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Properties of PEMs based on cross-linked sulfonated poly(ether ether ketone)[☆]

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Abstract

PEMs prepared from sulfonated poly(ether ether ketone) and cross-linked with simple polyols (ethylene glycol and glycerol), exhibited enhanced strength, stability in hot water and high proton conductivity. The properties and chemical structure of the cross-linked membranes were studied using TGA, ^{1}H NMR and FTIR. These data suggest that ethylene glycol and glycerol molecules do not link neighbouring main chains via sulfonic acid functions, but rather form alcohol–ether oligomers, bonded to $-SO_3-$ group and generating an interpenetrating network which interacts with the main chains. The thermal stability of cross-linked membranes is inferior to that of non-cross-linked ones. It is shown that splitting off of the sulfonic acid groups occurring above 200 °C is accompanied by main chain degradation in both initial and cross-linked membranes. The fact that the degradation temperature exceeds 200 °C suggests that this could be a promising and effective approach to cross-linking sulfonated membranes for FC application.

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

1. Introduction

The development of polymer electrolyte membranes (PEM) has attracted increasing interest, particularly for application in fuel cells intended for automotive and stationary power sources [1–3]. The most commonly utilized PEMs such as DuPont Nafion possess good mechanical and chemical stability and high proton conductivity, but suffer from a loss of conductivity above 80 °C. Together with the high cost inherent in fluorinated polymers, this impedes their large scale commercialization as a FC component [4,5]. Many efforts have been recently undertaken to develop less expensive hydrocarbon alternatives to Nafion. Among the various polymers with diverse properties and efficiency, which emerged over the last few years, membranes based on poly(ether ether ketone) (PEEK), were shown to be of considerable promise [6–11] due to their good thermal stability, appropriate mechanical strength and high proton conductivity, which increases with their degree of sulfonation (DS).

However, the mechanical properties of SPEEK tend to gradually deteriorate with increasing DS [12]. Moreover, the integrity of highly sulfonated polymers degrades in hot water due to excessive swelling, making questionable their long-term stability in FC conditions. The mechanical weakness of sulfonated polymers has initiated a number of attempts to prepare more stable and mechanically stronger cross-linked PEMs. Cross-linking of sulfonated aromatic poly-hydrocarbons might be conveniently achieved through bridging the reactive sulfonic acid functions by appropriate moieties. In [13] for instance, cross-linked sulfonated polyimides were prepared directly using a cross-linker containing sulfonic group and pre-sulfonated monomer. A series of studies focused on the development of covalently and ionically cross-linked polyarylenes has been carried out by Kerres et al. [14–16]. The covalent cross-linking there was achieved through alkylation of sulfinate groups with α,ω-dihalogenoalkanes [14] which brought about thermally stable but brittle final products. Ionically cross-linked membranes in [15,16] were prepared by blending the acidic ionomers with basic (aminated) polymers in binary and ternary compounds. Aromatic or aliphatic amines were also previously used in [17] for covalent cross-linking of SPEEK. In a later

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modification of this method a similar cross-linker with terminal amide functions was used in order to form imide functionality through a condensation reaction with the sulfonic acid groups of SPEEK [18]. Recently our group proposed another cross-linking route [19] using simple polyatomic alcohols (ethylene glycol, glycerol), added to the casting polymer solution. Subsequent thermal treatment supposedly activated inter-chain linkage, making the polymer mechanically stronger and reducing its swelling by water. Although the cross-linking allegedly occurred through the sulfonic acid group, a major portion of acid functions were not involved in cross-linking and remained available for proton transfer. Owing to this, membrane conductivities were found only moderately reduced, with values in some cases above 2×10^{-2} S/cm at room temperature. The structure and properties of the obtained cross-linked SPEEK membranes were not comprehensively studied in [19], which did not allow us to reach a definite conclusion on the cross-linking mechanism associated with the proposed method. The focus of this work is a more systematic and detailed examination of SPEEK cross-linking in order to better understand the cross-linking mechanism and resulting membrane structures. In this study different preparation conditions were tested in order to obtain the PEMs with improved properties. The proton conductivity, water uptake, thermal properties, chemical structure characteristics examined by ^{1}H NMR and FTIR, and the factors influencing these properties were analysed in this work.

2. Experimental

2.1. PEM preparation

The sulfonation of PEEK (Victrex PLC) was performed using concentrated sulfuric acid according to the procedure described elsewhere [10,19–21]. The reactions were carried out in the temperature range of 25–80 °C under vigorous mechanical stirring during periods ranging from several hours to a few days. To terminate the sulfonation reactions, the polymer solutions were decanted 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 pH 5 in order to eliminate the residual sulfuric acid. For water soluble samples with DS > 0.8, the residual acid was removed by placing the polymer solution into dialysis tubing and washing this tubing for several days until pH 5 was achieved for washing water. The polymer was then dried under vacuum for 1–2 days at 25–40 °C. The degree of sulfonation was determined both by ^{1}H NMR spectroscopy (described elsewhere [20,21]) and by titration with NaOH followed by back titration with HCl. Membranes were prepared from the dry SPEEK dissolved in dimethylacetamide (DMAc) or γ-butyrolactone (GBL) when the DS was lower than 80%, or in water–acetone, water alcohol mixtures at high DS. To the 10–15 wt% SPEEK solutions various amounts of a ethylene glycol (EG) or glycerol (GL) as 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 25–80 °C for a few more days. Despite containing water, aqueous acetone or alcohol polymer casting solutions resulted in clear non-porous films. The final curing continued under vacuum for 48–72 h at 130–150 °C. After curing, the membranes prepared with EG or GL in the casting solvent ceased to be soluble in boiling water, even those that were originally water soluble at room temperature. They became much stronger mechanically in comparison with initial high DS membranes, but remained thereby flexible and proton conductive.

2.2. Membrane characterization

The conductivity of the polymer membranes was measured by AC impedance spectroscopy as previously described in [19,21]. A strip 10 mm × 20 mm was cut from a membrane and placed in a closed frame cell, where it was clamped between two pairs of stainless steel electrodes. Tests were carried out at controlled temperature and 100%RH. The impedance data were corrected for the contribution from the empty and short-circuited cell.

Water absorption was measured by weighing films with area 5 mm × 50 mm immersed in deionized water at 25 and 80 °C for 24 and 3 h, respectively. It was found that at the higher temperature, equilibration occurred with 3 h. The weight and length gains of films were recorded.

FTIR spectra were recorded on a BIO-RAD FTS-60 Fourier transform spectrometer using powdered samples compressed in discs (1–3 wt% in KBr). Powders were prepared by milling of membranes samples and the initial PEEK granules frozen in liquid nitrogen.

The ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.961 MHz. For each analysis, a 2–5 wt% polymer solution was prepared in DMSO-d_6 and tetramethylsilane (TMS) was used as the internal standard.

A DuPont Instruments 951 and TA Hi-Res TGA 2950 thermogravimetric analyzer (TGA) were employed to study the thermal properties of SPEEK samples. The samples were heated under nitrogen flow from room temperature to 800 °C at 10 °C/min.

Mass-spectrometry analysis of the products, released in the course of thermolysis of the membranes, was carried out using a quadruple mass spectrometer (UTI-100) equipped with a capillary system for sampling. A specimen of the membrane was placed into U-shaped stainless steel reactor where it was heated at 10 °C/min under flow of He, used as a carrier gas. MS-signal was synchronized with the temperature of the furnace, which was coupled with the spectrometer.

A TA DSC 2920 differential scanning calorimetry (DSC) was employed to study the thermal transition behaviour of SPEEK samples. The samples were preheated under nitrogen from room temperature to 160 °C at 10 °C/min to remove moisture, then cooled down to 90 °C, and reheated from that temperature to 250 °C at 10 °C/min. The glass transition temperature, T_g was calculated at the intersection of the tangent to the corresponding DSC curve.

3. Experimental results

The aim of this study is the elucidation of the cross-linking mechanism associated with the introduction of EG or GL (*meso*-erythritol used in [19] was abandoned in this work as bringing about excessively fragile PEMs). Consequently in the following, pure SPEEK membranes will be compared with those containing different portions of a cross-linking agent. The samples are denoted in such a manner as to indicate the DS of the initial polymer, cross-linker used (or not used) and its content expressed as a mole ratio with respect to the SPEEK repeat unit. For example 96EG1.5 designates a membrane prepared from SPEEK with DS = 96%, with addition of ethylene glycol at mole ratio EG/SPEEK = 1.5. Membrane prepared from the initial non-cross-linked polymer will be denoted as 96PURE.

3.1. Glass transition temperature: DSC studies

Fig. 1 illustrates the influence of EG added to the casting mixture on the T_g of cross-linked SPEEK polymers. In the non-cross-linked membranes (EG/SPEEK = 0), presented as a reference, T_g increases with the DS due to ionomer effect of SO_3H (intermolecular interaction by hydrogen bonding) and increased molecular bulkiness. From the figure it can be seen that EG addition raises the glass transition temperatures of both polymers. The T_g increases with EG content indicating incremental restraints upon the motions of longer segments of the polymer main chain. T_g of SPEEK with DS = 78% increases from 199 to 212 °C (78EG3.5), while for SPEEK with DS = 96%, from 203 to 219 °C (96EG3.7). The fact that T_g of SPEEK with DS = 96% increases faster than when DS = 78% might be due to larger number of introduced EG molecules per repeat unit, which is proportional to DS. The stronger EG effect observed for higher DS polymer indicates an interaction between SO_3H functions and hydroxyl terminals of EG.

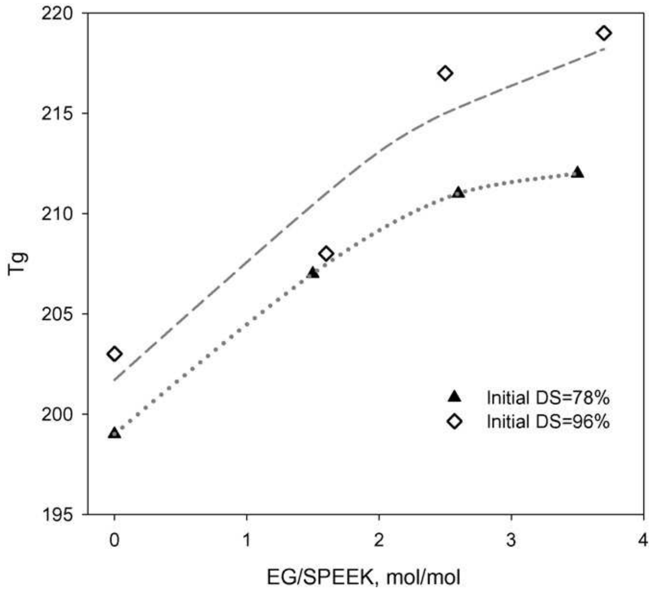

Fig. 1. Glass transition temperatures of cross-linked membranes, prepared from 78PURE and 96PURE polymers. Dashed lines are plotted as visual guides.

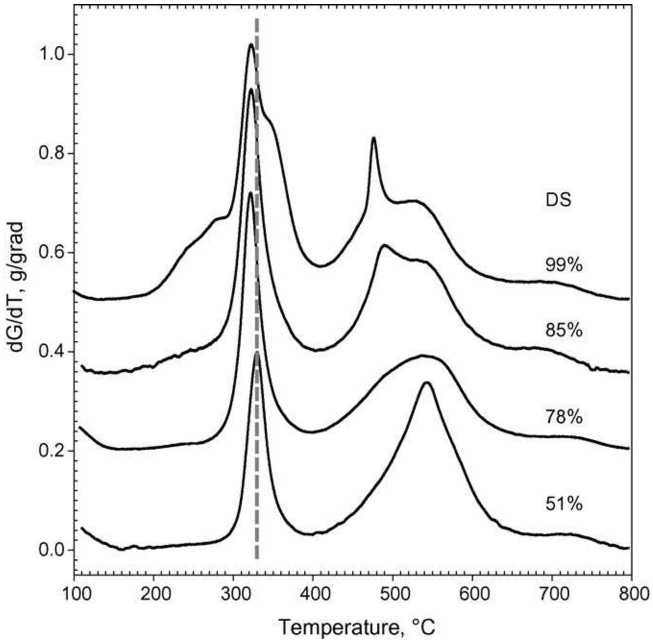

Fig. 2. Differential TGA signal for pure SPEEK membranes with different DS cast from DMAc.

3.2. Thermo-gravimetric analysis

Some differences in behaviour of a series of pure SPEEK membranes with various DS, cast from DMAc solutions, can be observed in the results of TGA experiments presented in Fig. 2 and complemented by Table 1. It follows from them that the process of thermal degradation grows more complex with increasing DS. Both maxima in the differential thermo-gravimetric (DTG) spectra (the first, associated with the loss of sulfonic acid groups and the second, originated from main chain decomposition) move to lower temperatures. The DTG spectrum of SPEEK with DS = 99% has a shoulder at 200–300 °C and a sharp peak at 476 °C in addition to a broad maximum at ~540 °C. The latter indicates some alternative strong reaction of main chain degradation, occurring against the background of decomposition, typical for less sulfonated SPEEK. The cause of this additional reaction is not completely clear. However, it may

Table 1
TGA parameters of SPEEK with different DS

Initial DS[a]	Sulfonic acid related peak		Main chain related peak	
	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
51 (12.2%)	330	14.0	544	32.8
78 (17.5%)	322	22.4	542	31.7
85 (18.8%)	321	23.2	489	26.1
99 (21.1%)	321	30.0	476	23.6

Casting solvent is DMAc. Corresponding differential thermogramms are in Fig. 2.

