indicating a high molecular weight of the product, it was precipitated in ethanol or water. As shown in Scheme 1, the sulfonate content and the nitrile group content in SPPEKN copolymers were balanced by varying the feed ratio of SDFB-Na to 2,6-DFBN. The sulfonate content (SC) is used to distinguish between different SPPEKN copolymers in the series and is expressed as the molar ratio of SDFB-Na units (bearing the –SO₃Na group) to 1.0 mol of DHPZ. For example, the average repeat unit of SPPEKN-30 copolymer is composed of 0.3 unit of SDFB-Na, 0.7 unit of 2,6-DFBN and 1.0 unit of DHPZ. Table 1 lists the polymerization conditions and details of the resulting polymers. In order to obtain the polymers with proton conductivities higher than 10⁻² S/cm, only SPPEKN copolymers with SC values ranged from 0.3 to 0.6 were synthesized. All SPPEKN copolymers had intrinsic viscosities higher than 0.6 in DMAc at 25 °C indicating the polymerizations proceeded to high molecular weights. All SPPEKN copolymers were cast into free-standing films, also confirming the high molecular weight of the resulting copolymers. Equivalent molecular weight (M_{eq}) and ionic exchange capability (IEC) were also calculated from the initial reagents ratios and listed in Table 1 for comparison.

3.2. FT-IR

FT-IR is a convenient method to confirm the sulfonate or nitrile groups in new polymers. Fig. 1 illustrates the FT-IR spectra of SPPEKN copolymers, along with a comparative spectrum of SPPEK-50 (0.5 unit of SDFB-Na, 0.5 unit of 4,4-difluorobenzophenone and 1.0 unit of DHPZ) for comparison. In all the spectra of SPPEKN copolymers characteristic bands of the aromatic sulfonate salt (symmetric and asymmetric stretching vibrations of S=O) were observed at 1027 and 1096 cm⁻¹ and the characteristic symmetric stretching vibration of nitrile groups at 2247 cm⁻¹ was observed, only in SPPEKN spectra. It

is seen that the intensity of two characteristic sulfonate absorption bands increases with SC, while the intensity of the nitrile absorption decrease with SC. This confirms that the number of sulfonate and nitrile groups, introduced into the copolymers, was the function of the monomer feed ratio. Some other characteristic absorptions in SPPEKN copolymers were also assigned. The absorption band at around 1600 cm⁻¹ is attributed to C=C stretching vibration in phenyl rings. The absorption bands around 1668 cm⁻¹ is attributed to carbonyl group. The characteristic absorption band of 1,4-aromatic ring substitutions at 1510 cm⁻¹ also decrease with SC values. The absorption bands at 1217 and 1260 cm⁻¹ are assigned to phenoxy group absorptions.

3.3. NMR

Fig. 2 displays the aromatic region of five polymers. The top and bottom spectra represent the polymers poly(phthalazinone ether nitrile) (PPEN) and SPPEK, respectively, whereas the three other spectra are related to SPPEKN with various SC. The assignment of the PPEN signals was done using ¹H and 2D-COSY and TOCSY NMR. The three different hydrogen spin systems (H-6,7,8,9; H-25,26; H-31,32,33) were easily detected and assigned using 2D spectroscopy. The analysis of SPPEK ¹H spectrum was performed earlier [12] and is shown in Fig. 2. These two fully-assigned spectra were incorporated into Fig. 2 in order to better visualize the signal changes taking place in the three SPPEKN spectra. The copolymer spectra are very complex as a result of the asymmetry of the phthalazinone monomer.

