



## NRC Publications Archive Archives des publications du CNRC

### **Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK)**

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

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.2004.01.004>

*Journal of Membrane Science, 233, 2004*

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

<https://nrc-publications.canada.ca/eng/view/object/?id=6a7c4d12-b290-413b-87c8-cc1d131686ac>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=6a7c4d12-b290-413b-87c8-cc1d131686ac>

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.



## Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK)<sup>☆</sup>

Serguei D. Mikhailenko<sup>a</sup>, Keping Wang<sup>a</sup>, Serge Kaliaguine<sup>a,\*</sup>, Peixiang Xing<sup>a,b</sup>, Gilles P. Robertson<sup>b</sup>, Michael D. Guiver<sup>b</sup>

<sup>a</sup> Chemical Engineering Department, Laval University, Sainte-Foy, Que., Canada G1K 7P4

<sup>b</sup> Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ont., Canada K1A 0R6

Received 3 September 2003; received in revised form 15 December 2003; accepted 9 January 2004

### Abstract

A new method for the preparation of proton exchange membranes (PEMs), based on cross-linked sulfonated poly(ether ether ketones) is reported. The cross-linking involves thermally activated bridging of the polymer chains with polyatomic alcohols, which makes the polymer mechanically stronger and reduces its swelling by water. Although the cross-linking occurs through the sulfonic acid group, a major portion of acid functions is not involved in cross-linking and remains available for proton transfer. Owing to this, membrane conductivities are only somewhat reduced, leaving some with values above  $2 \times 10^{-2}$  S/cm at room temperature.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Sulfonated poly(ether ether ketone); Proton conductivity; Proton exchange membrane; Cross-linking

### 1. Introduction

A fuel cell (FC) is a device that generates electricity by direct electrochemical conversion of a fuel and an oxidant. Since the process does not involve combustion of fuel, a FC is not thermodynamically restricted and thus its efficiency greatly surpasses that of conventional power generation devices. A FC consists essentially of two catalytic electrodes separated by an electrolyte which can be liquids, such as alkaline or H<sub>3</sub>PO<sub>4</sub> solutions, or solids, such as oxides or proton exchange membranes (PEMs). In the latter case the fuel is ionized on the anode, and the protons diffuse across the membrane to recombine with the oxygen ions on the surface of the cathode, while the electron current flowing from the anode to the cathode through an external load produces power.

The PEM separating the electrodes in a FC should have low resistance to the diffusion of ions from one electrode to the other, but must provide a barrier against fuel and

oxidant cross-leaks to keep them apart. Diffusion or leakage of the fuel or oxidant gases across the membrane leads to power loss and other undesirable consequences. The PEM should also have a high resistance to the electron flow since if the device is even partially shorted out, the power output is reduced.

For reasons of chemical stability, perfluorosulfonic acid polymer membranes, the best known example of which is DuPont's Nafion<sup>®</sup>, are most widely used both in fuel cell research and industry. However, they suffer from several shortcomings among which their high cost presents a major obstacle for widespread application in FC. In addition, a loss of proton conductivity above 80 °C and low resistance toward alcohols cross-leaks impose restrictions on the operating temperature and choice of possible fuels. Many efforts have been recently undertaken to develop hydrocarbon based alternatives to Nafion, which would be less expensive and free from other disadvantages of perfluorinated membranes. Among the various polymers with diverse mechanical and electrical properties, long-term stability, efficiency and cost, which emerged over the last few years, membranes based on poly(ether ether ketone) (PEEK), were shown to be of considerable promise [1–6]. They were found to possess good thermal stability, appropriate mechanical strength and high

<sup>☆</sup> NRCC No: 46458

\* Corresponding author. Tel.: +1-418-656-2708; fax: +1-418-656-3810.

E-mail address: [serge.kaliaguine@gch.ulaval.ca](mailto:serge.kaliaguine@gch.ulaval.ca) (S. Kaliaguine).

proton conductivity, which depend on their degree of sulfonation (DS). However, the mechanical properties of PEEK tend to deteriorate progressively with sulfonation [7], which makes the long-term stability of highly sulfonated polymers questionable. The mechanical weakness of non-cross-linked sulfonated polymers has initiated a number of attempts to prepare more stable and mechanically stronger cross-linked PEMs. Sulfonated PEEK (SPEEK) can be conveniently cross-linked through bridging links to the reactive sulfonic acid functions. The first reported cross-linking of SPEEK was carried out using suitable aromatic or aliphatic amines [8]. Later a modification of this preparation method was patented [9] where it was proposed to use a similar cross-linker also having terminal amide functions, which forms imide functionality through a condensation reaction with the sulfonic acid groups of SPEEK. The imide group is supposed to be acidic and therefore able to participate in proton transfer, contributing to the proton conductivity of the polymer.