[a] Values in parantheses are the SO_3H contents in the polymers (in wt%).

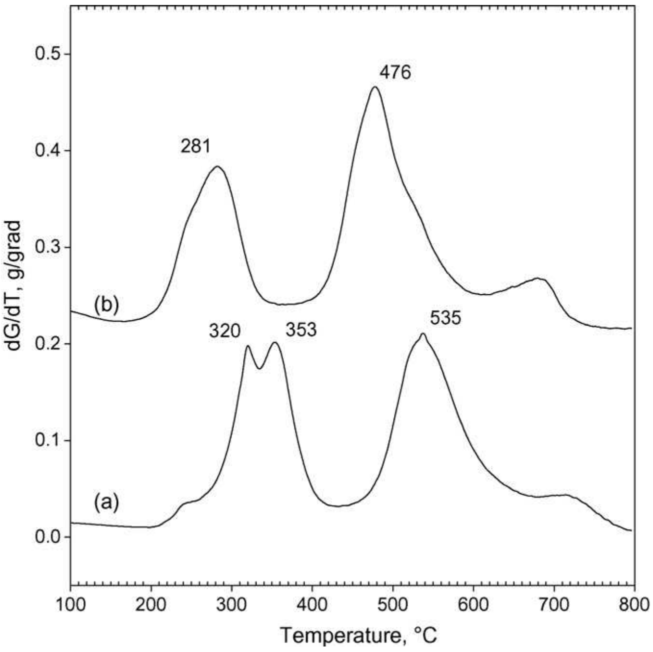

Fig. 3. Differential TGA signal for (a) 85PURE and (b) 85GL3.5 SPEEK membranes cast from GBL.

be assumed to be associated with a larger amount of released sulfur–oxygen compounds, which also show up as the shoulder at 200–300 °C. It is important to note that for the non-cross-linked SPEEK polymers, the first weight loss is larger than the SO_3H portion in the polymers with DS = 51–99% (Table 1), which indicates that apart from sulfonic acid groups, some other fragments of the polymer chain are splitting-off at these temperatures.

Similar results (weight loss exceeding SO_3H content) were obtained for unmodified 85% SPEEK cast from GBL solution (Fig. 3a and Table 2). The cross-linked membrane, prepared from the same polymer with addition of glycerol and cured at 140 °C, exhibited significant shifts of decomposition maxima to lower temperatures (Fig. 3b). At the same time the weight loss associated with sulfonic acid functions decreased for this sample below stoichiometric value (Table 2). The influence of the casting solvent is evident from comparison of Figs. 2 and 3 with Fig. 4, where DTG spectra of samples cast in absence of organic solvent are shown. The membrane prepared using water as solvent (Fig. 4a) has a first maximum at a temperature about 20 °C higher than those where DMAc (Fig. 2) or GBL (Fig. 3a) were used, indicating that degradation occurs differently depending on membrane preparation conditions. It is interesting to note that the amount of a cross-linker (GL here) does not affect the first maximum, but strongly alters the thermal stability of the polymer backbone, shifting the corresponding maximum further to lower temperatures when more GL is added to the casting solution (compare Fig. 4b and c). Similar results are obtained with EG used as a cross-linker (Fig. 5 and Table 2) except weight loss at 250–450 °C in that case is still larger and the main chain stability is less affected than it was with GL.

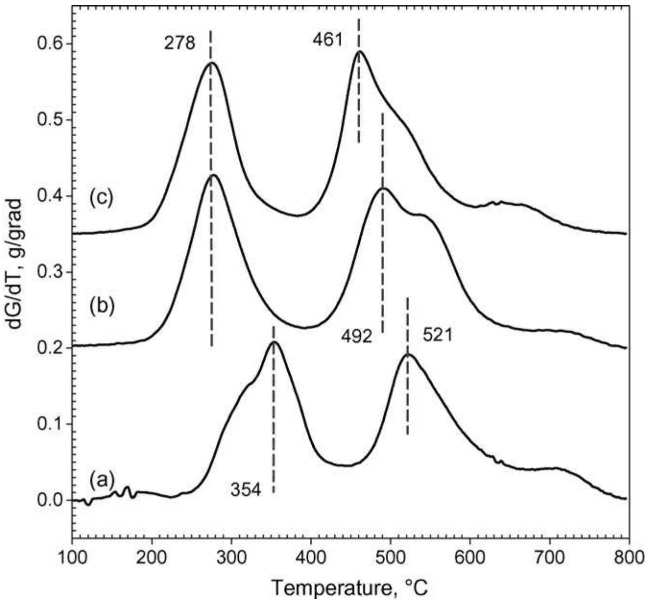

Fig. 4. Differential TGA signals for (a) 95PURE, (b) 95GL1 and (c) 95GL3 SPEEK membranes cast from water/acetone solution.

The following experiments were aimed at providing more detailed information on the thermal decomposition of SPEEK, wherein the products were monitored as a function of linearly increasing temperature in a flux of He. Fig. 6b shows the results of mass spectroscopy analysis of the products evolved and DTG curve obtained for membrane 78EG3.3 prepared using a water/ethanol mixture as solvent. Among all monitored *m*/*e*

Table 2
TGA parameters of SPEEK with different DS, casting solvents and cross-linking conditions

Initial DS[a]	Casting solvent	Figure	Cross-linker/SPEEK (mol/mol)	Sulfonic acid related peak		Main chain related peak	
				T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
78 (17.5%)	H_2O	Fig. 6a	–	340	19.7	–	–
		Fig. 6b	EG/SP = 3.3	281	18.9	–	–
85 (18.8%)	GBL	Fig. 3a	–	320–353	22.4	535	27.5
		Fig. 3b	GL/SP = 3	281	16.7	476	29.0
95 (20.5%)	H_2O	Fig. 4a	–	354	21.3	521	24.6
		Fig. 4b	GL/SP = 1	280	20.5	492	31.3
		Fig. 4c	GL/SP = 3	278	20.0	461	25.6
		Fig. 5b	EG/SP = 2.5	273–302	25.1	509	26.4

[a] Values in parantheses are the SO_3H contents in the polymers (in wt%).