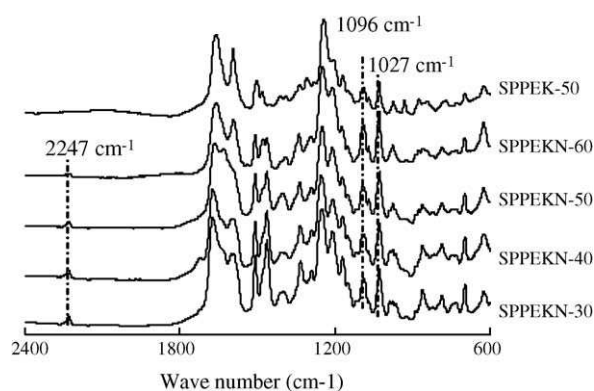


Fig. 1. FT-IR spectra of SPPEKN copolymers in sodium form.

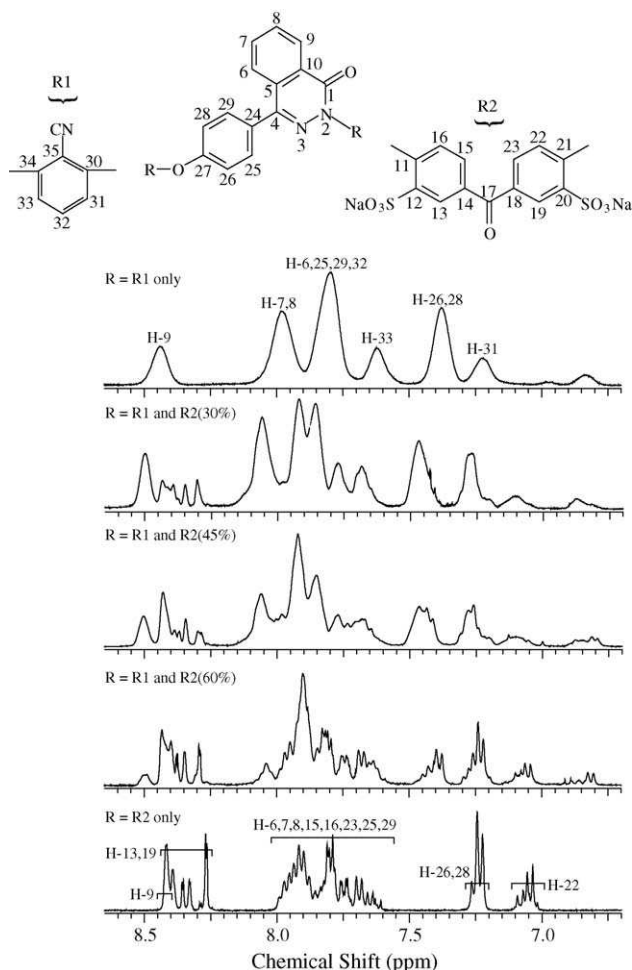


Fig. 2. ^1H NMR stacked spectra of PPEKN (top), SPPEK (bottom) and SPPEKN with SC of 30, 45 and 60%.

As illustrated in Fig. 2, both R groups for the copolymers can either be nitrile or sulfonated monomers. The different feed ratios of sulfonated monomer also add complexity to the spectra. Therefore, we did not attempt to assign all the signals from the three SPPEKN copolymers. Nevertheless, Fig. 2 clearly shows increasing downfield signals for the sulfonated monomer and decreasing upfield growing for the nitrile monomer. Previous experience [12] in measuring the SC by ^1H NMR has shown that the SC is usually consistent with the feed ratio of monomers. One can observe in Fig. 2 that sulfonated repeat unit signals increase with SC while nitrile signals decrease. The smaller signals at lower frequency may be attributed to chain end groups or resulted from one of the possible RU configuration due to the factors described above.