Another way to perform cross-linking of SPEEK, as asserted by the authors of a US patent [10], can be accomplished through intra/inter chain condensation of sulfonic acid functionalities, allegedly initiated simply by appropriate thermal treatment. This technique will be discussed more thoroughly below.

The cross-linked SPEEK membranes were found to be much less susceptible to swelling than non-cross-linked SPEEK and comparable to commercial Nafion in terms of their mechanical strength, stability and proton conductivity. However no fuel cell performance data for these membranes are currently available in the literature. It should be also mentioned that when amine functions are employed in the cross-linking reactions with sulfonic acid groups as was performed in refs. [8,9], sulfanilamide is produced. The hydrolytic stability of sulfanilamide is questionable which casts much doubt upon the membrane durability under fuel cell operating conditions.

As follows from the above, the need for an inexpensive, mechanically and chemically stable proton conducting polymer might be satisfied by developing a technique for preparation of cross-linked SPEEK. The objective of this work is therefore to produce a high proton conductivity, low electronic conductivity membrane, which is mechanically strong and chemically stable and can prevent the cross-leaks of molecular gases. This was accomplished by a method developed in this study, which allows the production of cross-linked acidic SPEEK polymers and films thereof.

## 2. Experimental

### 2.1. PEEK sulfonation

PEEK extrudate samples used in this work were Vitrex<sup>®</sup> PEEK<sup>™</sup> kindly provided by Victrex. Typically 20 g of PEEK was dried in a vacuum oven at 100 °C and then dis-

solved in 500 ml of concentrated (95–98% H<sub>2</sub>SO<sub>4</sub>) sulfuric acid at 50–90 °C under vigorous mechanical stirring. The reaction time ranged from 1 to 6.5 h. The sulfonation reaction was terminated by decanting the polymer solution into a large excess of ice-cold water under continuous mechanical agitation. For samples with a DS of <0.8, the polymer precipitate was filtered and washed several times with distilled water until the pH was neutral. For water swellable or soluble samples with DS > 0.8, residual sulfuric acid was removed by dialysing the polymer. The polymer was then dried under vacuum for 1–2 days at 25–40 °C. The DS was determined by <sup>1</sup>H NMR according to the technique described elsewhere [5].

### 2.2. Membrane preparation

The dry SPEEK polymer was first dissolved in one of the following solvents: dimethylacetamide (DMAc), dimethylformamide (DMF), *N*-methyl-pyrrolidinone (NMP), water–acetone or water–alcohol mixtures. To the 10–15 wt.% SPEEK solutions various amounts of a cross-linker were added, agitated for 30 min and after vacuum outgassing for 30 min cast onto a glass plate. The samples were dried under ambient conditions for several days and then cured under vacuum at 25–150 °C for a few more days.

### 2.3. Characterization of SPEEK membranes

The <sup>1</sup>H NMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz. For each analysis, a 2–5 wt.% polymer solution was prepared in DMSO-*d*<sub>6</sub> and tetramethylsilane (TMS) was used as the internal standard. The DS was determined by comparative integration of distinct aromatic signals [5]. Alternatively the degree of sulfonation was determined by titration: 1–2 g of the SPEEK was placed in 0.5 M aqueous NaOH and kept for 1 day. The solution was then back titrated with 0.5 M HCl using phenolphthalein as an indicator.

The amount of water absorbed in SPEEK membranes was determined by comparison of weights of a blotted soaked membrane and vacuum dried one. The water uptake was calculated with reference to the weight of the dry specimen:  $(W_{\text{wet}}/W_{\text{dry}} - 1) \times 100\%$ .