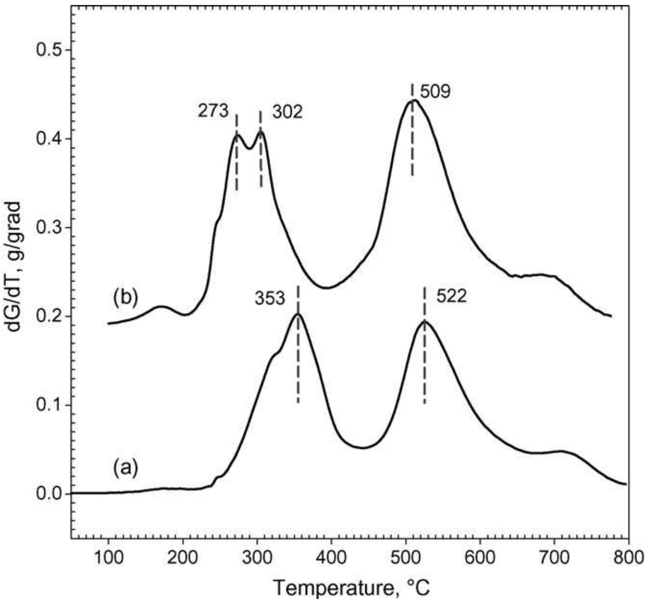

Fig. 5. Differential TGA signal for (a) 96PURE and (b) 96EG2.5 membranes cast from water/acetone solution.

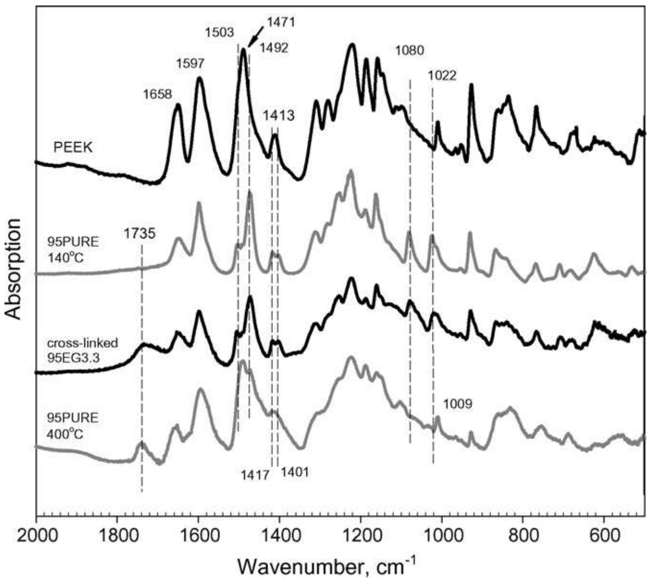

Fig. 7. FTIR spectra of PEEK and SPEEK samples.

numbers (18, 28, 32, 44, 64, 80) the most significant evolutions were observed for $m/e = 44$ and 64 corresponding to CO_2 and SO_2. It can be seen from Fig. 6a, illustrating the initial polymer behaviour, that contrary to what might be expected CO_2 is released prior to SO_2 evolution, with a delay between evolution maximums of about 35 °C. The possible origin of this carbon dioxide is discussed below. MS-TGA spectra of cross-linked membranes are quite different from those of non-cross-linked ones. Both their derivatives shifted to lower temperatures by 50–80 °C, and their maxima now coincided at 283 °C. In the latter case, however, CO_2 evolution has a broad shoulder, starting at 180 °C, preceding SO_2 by about 50 °C.

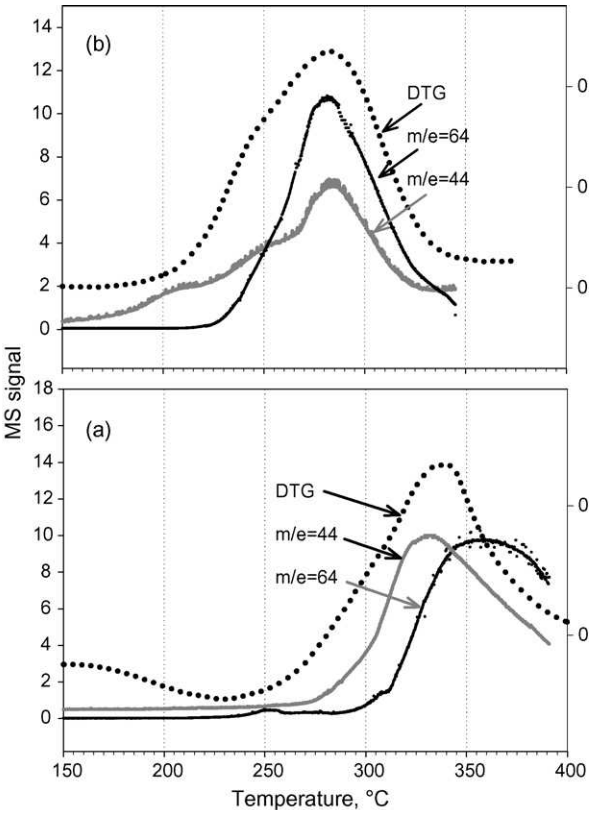

Fig. 6. MS and DTG signals of initial (a) and cross-linked (b) SPEEK, obtained at heating rate of 10 °C/min in N_2 (DTG) and He (MS).

3.3. FTIR spectroscopy

Spectra of the initial PEEK material, its sulfonated form 95PURE, the same 95PURE SPEEK annealed at 400 °C and of cross-linked membrane 95EG3.3 are presented in Figs. 7 and 8. All samples yielded a characteristic absorption at 1658 cm^{-1} attributed to stretching vibration of backbone carbonyl group, and a peak at 1597 cm^{-1} corresponding to aromatic C=C stretching. The band at 1492 cm^{-1}, observed both in PEEK and thermally treated SPEEK and assigned to di-substituted phenyl rings, splits into 1471 and 1503 cm^{-1}

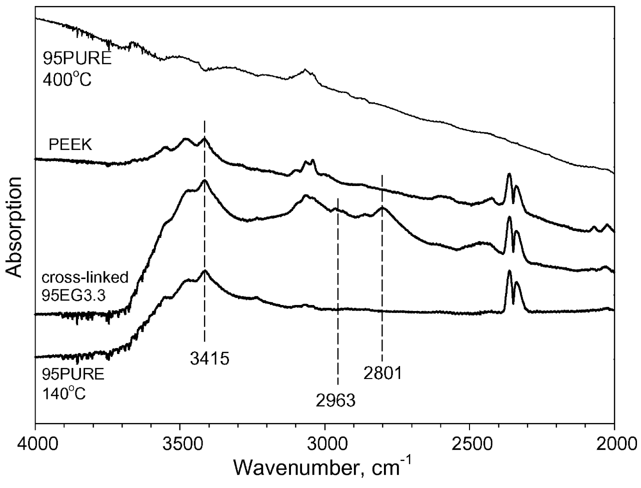

Fig. 8. FTIR spectra of PEEK and SPEEK samples.