3.4. Thermal properties

The thermal properties of SPPEKN copolymers in both salt and acid forms are listed in Table 2 and illustrated in Fig. 3. There is only one weight loss step in the TGA curves of salt form SPPEKN copolymers (Fig. 3), which is assigned to the degradation of polymer main chain. Compared with PPEK and SPPEKS [12], no obvious difference in the thermal stability of salt form

Table 2

Thermal properties of SPPEKN copolymers

Polymer	T_g ($^{\circ}\text{C}$)		$T_d(5\%)$ ($^{\circ}\text{C}$)		T_d ($^{\circ}\text{C}$) extrapolated onset for first weight loss	
	Sodium form	Acid form	Sodium form	Acid form	Sodium form	Acid form
PPEK	263		487		470	
SPPEK-40 ¹²	367	294	475	340	456	302
SPPEK-50 ¹²	390	ND	482	322	458	294
SPPEK-60 ¹²	ND	ND	484	339	461	307
SPPEKN-30	359	ND	475	327	463	278
SPPEKN-35	362	ND	480	348	473	293
SPPEKN-40	365	ND	483	342	479	298
SPPEKN-45	372	ND	483	342	476	303
SPPEKN-50	ND	ND	479	317	475	282
SPPEKN-55	ND	ND	479	310	474	337
SPPEKN-60	384	ND	466	327	476	296

ND: not detected.

SPPEKN copolymers was observed and all their 5% weight loss temperatures and the extrapolated onset temperatures are higher than 450°C , indicating the high thermal stabilities of sodium form SPPEKN copolymers. In similarity with observations made previously [11–13,23] there are two distinct weight loss steps in the TGA curves of SPPEKNH copolymers. The 5% weight loss temperatures and the extrapolated onset temperatures for the first weight loss of SPPEKNH (caused by the loss of sulfonic acid groups) are all higher than 280°C , and decrease with increasing SC. The second thermal degradation around 480°C is assigned to the degradation of the polymer main chain. In comparison with SPPEK, the introduction of nitrile groups into the polymer chain did not have an obvious effect on the thermal properties of SPPEKN either in salt or in acid forms.

Table 2 also lists the T_g 's of SPPEKN copolymers. SPPEKNH copolymers were not detectable as their weight loss started earlier than glass transition (T_g 's > T_d 's). SPPEKN copolymers in sodium salt form showed T_g 's increasing with SC from 359 to 384°C , which is higher than the T_g of non-sulfonated PPEK.

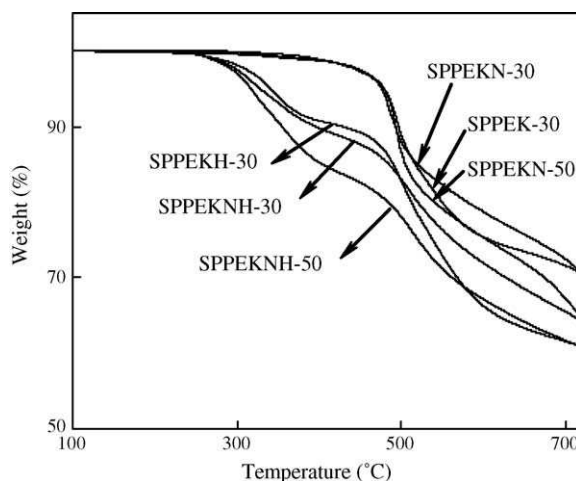


Fig. 3. TGA traces of copolymers.

The increase in the T_g 's of SPPEKN copolymers are the result of the introduction of sodium sulfonate or sulfonic acid groups, which increases intermolecular interaction by pendant ions or by hydrogen bonding and molecular bulkiness and hinder the internal rotation of high molecular chain segments. The introduction of nitrile groups, as follows from the comparison with SPPEK data, did not reduce the T_g 's of copolymers.