The proton conductivity of the polymer membranes was measured by AC impedance spectroscopy using a Solartron 1260 analyzer across 13 mm diameter samples clamped between two blocking stainless steel electrodes. The sample discs were hydrated by soaking in water overnight and placed wet in the measurement cell. The conductivity  $\sigma$  of the samples was calculated from the impedance data, using the relation  $\sigma = d/RS$  where  $d$  and  $S$  are the thickness and face area of the sample, respectively, 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 the empty and short-circuited cell.

### 3. Results and discussion

#### 3.1. Cross-linking of SPEEK with polyatomic alcohols

A series of the experiments was carried out in this work as an attempt to obtain cross-linked SPEEK through intra/inter chain condensation of sulfonic acid functionalities by thermal treatment as suggested in ref. [10]. It was found, however, that cross-linking of SPEEK did not occur after this treatment if no cross-linker was added. Indeed, in our experimental preparations all SPEEK membranes with DS ranging from 0.6 to 1.0 cast from solutions in DMF, DMAc, NMP, water–ethanol or water–acetone mixtures remained soluble in these solvents after drying and curing under vacuum at 120–150 °C for several days. This will be discussed below in more details using Fig. 1. In this figure, the far left column shows DS of various samples of initial SPEEK, and every stroke within the rectangles corresponds to an attempt

to prepare a cross-linked membrane. The left hand rectangle, where casting mixtures did not contain a cross-linker or its concentration was too low, corresponds to preparations, where no cross-linking was observed.

These experiments suggest that the thermal treatment alone does not induce any significant cross-linking, at least below 120–150 °C. This result is in contradiction with the assertions made in ref. [10], which suggest that heating high DS SPEEK to 120 °C is sufficient to initiate thermal cross-linking.

It is worth mentioning at this point that further heating of our high DS SPEEK samples up to 250 °C under vacuum resulted in membranes, which are insoluble in any solvent (except H<sub>2</sub>SO<sub>4</sub>) and stable in boiling water. In some instances this thermally induced transformation started at 220 °C. However, the chemical analysis of these samples has shown that heating above 200 °C brings about desulfonation of SPEEK, likely to be accompanied by SO<sub>3</sub> release.