bands in sulfonated and cross-linked SPEEK due to the third substitution in hydroquinone segment by a sulfonic acid group. The sulfonic acid group yielded its own absorptions at 1080 and 1022 cm^{-1}, attributed to asymmetric and symmetric O=S=O stretching vibrations. One more sulfonic acid associated band at 1258 cm^{-1} is observed next to the aromatic ether link at 1224 cm^{-1}, dominating in all four spectra. A new absorption appeared in the spectra of cross-linked and annealed SPEEK at 1735 cm^{-1}. In the frequency region corresponding to hydrogen bond vibrations (Fig. 8), apart from broad bands at 3415, 3481 and 3554 cm^{-1} from water absorbed by pellets, two new signals at 2963 and 2801 cm^{-1} specific for cross-linked SPEEK most likely should be assigned to asymmetric C–H stretching [22,23]. The main difference in FTIR patterns brought about by cross-linking and by annealing of SPEEK is the occurrence of a new band at 1735 cm^{-1}. This frequency is characteristic for a carbonyl group, which however being incorporated into PEEK main chain already yielded its own absorption at 1658 cm^{-1}. In the literature there are references [22] on a hydrogen bonding interaction with C=O, that could supposedly result in a band above 1700 cm^{-1}. However, H-bonding with a backbone carbonyl group would only move this band to a lower frequency as it should decrease electron density along C=O bond. The new absorption at 1735 cm^{-1} can be attributed to a new function also containing the C=O group which may be an ester, an acid or an aldehyde [23]. A new band at 2801 cm^{-1} might be caused by either the C–H or OH bonds, which makes impossible to distinguish between aldehyde and acid options. The origin of the new functions will be discussed below.

3.4. ^{1}H NMR study

As discussed in the previous section, SPEEK degradation below 400 °C, usually attributed to sulfonic acid group detachment [20,24], is more complex in the cross-linked material and supposedly involves different polymer functions. In the isothermal TGA test illustrated by Fig. 9 it was observed that 99PURE SPEEK remains stable at 160 °C (note that curing was carried out below 150 °C) but that it continuously loses weight at 210 °C. Fig. 10 shows the ^{1}H NMR spectra of these two samples after 10 h of isothermal treatment at 160 °C, evidencing that SPEEK structure was not changed. The spectra correspond to the most commonly observed pattern [21], where the doublet at 7.55 ppm is attributed to a proton in the hydroquinone ring, adjacent to sulfonic acid group and the multiple signals shifted still further downfield is assigned to the four protons, neighbouring a carbonyl group. The SPEEK treated at 210 °C yielded a significantly different pattern. Here a signal at 7.55 ppm has decreased in intensity indicating desulfonation of the polymer. Yet more significant are the general changes in the whole spectrum at 7–8 ppm, revealing a degradation of the main chain, despite rather low weight changes of only 1.8% after 10 h of treatment. This may be accounted for only by incomplete SO_3H release from the polymer after its splitting off, which instead interacts with the main chain, inducing its cleavage and rearrangement.

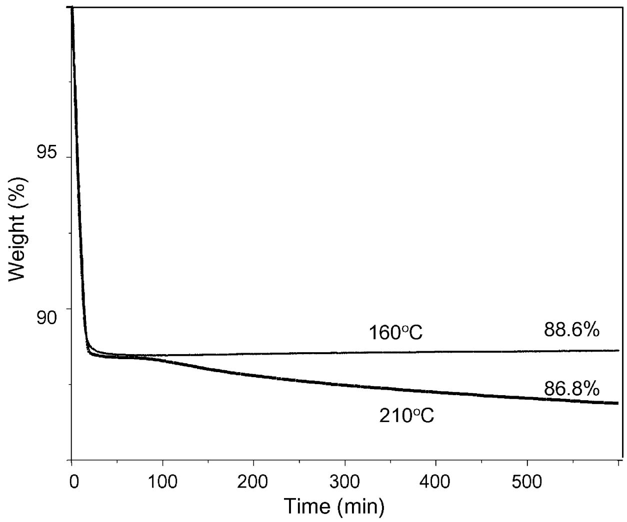

Fig. 9. Weight changes in the course of isothermal treatment of SPEEK DS = 99% in nitrogen.

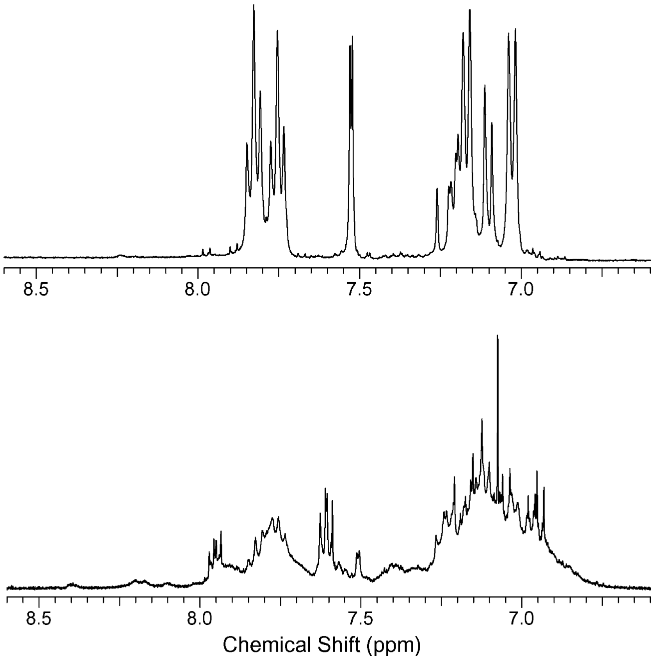

Fig. 10. ^{1}H NMR spectra of SPEEK DS = 99% treated at 160 °C (top) and 210 °C (bottom) in air.