3.5. Water uptake and swelling ratio

It was reported that some sulfonated polymers are nanophase separated into hydrophilic and hydrophobic domains wherein sulfonate or sulfonic acid groups and polymer backbones aggregate separately [8,19,25,30]. The hydrophobic part provides the hydrated sulfonated polymer membrane films with morphological and mechanical stability, whereas the hydrophilic domains imbibe water and ensure proton conductivity. Since PEMs in fuel cells are generally operated at temperatures close to 80 °C, water uptake and swelling ratio of SPPEKN copolymers were measured at both room temperature and 80 °C as functions of the SC and of the counter ion nature. The results are shown in Table 3. SPPEKN-55 in sodium form was brittle when fully dehydrated, which made it difficult to measure its length and weight. Therefore, no data on this sample were reported, despite the fact that its sodium form maintained its shape when hydrated at room temperature. In general, the water uptake and swelling ratio of SPPEKN copolymers in both salt and acid forms increase with SC (or IEC) and temperature. Membrane films in acid form have higher water uptake and swelling values than their salt form films because of the hydrogen bond interactions between H₂O and sulfonic acid groups. Compared with Nafion® 117 (IEC = 0.91 mmol/g, water uptake 35% at room temperature [31]) and previously SPPEK copolymers [12] (prepared from DHPZ, 4,4'-SDFB-Na and 4,4'-difluorobenzophenone), SPPEKN copolymers with similar IEC have lower water uptake. As a comparison, polymers with and without nitrile groups are discussed. SPPEKH (no nitrile) and SPPEKNH (nitrile) have different types of repeat units, so it is more meaningful to compare derivatives with similar EW than those with similar SC in order to get truly comparative ionic content. SPPEKH-50

has an EW of 568 that is similar to SPPEKNH-40, which has a value of 562. At 80 °C, SPPEKH-50 had a water uptake of 210 wt.% and a swelling ratio of 50%, whereas SPPEKNH-40 had a water uptake of 99 wt.% and a swelling ratio of 31%. In other words, SPPEKNH copolymers imbibe less water and swell less than similarly structured polymers that do not contain the nitrile group under the same conditions. Since the aggregation of hydrophilic sulfonic acid groups in SPPEKNH membrane films appears to be similar to those in SPPEK, relative decrease in the water uptake and swelling may be assigned to the greater hydrophobic aggregation occurring in SPPEKNH. The use of 2,6-DFBN for the SPPEKN copolymerizations instead of 4,4'-difluorobenzophenone employed in synthesis of SPPEK resulted in the strongly polar nitrile groups, pendant on aromatic rings of SPPEKN copolymers, instead of the more weakly-interactive ketone groups in the polymer main chains of SPPEK copolymers. The presence of strongly polar nitrile groups obviously enhances the intra/intermolecular interaction in the polymer and enhances the toughness of the hydrophobic network structure. As a result, free volume for water adsorption in SPPEKN membrane films is restricted, thereby reducing the water uptake. Consequently the dimensional stability of membrane films is improved.

3.6. Tensile properties

Besides the thermal and dimensional stability, an important requirement imposed on PEMs for fuel cells is adequate mechanical strength. The tensile properties of SPPEKNH copolymers were tested at room temperature in both the dry and fully hydrated states and the results are presented in Table 4. It can be seen that all SPPEKNH copolymers exhibited good tensile strength ranging from 22 to 52 MPa and an elongation at break ranging from 3.7 to 5.8%. SPPEKNH-55 exhibited lower tensile strength than other SPPEKNH copolymers, since SPPEKNH-55 had lower molecular weight than other copolymers. For comparison, Nafion® 117 was also tested under the same conditions and the results are also shown in Table 4. Compared with Nafion® 117, all SPPEKNH copolymers exhibited much higher tensile strength values and less elongation at

Table 3
Water uptake and swelling ratio of SPPEKN copolymers

Polymer	EW (IEC), calculated (g/mol SO ₃ (milliequiv. g ⁻¹))	Room temperature				80 °C			
		Water uptake (%)		Swelling ratio (%)		Water uptake (%)		Swelling ratio (%)	
		Sodium form	Acid form	Sodium form	Acid form	Sodium form	Acid form	Sodium form	Acid form
SPPEK-40 ¹²	698 (1.43)	21	24	6.0	9.5	26	28	7.5	11
SPPEK-50 ¹²	568 (1.76)	33	42	11	15	101	210	29	50
SPPEK-60 ¹²	482 (2.07)	47	60	14	20	410	2300	87	150
SPPEKN-30	702 (1.42)	14	16	4.5	7.4	18	32	5.2	10
SPPEKN-35	631 (1.58)	16	20	5.6	8.5	20	40	6.8	14
SPPEKN-40	562 (1.78)	26	29	7.4	13	44	99	16	31
SPPEKN-45	515 (1.94)	31	34	7.9	15	65	150	20	42
SPPEKN-50	478 (2.09)	36	51	8.3	18	92	1100	25	145
SPPEKN-55	447 (2.24)	–	79	–	29	–	Dissolved	–	Dissolved
SPPEKN-60	422 (2.37)	220	Swelled	52	Swelled	Dissolved	Dissolved	Dissolved	Dissolved