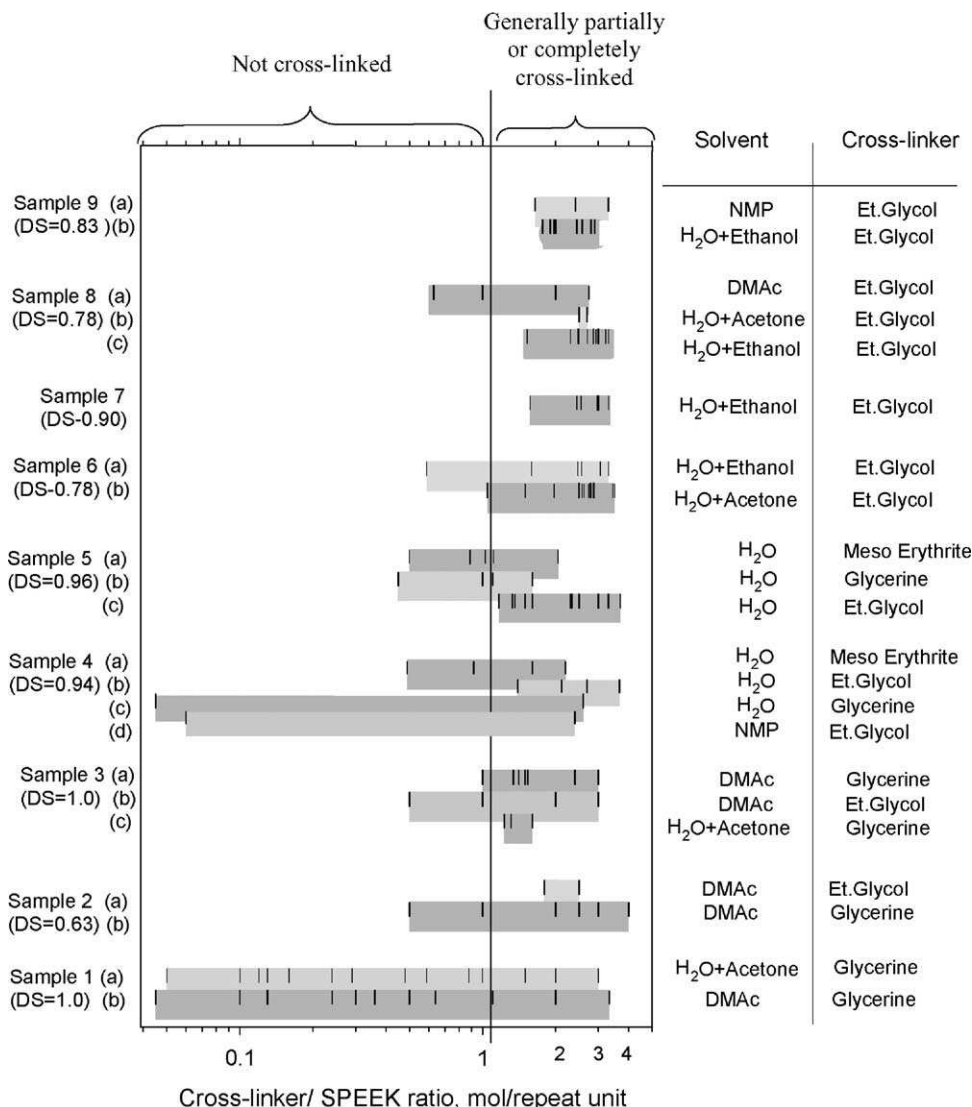


Fig. 1. The preparation formulations of different SPEEK samples.

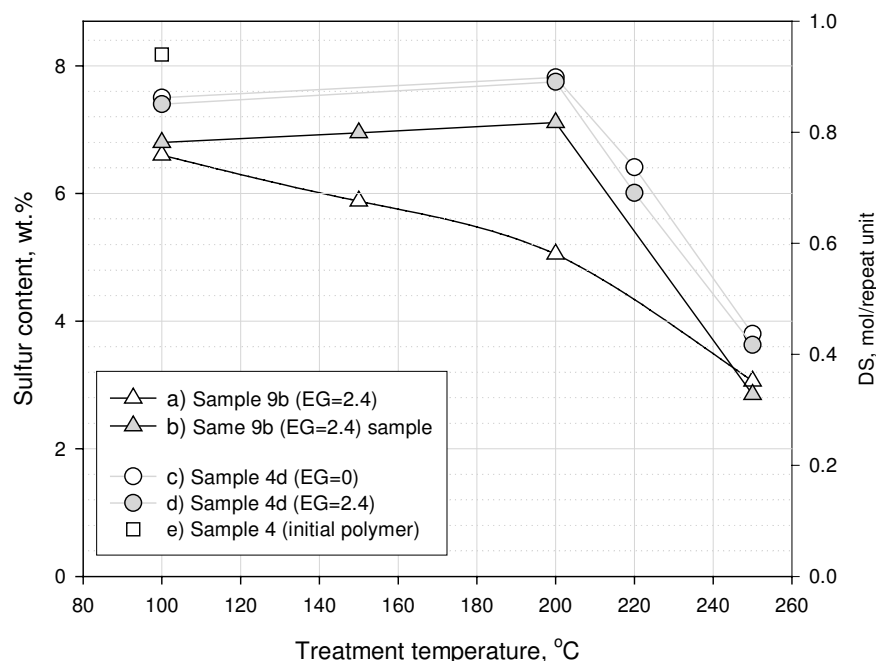


Fig. 2. Sulfur content in cross-linked and non-cross-linked SPEEK membranes as function of the treatment temperature: (a) DS determined by titration; sulfur content calculated from DS; (b, c and d) sulfur content determined by elemental analysis; DS calculated from sulfur content; (e) DS determined by  $^1\text{H}$  NMR; sulfur content calculated from DS. For sample designation see Table 1 and Fig. 1.

The results of sulfur elemental analysis for four membrane samples treated at different temperatures are presented in Fig. 2. A pure (containing no cross-linker) SPEEK membrane cast from NMP solution and treated at different temperatures is represented by curve (c) in Fig. 2. The sample studied had a DS 0.94 according to  $^1\text{H}$  NMR analysis (see Table 1), which corresponds to a calculated value of 8.2 wt.% of sulfur. It can be seen from the plot that the initial (sample 4d dried at 100 °C) sulfur content determined by chemical analysis is 9% lower than the value calculated from NMR. Heating to 200 °C reduced the discrepancy between the results of these two analytical techniques, which suggests that this difference may be associated with the presence of residual NMP solvent in the membrane. However, NMP is difficult to remove completely as its boiling point is 202 °C.