It should be noted that liquid phase ^{1}H NMR usually used for organic structure determination has a limited application in this case due to the poor solubility or complete insolubility of cross-linked polymers. Solid state ^{1}H MAS NMR spectroscopy proved to be even less effective here than the liquid phase method, producing only a very broad signal bearing no information on the polymer structure. Thereafter some ^{1}H NMR experiments in the liquid phase were carried out in conditions, imitating preparation of cross-linked membranes in an attempt to observe transitional states and compounds formed during the cross-linking. In these experiments 30 mg of 99PURE SPEEK mixed with 0.3 g EG were dissolved in DMSO-d_6 and heated at 90, 110 and finally at 160 °C for 20 h. In two blank experiments the solutions contained only SPEEK and only EG. Treatment at temperatures up to 110 °C produced no changes in NMR

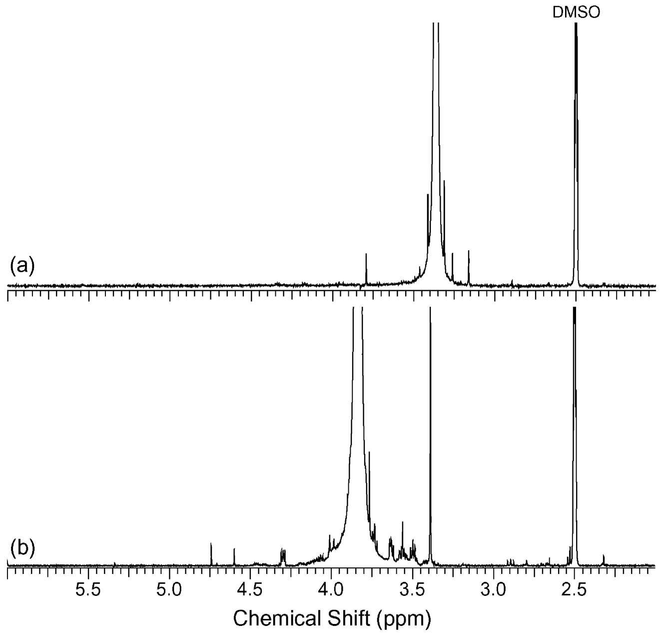

Fig. 11. ^{1}H NMR spectra of (a) EG and (b) SPEEK + EG. Samples were dissolved in DMSO-d_6 and pretreated at 160 °C in the NMR tube. Intensity scales are the same for (a) and (b).

spectra of all three mixtures. Heating at 160 °C for 20 h did not change NMR pattern of pure SPEEK either, but affected the spectrum of SPEEK/EG mixture. Moreover, some new small resonances emerged in the spectrum of pure EG (Fig. 11). This latter observation deserves more attention.

The chemistry of ethylene glycol is well investigated [25] and it is known that EG can be easily oxidized by a number of oxidizing agents, including oxygen (which was not eliminated in the experiment). The typical oxidation products, derived from the alcoholic functions are $HOCH_2CHO$, $HOCH_2COOH$, CHOCHO, HCOCOOH, HOOCCOOH, HCHO and HCOOH. Further interaction of EG with its derivatives might result in formation of cyclic compounds, such as dioxolanes or dioxane. The presence of two hydroxyl groups may also lead to formation of mono and di-ethers and esters.

The diversity of potential products of EG reactions makes difficult unambiguous assignment of all NMR resonances observed in the experiment. However when Fig. 11b is compared with Fig. 11a, it is apparent that liquid phase oxidation or/and oligomerization of EG occurs much faster in the presence of SPEEK, clearly due to catalytic effect of sulfonic acid groups. The shift toward higher frequencies of the EG signal of Fig. 11b is explained by increased hydrogen bonding in the DMSO solution between EG, $-SO_3H$ groups and water, all showing up as one large signal at 3.87 ppm.

In order to overcome the difficulties associated with insolubility of fully formed cross-linked membranes in DMSO, several experiments were also carried out on the partially cured samples. SPEEK and EG were dissolved in D_2O/acetone-d_6 mixture and treated at 130–160 °C for 2 h instead of the usual several days. These membranes remained DMSO soluble. Their NMR spectra did not reveal obvious changes in the aromatic domain but similarly to the pattern illustrated by Fig. 11 exhibited multiple signals at 3–5 ppm (Fig. 12a) signifying an interaction of EG with the polymer.

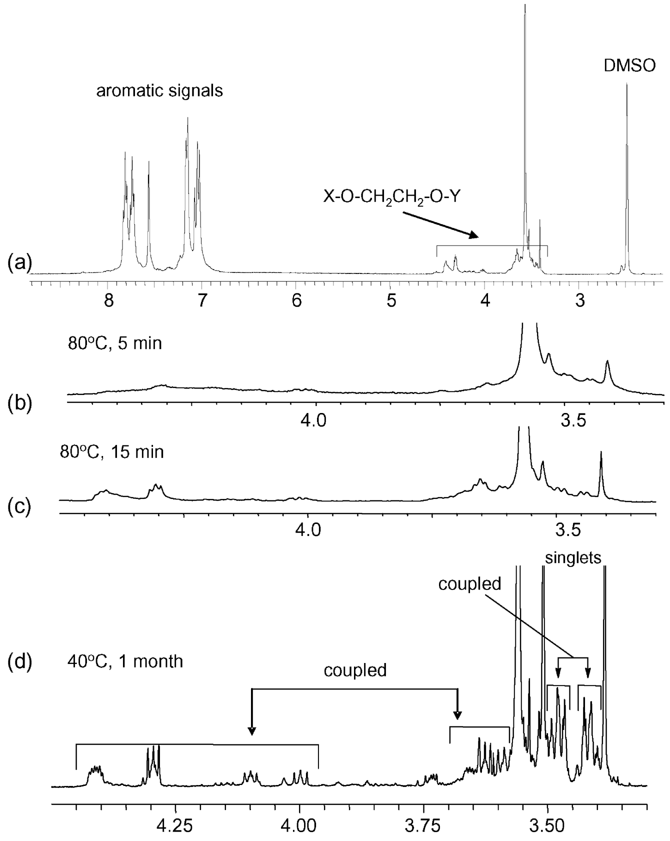

Fig. 12. NMR-spectra of SPEEK partially cross-linked with EG (DS = 99%) immediately after dissolution in DMSO at 80 °C (a and b), 15 min later (c), and after 1 month in DMSO (recorded at 40 °C) (d).

It should be mentioned, that even the partially cross-linked polymer was difficult to dissolve in DMSO. Fig. 12 shows a series of spectra, obtained at different periods of time after addition of DMSO-d_6 into the NMR tube containing partially cross-linked SPEEK specimen and EG. If at first it was a gel-like substance, giving poor resolution spectra (Fig. 12a–c), a long-term storage of the sample tube resulted in a liquid, yielding a spectrum with sharp signals (Fig. 12d) which could be analyzed with better precision.