Table 4
Tensile properties of SPPEKNH copolymers

Polymer	Dry membranes		Hydrated membranes	
	Tensile strength (MPa)	Elongation at break (%)	Tensile strength at break (MPa)	Elongation at break (%)
SPPEKNH-30	39	5.4	36	6.8
SPPEKNH-35	52	4.1	48	5.4
SPPEKNH-40	43	3.8	37	3.9
SPPEKNH-45	37	3.7	36	4.9
SPPEKNH-50	42	3.9	21	4.2
SPPEKNH-55	22	3.0	25	3.8
SPPEKNH-60	35	5.8	–	–
Nafion®117	10	623	–	–

break. After immersion in deionized water at room temperature for 24 h, during which time the polymer membrane films are normally fully hydrated [12,25], SPPEKNH copolymers exhibited decreases in tensile strength and increase in elongations at break except SPPEKNH-55, which maintained its tensile strength. SPPEKNH-60 swelled excessively and lost its mechanical strength in the fully hydrated state. The decreases in tensile strengths were the result of water plasticization in membrane films. In the dry state the sulfonic acid groups contribute to the tensile strength of membrane films via ionic interaction. However, in hydrated membranes the ionic interaction is partly replaced by hydrogen-bonding between H₂O and sulfonic acid groups. The film is growing in size due to imbibed water and the rigid network structure of the membrane is weakened, resulting in a decrease in its tensile strength. However, all hydrated SPPEKNH membrane films still show higher tensile strength than Nafion®117 and obviously suited to the tensile strength requirements for PEM intended for fuel cells applications.

3.7. Proton conductivity

Proton conductivities of SPPEKNH copolymers as functions of SC and temperature were measured in air at 100% relative humidity in the longitudinal direction by AC impedance spectroscopy and shown in Fig. 4. For comparison, the proton conductivity of Nafion®117 was also measured under the same conditions.

The SPPEKNH membrane film series showed room temperature proton conductivities in the range of around 10^{-2} to 10^{-1} S/cm depending on the SC values. SPPEKNH-60 swelled excessively even at room temperature; thus its proton conductivity could not be measured. The other films of the series showed an increase in proton conductivities with temperature and the values from 8.3×10^{-3} to 1.7×10^{-1} S/cm were observed for different SCs. This is close to the results, obtained for Nafion®117 which shown proton conductivities from 7.5×10^{-2} at room temperature to 1.6×10^{-1} S/cm at 97 °C. SPPEKNH-50 and SPPEKNH-55 exhibited conductivities, higher than or close to Nafion®117; they, however, suffer from excessive swelling at elevated temperatures or even dissolves in hot water. This makes them unsuitable for PEM applications at elevated temperatures, although they may be used at room temperature. SPPEKNH-