Heating above 200 °C under vacuum strongly reduces the sulfur content below the values corresponding to DS 0.5, as follows from Fig. 2c. These SPEEK samples become insoluble in many solvents and might be mistaken for thermally cross-linked. However, this increase of chemical stability should be mostly caused by desulfonation as it is known that at low DS pure SPEEK is insoluble in any solvents except concentrated  $\text{H}_2\text{SO}_4$ . At the same time when initially the same samples were treated under vacuum not above 200 °C but at 150 °C for several days, these membranes remained soluble and did not show any properties of cross-linked polymers.

The authors of patent [10] reported cross-linking of SPEEK with a treatment temperature of 120 °C, which is significantly lower than the onset temperature of desulfona-

tion. A plausible explanation for this observed cross-linking at this low temperature is that some other fortuitous reactions occurred in the experiments reported in [10] during curing of the SPEEK. It was mentioned in ref. [10], that in the course of membrane preparation some glycerine was added (evidently as a plasticizer) to SPEEK, dissolved in a water–acetone mixed solvent. Our experiments revealed the role of the polyols, in cross-linking of sulfonated linear polymers. In all our experimental preparations, where the casting medium contained certain amounts of glycerol, cross-linking indeed has been observed: membranes changed colour from brownish-yellow to black and became mechanically stronger and insoluble in any of the solvents used. That occurred, when the ratio of glycerine to SPEEK was at least 1 molecule per repeat unit of the polymer. This can be seen in Fig. 1, where the stroke marks indicate numerous preparations that make a rather representative set of statistical data.

The chemical reaction assumed to be involved in such cross-linking is shown in Fig. 3. The glycerine, participating in the bridging of SPEEK fragments, may be replaced by any polyol. In order to verify this, a number of preparations has been carried out using ethylene-glycol (two-carbon) and mesoerythrite (four-carbon) polyols (see Fig. 3). It was observed, that starting from a certain molar ratio of cross-linker to SPEEK the reaction of polycondensation apparently occurs and some of the products obtained became insoluble in boiling water and organic solvents. The preparation formulations of different SPEEK membranes, including casting solvent and cross-linking polyol used, are listed in Fig. 1. In order to initiate cross-linking the films were dried after