This spectrum (Fig. 12d) shows the multiplets at 3.95–4.45 ppm being spin-coupled to the multiplets at 3.58–3.70 ppm. High frequency signals are typical of hydrogen in CH_2 groups near electron withdrawing functions, such as sulfonic acids and esters. Signals in the 3.58–3.70 ppm region are usually attributed to CH_2 groups adjacent to ethers or hydroxyls. It might be assumed therefore that this pattern originates from structures, similar to the one, illustrated in Fig. 13a and b as an example of EG multi-additive reaction with SPEEK. In the mixture of different $-O-CH_2-CH_2-O-$ signals in the spectrum shown in Fig. 12, the signals at 3.58–3.70 and 3.95–4.45 ppm could be assigned to hydrogen atoms in *a–d* positions of Fig. 13. The singlets on the spectra most probably originate from EG (or EG oligomer) protons such as *f* and *g* segments in Fig. 13 or from isolated CH_2 groups (*e*-position). The coupled multiplets

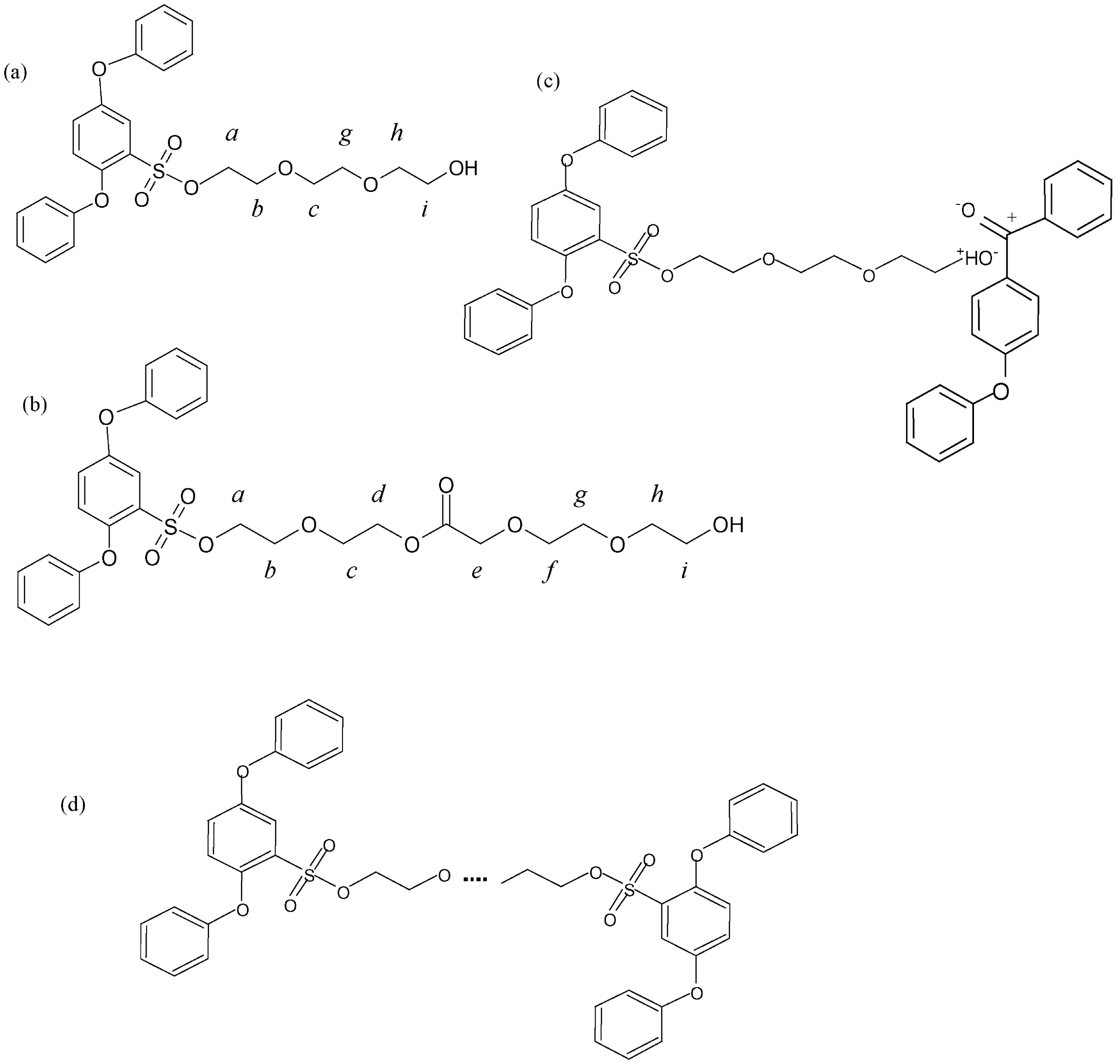

Fig. 13. Structures possibly formed in the course of curing of membranes, containing EG in their formulation: (a) EG trimer attached to the SPEEK; (b) example of structure including some of the potential functional groups. Partial cross-linking; (c) interaction of one of these structures with a carbonyl of main chain; (d) example of complete cross-linking via EG oligomers.

at 3.40–3.51 ppm are typical signals for structures corresponding to protons in *h* and *i* position of Fig. 13.

These observations suggest that the EG molecule initially attached to sulfonic acid group will preferably react with another EG molecule or its derivative, forming EG dimers, trimers or polyfunctional moieties. This is also supported by the fact that linking EG with a SO_3 group provokes electron depletion in the CH_2 adjacent to hydroxyl in the molecule, making it even more reactive for substitution than free EG. Thus, NMR studies of partially cross-linked polymers shows that treatment at 120–150 °C initiates the attachment of an EG molecule to $–SO_3H$ group which, being activated by the influence of the sulfonic acid group, then forms polyaddition products most probably terminated by an –OH group.

4. Discussion

The main distinctions between the cross-linked SPEEK membranes and the initial non-cross-linked ones are as follows: (1) significant decrease of the temperatures of the two steps of degradation associated with both pendant sulfonic acid group and main polymer chain; (2) emerging in the FTIR spectra a band at $1735\,cm^{-1}$ associated with a carbonyl stretching vibration, different from a backbone carbonyl of SPEEK; (3) appearance in the ^{1}H NMR spectra of signals suggesting interactions of EG or GL with sulfonic groups as well as (4) signals, indicating formation of multifunctional structures from EG molecules and derivatives.