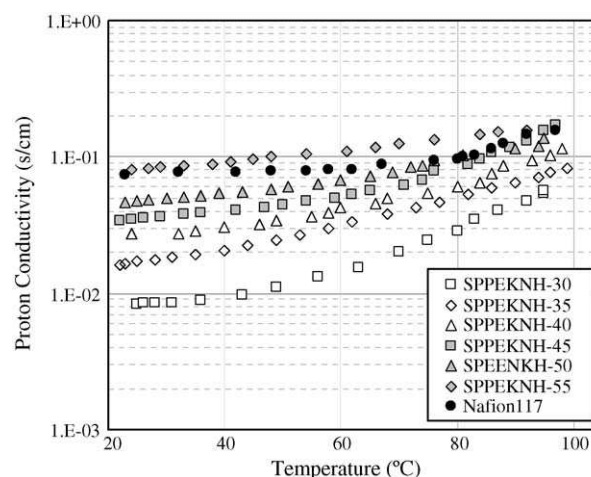


Fig. 4. Proton conductivities measured longitudinally of SPPEKNH copolymers compared with Nafion®117.

35, SPPEKNH-40 and SPPEKNH-45 films showed high proton conductivities from 10^{-2} to 10^{-1} S/cm at different temperatures, close to the values of Nafion®117. In addition, since they maintained reasonable dimensional stabilities and tensile strengths in both the dry and hydrated states, they could be considered as promising candidates for PEMs applications. Compared with Nafion®117, SPPEKNH copolymers exhibited a more rapid increase in proton conductivities with temperature, suggesting that SPPEKNH copolymers have higher activation energy for proton conductivity.

Since in our previous study the proton conductivities of SPPEKH copolymers (Fig. 5) were measured in their transverse direction (between film faces), those data are not directly comparable with the ones, obtained for SPPEKNH copolymers in the longitudinal direction in this study. Previously it was observed that proton conductivity values measured transversely are typically 3–5 times lower than those measured longitudinally [32]. The comparisons of each series were made against Nafion®117 which were measured either in the transverse and longitudinal directions. It can be seen from Figs. 4 and 5, that SPPEKH

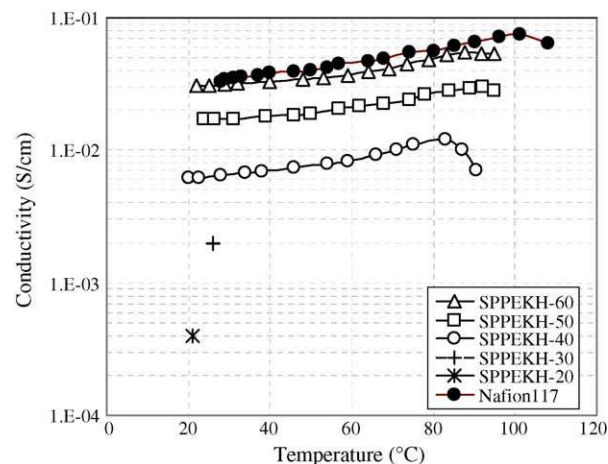


Fig. 5. Proton conductivities measured transversely of SPPEKH copolymers compared with Nafion®117.

and SPPEKNH showed proton conductivities close to the values obtained for Nafion[®] 117 with the similar dependence of the conductivity on SC with respect to the reference (Nafion). The introduction of nitrile groups did not provoke any significant decrease in the proton conductivities of copolymers.

4. Conclusions

Sulfonated poly(phthalazinone ether ketone nitrile) copolymers with high molecular weight were prepared by direct copolymerization reaction of disodium 3,3'-disulfonate-4,4'-difluorobenzophenone (SDFB-Na), 2,6-difluorobenzonitrile (2,6-DFBN), and 4-(4-hydroxyphenyl)-1(2*H*)-phthalazinone (DHPZ) under general polycondensation reaction conditions. The sulfonic acid group content (SC) and nitrile content in the copolymers were balanced by varying the feed ratio of sulfonated monomer SDFB-Na to unsulfonated monomer 2,6-DFBN and characterized by FT-IR and NMR spectroscopies. All SPEKNH copolymers exhibited thermal stabilities up to 270 °C, but no T_g 's were observed up to their degradation temperatures. The presence of highly polar nitrile groups in SPPEKNH renders the copolymers less moisture absorbable and swellable than the previously prepared SPPEKH copolymers, when comparing polymers of similar EW. The SPPEKNH copolymers exhibited tensile strength stronger than Nafion[®] 117 and reasonable flexibility in both the dry and hydrated states. The proton conductivities of SPPEKNH copolymers increase with SC and temperature and were found in the range of 10^{-2} to 10^{-1} S/cm, which is not inferior to Nafion[®] 117, measured under the same conditions. Nitrile groups are also anticipated to promote adhesion of the polymers to catalyst and carbon black in membrane electrolyte assembly (MEA) or to solid inorganic ionic compounds, such as heteropolyacids in composite membranes [25]. Considering the advantages of the prepared membranes, such as their thermal properties, tensile strength, dimensional stability in the hydrated state and high proton conductivity, it appears that SPPEKNH-35, -40 and -45 might be potential proton exchange membrane materials for fuel cells applications.