Table 1  
Properties of the SPEEK membranes after cross-linking procedure

Sample (DS) <sup>a</sup>	Solvent	Cross-linker	Cross-linker/SPEEK ratio (mol/repeat unit)	Cure condition		Conductivity at 25 °C (S/cm)	Comments
				T (°C)	Time (h)		
1a (1.0)	DMAc	Glycerol	<1	125	36	–	Soluble in water
			>1	130	72	$\leq 1.5 \times 10^{-2}$	Partially soluble in DMAc, H <sub>2</sub> O
1b (1.0)	Water + acetone	Glycerol	<1	125	48	–	Soluble in water
			>1	120	48	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
2a (0.63)	DMAc	Ethylene-glycol	>1	125	48	–	Partially soluble in DMAc
2b (0.63)	DMAc	Glycerol	<1	125	48	$\leq 2 \times 10^{-3}$	Soluble in DMAc
			>1			$\leq 5.7 \times 10^{-3}$	Partially soluble in DMAc
3a (1.0)	DMAc	Glycerol	=1	130	66	$7.8 \times 10^{-3}$	Soluble in water
			>1	130	66	$\leq 1 \times 10^{-2}$	Partially soluble in DMAc
3b (1.0)	DMAc	Ethylene-glycol	>1	130	66	$\leq 1.5 \times 10^{-2}$	Partially soluble in DMAc
3c (1.0)	Water + acetone	Glycerol	>1	125	60	–	Complete cross-linking
4a (0.94)	Water	Meso-erythritol	<1	135	60	–	Soluble in water
			>1	135	60	$\leq 2.2 \times 10^{-2}$	Complete cross-linking, brittle
4b (0.94)	Water	Ethylene-glycol	=1.4	135	60	$2.2 \times 10^{-2}$	Soluble in water
			>1.4	135	60	$\leq 2.2 \times 10^{-2}$	Complete cross-linking
4c (0.94)	Water	Glycerol	2.6	135	60	$2.2 \times 10^{-2}$	Complete cross-linking
4d (0.94)	NMP	Ethylene-glycol	<2.7	150	60	$\leq 4 \times 10^{-2}$	Soluble in hot water
5a (0.96)	Water	Meso-Erythritol	0.5–0.9	140	48	–	Soluble in water
			1–2	140	48	–	Cross-linked, brittle
5b (0.96)	Water	Glycerol	>1	140	48	$\leq 1.2 \times 10^{-2}$	Complete cross-linking
5c (0.96)	Water	Ethylene-glycol	$\leq 1.5$	140	48	$\leq 2.2 \times 10^{-2}$	Soluble in water at 100 °C
			>1.5	140	48	$\leq 2.7 \times 10^{-2}$	Complete cross-linking
6a (0.78)	Water + alcohol	Ethylene-glycol	0.6	140	60	–	Soluble in water
			>1.6	140	60	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
6b (0.78)	Water + acetone	Ethylene-glycol	<1.5	140	60	$\leq 1.6 \times 10^{-2}$	Soluble in water at 100 °C
			>1.5	140	60	$\leq 2.5 \times 10^{-2}$	Complete cross-linking
7 (0.90)	Water + alcohol	Ethylene-glycol	>1.6	140	60	$\leq 4.2 \times 10^{-2}$	Complete cross-linking
8a (0.78)	DMAc	Ethylene-glycol	<1	150	68	–	Soluble in DMAc, hot water
			>1	150	68	–	Partially soluble in DMAc
8c (0.78)	Water + alcohol	Ethylene-glycol	1.5	150	68	$\leq 2.6 \times 10^{-2}$	Complete cross-linking
9a (0.83)	NMP	Ethylene-glycol	1.65–3.3	150	68	$\leq 4.6 \times 10^{-2}$	Soluble in water at 100 °C
9b (0.83)	Water + alcohol	Ethylene-glycol	<1.9	150	68	$\leq 6.5 \times 10^{-2}$	Soluble in water at 100 °C
			>1.9	150	68	$\leq 4 \times 10^{-2}$	Complete cross-linking

<sup>a</sup> Measured by NMR before membrane casting.

casting and cured according to the procedure described in ref. [10] or even sometimes under more stringent conditions (curing temperature up to 150 °C instead of 120 °C).

In Table 1, the results of the cross-linking procedure along with the conductivity values are presented more comprehensively than in Fig. 1. It follows from this table that sample 1 with DS 1.0 is rendered completely cross-linked (insoluble in any solvent) only when cast from water–acetone solution and when the glycerine content is higher than one molecule per repeat unit of SPEEK (sample 1b). However, when DMAc was used as casting solvent, no (or only partial) cross-linking occurred even at high glycerine concentration.

The same was observed for all samples, whether they were low DS (samples 2a, 2b), high DS (samples 1a, 3a, 3b) or mid-DS (sample 8a). When the membranes were prepared using low cross-linker concentration, the membranes (samples 1, 3) remained soluble even in cold water, indicating that no or only little cross-linking occurred. At higher cross-linker concentration, membranes were partially soluble in DMAc indicating that cross-linking was incomplete. The same was observed for another casting solvent NMP (samples 4d, 9a). It is apparent that cross-linking is blocked by the competing reaction of sulfonic acid groups with DMAc or NMP. Recently it has been shown that DMAc and

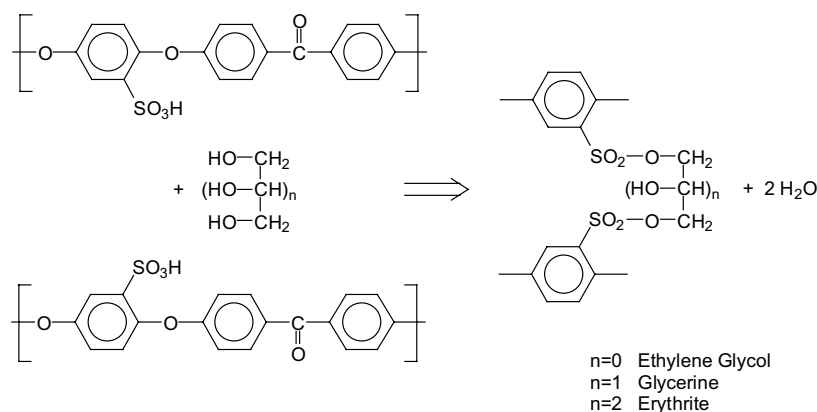


Fig. 3. Possible reaction of SPEEK cross-linking.