Acknowledgement

This work was supported primarily by the National Research Council of Canada Fuel Cell program. Partial support was also provided by the Natural Sciences and Engineering Research Council (NSERC) and by the National Natural Science Foundation of China (Contract grant number: 20104001).

References

- [1] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature* 414 (2001) 345–352.
- [2] O. Savadogo, Emerging membrane for electrochemical systems. I. Solid polymer electrolyte membranes for fuel cell systems, *J. New Mater. Electrochem. Syst.* 1 (1998) 47–66.
- [3] M. Rikukawa, K. Sanui, Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, *Prog. Polym. Sci.* 25 (2000) 1463–1502.
- [4] S.-P.S. Yen, S.R. Narayanan, G. Halpert, E. Graham, A. Yavrouian, US Patent 5,769,496 (1998).
- [5] F. Helmer-Metzmann, F. Osan, A. Schneller, H. Ritter, K. Ledjeff, R. Nolte, R. Thorwirth, US Patent 5,438,082 (1995).
- [6] T. Kobayashi, M. Rikukawa, K. Sanui, N. Ogata, Proton-conducting polymers derived from poly(ether-ether ketone) and poly(4-phenoxybenzoyl-1,4-phenylene), *Solid State Ionics* 106 (1998) 219–225.
- [7] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications, *J. Membr. Sci.* 173 (2000) 17–34.
- [8] 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) 231–242.
- [9] Y.S. Kim, L. Dong, M.A. Hickner, J.E. McGrath, State of water in disulfonated poly(arylene ether sulfone) copolymers and a perfluorosulfonic acid copolymer (Nafion) and its effect on physical and electrochemical properties, *Macromolecules* 36 (2003) 6281–6285.
- [10] W.L. Harrison, F. Wang, J.B. Mecham, V.A. Bhanu, M. Hill, Y.S. Kim, J.E. McGrath, Influence of the bisphenol structure on the direct synthesis of sulfonated poly(arylene ether) copolymers, *J. Polym. Sci., Part A: Polym. Chem.* 41 (2003) 2264–2276.
- [11] Y. Gao, G.P. Robertson, M.D. Guiver, X. Jian, Synthesis and characterization of sulfonated poly(phthalazinone ether ketone) for proton exchange membrane materials, *J. Polym. Sci., Part A: Polym. Chem.* 41 (2003) 497–507.
- [12] Y. Gao, G.P. Robertson, M.D. Guiver, X. Jian, S.D. Mikhailenko, K. Wang, S. Kaliaguine, Direct copolymerization of sulfonated poly(phthalazinone arylene ether)s for proton-exchange-membrane materials, *J. Polym. Sci., Part A: Polym. Chem.* 41 (2003) 2731–2742.
- [13] Y. Gao, G.P. Robertson, M.D. Guiver, X. Jian, S.D. Mikhailenko, K. Wang, S. Kaliaguine, Sulfonation of poly(phthalazinones) with fuming sulfuric acid mixtures for proton exchange membrane materials, *J. Membr. Sci.* 227 (2003) 39–50.
- [14] G. Xiao, G. Sun, D. Yan, P. Zhu, P. Tao, Synthesis of sulfonated poly(phthalazinone ether sulfone)s by direct polymerization, *Polymer* 43 (2002) 5335–5339.
- [15] G. Xiao, G. Sun, D. Yan, Polyelectrolytes for fuel cells made of sulfonated poly(phthalazinone ether ketone)s, *Macromol. Rapid Commun.* 23 (2002) 488–492.
- [16] J. Kerres, W. Cui, S. Reichle, New sulfonated engineering polymers via the metalation route. I. Sulfonated poly(ethersulfone) PSU Udel via metalation-sulfonation-oxidation, *J. Polym. Sci., Part A: Polym. Chem.* 34 (1996) 2421–2438.
- [17] J. Kerres, W. Zhang, W. Cui, New sulfonated engineering polymers via the metalation route. II. Sulfonated/sulfonated poly(ether sulfone) PSU Udel and its crosslinking, *J. Polym. Sci., Part A: Polym. Chem. Ed.* 36 (1998) 1441–1448.
- [18] J.A. Kerres, Development of ionomer membranes for fuel cells, *J. Membr. Sci.* 185 (2001) 3–27.
- [19] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *J. Membr. Sci.* 185 (2001) 29–39.
- [20] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes, *J. Membr. Sci.* 229 (2004) 95–106.
- [21] B. Lafitte, L.E. Karlsson, P. Jannasch, Sulfophenylation of polysulfones for proton-conducting fuel cell membranes, *Macromol. Rapid Commun.* 23 (2002) 896–900.
- [22] M.D. Guiver, J.W. ApSimon, O. Kutowy, The modification of polysulfone by metalation, *J. Polym. Sci., Polym. Lett. Ed.* 26 (1988) 123–127.
- [23] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Synthesis of poly(arylene ether ether ketone ketone) copolymers containing pendant sulfonic acid groups bonded to naphthalene as proton exchange membrane materials, *Macromolecules* 37 (2004) 6748–6754.