especially DMF form strong hydrogen bonding with sulfonated PEEK [11,12]. Moreover, both solvents have been found to be prone to thermally activated decomposition, accelerated by sulfonic acid functions and the produced dimethylamine also forms strong bonding with SPEEK [11,12]. It is therefore preferable to avoid these solvents for membrane casting, replacing them wherever possible (SPEEK with  $DS > 0.8$ ) by water or water–acetone mixtures. Water–alcohol mixture also may be used, because there is little likelihood of hydroxyl interaction with acid groups due to the very low boiling point of ethanol, which is about 4 °C under vacuum. This is sustained by the fact that the proton conductivity of a water–alcohol cast membrane is no different from that obtained from water–acetone solution (compare completely cross-linked samples 6a and 6b).

It is interesting to note that the introduction of the cross-linker does not change the sulfur content of the membranes treated at different temperatures, as can be seen from the comparison of curves (c) and (d) in Fig. 2. However, the results of titration turned out to be very different from that of elemental chemical analysis for sulfur for the cross-linked samples (compare plots a and b in Fig. 2). The disparity in these two curves corresponds to the difference between the amount of sulfur comprised only in sulfonic acid functions (available for ion exchange as used in titration), and the total sulfur content, including bridging  $-\text{SO}_2-$  functions not detectable by titration but measurable by elemental analysis. Therefore, the difference between S content according to the results of elemental analysis and titration can be a measure of degree of cross-linking: the larger this difference, the greater number of sulfonic functions became bridging.

Among the three cross-linkers used, the best membranes were obtained with ethylene-glycol. They were most strong mechanically, flexible and less liable to deformation. Glycerine gave slightly less strong membranes, which sometimes were also less conductive than the ones made with ethylene-glycol (compare for example samples 5b and 5c). Mesoerythrite, despite the fact that it also ensures SPEEK cross-linking, results in membranes that are too brittle to be of any practical use (samples 4a, 5a).

In summary it may be said that the best cross-linked SPEEK membranes are obtained from SPEEK with  $0.75 < DS < 1.0$  using water–acetone or water–alcohol mixture as a casting solvent and ethylene-glycol as a cross-linker at ratio between 1.5 and 3 molecules per SPEEK repeat unit. The 18 wt.% solution cast on the glass plate should be dried at room conditions for 2 days, and then under vacuum for 3 days at temperature gradually increasing from 25 to 150 °C over 2 days.

### 3.2. Properties of cross-linked SPEEK membranes

The swelling of a SPEEK membrane in water is commonly thought to be inversely related to its mechanical strength. In Fig. 4 the room temperature water uptake along with conductivity of a series of cross-linked membranes are presented as functions of their DSs, measured by titration as the number of sulfonic acid functions per repeat unit. As can be seen from Fig. 2, sulfur contents measured by titration (accounting only for sulfonic acid groups, available

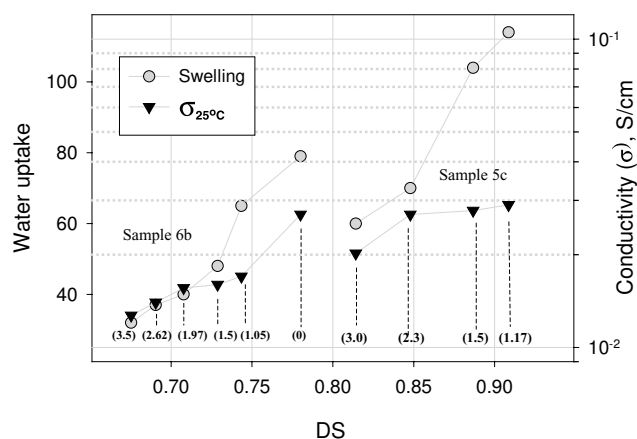


Fig. 4. Swelling and proton conductivity of cross-linked SPEEK membranes as function of DS, measured by titration (Nafion 117 conductivity measured in the same cell and under the same conditions was  $\sigma_{25^\circ\text{C}} = 3.3 \times 10^{-2}$  S/cm). Values in parentheses are ethylene-glycol/SPEEK molar ratios, used in membrane preparation.

for ion exchange) are lower than the total sulfur concentration, defined by elemental analysis. From Fig. 4 it follows that introduction of increasing amounts of ethylene-glycol into sample 6 caused a gradual decrease in the DS from 0.78 to 0.68, accompanied by more than a twofold water uptake decrease from 79 to 32 wt.%. At the same time the conductivity decreased less significantly from  $2.7 \times 10^{-2}$  to  $1.4 \times 10^{-2}$  S/cm and remained within the usable range, where PEMs are still suitable for fuel cell application. The resulting membranes from DS 0.71 (corresponding to EtGly/SPEEK = 1.97) were completely cross-linked and maintained good mechanical strength even when swollen. It is worth mentioning that conductivity measurements were performed on the membranes that were subjected to boiling in water.

Sample 5c having DS 0.96 was initially soluble in water and therefore its water uptake may be considered as infinity. However at EtGly/SPEEK ratio 2.3 and higher it became fully cross-linked, with water uptake below 70 wt.% and conductivity above  $2 \times 10^{-2}$  S/cm. Such a high conductivity suggests that a major portion of sulfonic acid functions was not involved in cross-linking and remained available for proton transfer. It is important to note that despite cross-linking being far from complete, the membranes were rigid and strong at ambient conditions, and at the same time, become moldable and pliable at temperatures above 150 °C. That allows their use in the preparation of membrane-electrode assemblies for FC.

#### 4. Conclusions

A method for cross-linking of sulfonated poly(ether ether ketones) was developed in this study. It is based on the thermally activated bridging of the polymer chains with polyatomic alcohols through condensation reaction with sulfonic acid functions. Cross-linking greatly increases the polymer mechanical strength and reduces its swelling in water. Although the cross-linking decreases the number of sulfonic acid groups available for proton transfer, the

SPEEK membrane conductivities are only slightly reduced. Some of the samples exhibited a room temperature conductivity of above  $2 \times 10^{-2}$  S/cm.

#### References

- [1] G. Pourcelly, C. Gavach, Perfluorinated membranes, in: Ph. Colomban (Ed.), *Proton Conductors: Solids, Membranes and Gels-Materials and Devices*, Cambridge University Press, New York, 1992, pp 294–310.
- [2] O. Savadogo, Emerging membranes for electrochemical systems: (I) solid polymer electrolyte membranes for fuel cell systems, *J. New Mat. Electrochem. Syst.* 1 (1998) 47.
- [3] 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.
- [4] J. Kerres, A. Ullrich, Th. Haring, New ionomer membranes and their fuel cell application: 1. Preparation and characterization, in: *3rd International Symposium on New Materials for Electrochemical Systems*, Montreal, Canada, July 1999, p. 230.
- [5] 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.
- [6] B. Bonnet, D.J. Jones, J. Rosière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, B. Bauer, A. Peraio, E. Ramunni, Hybrid organic-inorganic membranes for a medium temperature fuel cell, *J. New Mat. Electrochem. Syst.* 3 (2000) 87.
- [7] X. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, A sulfonated poly(aryl-ether-ketone), *Br. Polym. J.* 17 (1985) 4.
- [8] F. Helmer-Metzmann, F. Osan, A. Schneller, H. Ritter, K. Ledjeff, R. Nolte, R. Thorwirth, Polymer electrolyte membrane, and process for the production thereof, US Patent 5,438,082 (1995).
- [9] S.S. Mao, S.J. Hamrock, D.A. Ylitalo, Crosslinked ion conductive membranes, US Patent 6,090,895 (2000).
- [10] S.P.S. Yen, S.R. Narayanan, G. Halpert, E. Graham, A. Yavrouian, Polymer material for electrolytic membranes in fuel cells, US Patent 5,795,496 (1998).
- [11] G.P. Robertson, S.D. Mikhailenko, K.P. 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.
- [12] S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, M. Guver, Properties of SPEEK based PEMs for fuel cell application, *Catal. Today* 82 (2003) 213.