- [24] Y. Sakaguchi, K. Kitamura, S. Nagahara, S. Takase, Preparation of sulfonated poly(ether sulfone nitrile)s and characterization as proton conducting materials, *Polym. Prepr.* 45 (2004) 56–57.
- [25] M.J. Sumner, W.L. Harrison, R.M. Weyers, Y.S. Kim, J.E. McGrath, J.S. Riffle, A. Brink, M.H. Brink, Novel proton conducting sulfonated poly(arylene ether) copolymers containing aromatic nitriles, *J. Membr. Sci.* 239 (2004) 199–211.
- [26] X.G. Jian, Y.Z. Meng, H.B. Zheng, Chinese Patent 93109180.2 (1993).
- [27] X.G. Jian, Y.Z. Meng, H.B. Zheng, Chinese Patent 93109179.9 (1993).
- [28] S. Yoshida, A.S. Hay, Synthesis of all aromatic phthalazinone containing polymers by a novel N–C coupling reaction, *Macromolecules* 36 (1995) 2579–2581.
- [29] Y. Ding, A.R. Hlil, A.S. Hay, Novel poly(arylene thioether)s containing the 1,2-dihydro-4-phenyl(2*H*)phthalazinone moiety, *Polym. Prepr.* 38 (1997) 187–188.
- [30] T.D. Gieke, G.E. Munn, F.C. Wilson, The morphology in Nafion perfluorinated membrane products, as determined by wide- and small-angle X-ray studies, *J. Polym. Sci.: Polym. Phys.* 19 (1981) 1687–1740.
- [31] T.A. Zawodzinski, C. Derouin, S. Raszinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, Water uptake by and transport through Nafion®117 membranes, *J. Electrochem. Soc.* 140 (1993) 1041–1047.
- [32] S. Kaliaguine, S.D. Mikhailenko, K. Wang, P. Xing, G. Robertson, M. Guiver, Properties of SPEEK based PEMs for fuel cell application, *Catal. Today* 82 (2003) 213–222.