Apart from these observations it is pertinent to consider the additional data on the proton conductivity and water absorption of SPEEK membranes as function of their preparation conditions. They are shown in Table 3. It is clear from this Table that the casting solvent interacts with sulfonic groups, reducing water uptake (compare 78PURE and 84PURE cast from water/acetone with the ones cast from DMAc). The strong interaction of $–SO_3H$ groups with DMAc and especially with DMF was previously discussed in [20,21]. Solvent–SO_3H interaction is also confirmed by the loss in the membrane conductivity. As can be

Table 3
Conductivity and water absorption by cross-linked and non-cross-linked membranes

Initial polymer (DS%, solvent)	EG/SPEEK (mol/mol)	Uptake at 25 °C for 24 h (wt%)	Uptake at 80 °C for 3 h (wt%)	Conductivity at 25 °C (mS/cm)
59 (DMF)	–	21	31	0.65
69 (DMAc)	–	28	78	22.0
79 (DMAc)	–	42	–	26.0
84 (DMAc)	–	39	Soluble	39.0
96 (DMF)	–	Soluble	Soluble	4.3
96 (DMAc)		Soluble	Soluble	110.0
78 (water/acetone)	–	79	124	28.0
	1.1	65	–	17.0
	2.0	40	–	15.6
	2.6	37	–	14.0
	3.5	32	2100	12.7
85 (water/acetone)	0	124	Soluble	48.0
	3.5[a]	47	2900	31.0
96 (water/acetone)	0	Soluble	Soluble	–
	1.2	114	Soluble	29.0
	1.5	104	Soluble	27.8
	2.3	70	Gel-like	27.1
	3.0	60	3600	20.2

[a] Glycerol used instead of EG.

seen from Table 3, the conductivity of 96PURE membrane cast from DMF is 25 times lower than that of same polymer cast from DMAc. The membrane 96PURE cast from water/acetone solution being hydrated produced gel-like substance, the conductivity of which was not measured. It was shown in [19] that organic solvents also hinder cross-linking with polyatomic alcohols, resulting in membranes, partially or entirely soluble in water when prepared from high DS SPEEK. Only organic solvent free casting mixtures allowed completely cross-linked membranes to be obtained. This means that DMAc, DMF, NMP and GBL compete with EG or GL—for interactions with SO_3H, preventing the SPEEK membranes from complete cross-linking. It is important to note that the best cross-linked membranes were obtained when GL or EG contents corresponded to 3 molecules per SO_3H group (samples with DS = 96%, Table 3). At lesser mole ratio cross-linking was not complete. This observation correlates with the results of ^1H NMR spectroscopy, suggesting formation of polyfunctional groups from EG as shown in Fig. 13.

It is worth mentioning, that when EG/SPEEK mole ratio exceeded 3, the cross-linking product grew brittle indicating excessive cross-linking. Less strong cross-linking at EG/SPEEK = 3 allowed the polymer to remain flexible. More cross-linked structures must contain larger amount of completed bridges (Fig. 3d) at the expense of incomplete linkages (Fig. 13a and b). That probably explains the increase of CO_2 signal in DTG curves of cross-linked samples compared with non-cross-linked ones as seen in Fig. 6. Maximums of CO_2 and SO_2 evolution coincide in cross-linked materials and both signals are shifted to lower temperatures when compared with the initial membranes. These changes in thermo-gravimetric behaviour are caused by the increased easiness of splitting off of the sulfonic acid group with attached EG polyaddition products compared with the lone $–SO_3H$ group in non-cross-linked SPEEK. Similar effect but to a lower extent is exerted by organic solvents, which was shown above, facilitates the desulfonation of the polymer. It follows for instance from comparison of Tables 1 and 2, where the temperature of the first maxima of 78PURE cast from DMAc was 322 °C while the one cast from H_2O was 340 °C. Another example is that first maxima of both 85PURE and 99PURE cast from DMAc are at 321 °C while for 95PURE cast from water it falls on 354 °C. Thus, the presence of organic solvents strongly reduces cross-linking because of increased competition for acid functions.

Previously it was suggested [26] that cross-linking occurs through condensation of sulfonic acid functionalities according to: $Ar–SO_3H + HO_3S–Ar = Ar–SO_2–Ar + H_2SO_4$. It was shown elsewhere [19] that this cross-linking reaction actually does not occur, as there were no any changes observed in membrane mechanical properties if a cross-linker was not added. This seems reasonable due to the fact that $–SO_3H$ groups pendant to rigid SPEEK polymer chains have much more difficult access to each other than the small and mobile EG molecules. Thereupon it can be supposed that EG derivatives first bonded with SPEEK chains, and then underwent polyaddition reactions, resulting in an interpenetrating network grafted to the polymer. At this stage the polymer remains soluble (partially cross-linked). Further curing finally results in complete cross-linking when the terminal hydroxyls of this network will interact with remaining SO_3H of SPEEK as shown in Fig. 13d. A possibility also exists that the hydroxyl-terminated EG oligomers can interact with positively charged carbons in the main chain carbonyls by a dipolar interaction (Fig. 13c).

The possibility of involvement of >C=O function in the cross-linking is ensued from FTIR results shown above (Fig. 7), where the new absorption at 1735 cm^{-1} should be attributed to a new function containing the C=O group. It is interesting that in the FTIR spectra of unmodified SPEEK annealed above 250 °C the same absorption at $1735\,\mathrm{cm}^{-1}$ is also always present (Fig. 7). This frequency is characteristic to stretching vibrations of a carbonyl in ester, acid or aldehyde functions [23] and is obviously resulting from carbonyl interaction with evolving SO_3H. It is worth reminding that in the MS-TGA experiment SO_2 signal with $m/e = 64$ was registered instead of SO_3, that might be expected in the course of thermal desulfonation of SPEEK (Fig. 6). In a view of the fact that CO_2 evolution occurs prior to sulfur dioxide, one may assume that at first a hydroxyl radical fragment split off and immediately enters into interaction with the main chain. This hypothesis agrees with the results of [27], where SO_2 (not SO_3) evolution was also observed at 350 °C, accompanied by organic fragments including carbonic acid and a number of other products, such as diphenyl ether, dibenzofuran, phenoxyphenol, etc. The authors of [27] came to conclusion that a radical mechanism plays a significant role in the thermally driven decomposition of SPEEK. It is reasonable then that the thermolysis might begin with hydroxyl cleavage from $–SO_2–OH$ group, which is consistent with the relative bond strength of a C–S ($\Delta H = 714$ kJ/mol) in comparison with a SO_2–O bond ($\Delta H = 348$ kJ/mol).

Scission of the polymer backbone, provoked by –OH interaction with the carbonyl link in the course of the polymer thermolysis, leads to formation of a terminal function, most probably of an acid or aldehyde. This can explain the shift of main chain degradation temperature from 600 °C for PEEK to <550 °C for SPEEK observed in [10]. Still further lowering of the temperature of degradation of the cross-linked membranes compared with non-cross-linked ones (see Table 2 and Figs. 3–5) can be explained then by involvement of EG molecules (in addition to SO_3H) in interaction with the main chain carbonyl groups.

Emergence of the same (supposedly aldehyde or acid) absorption in the FTIR spectra of both the cross-linked SPEEK and annealed non-cross-linked SPEEK leads to assumption of certain similarity in their structures. It is conceivable that some part of hydroxyl terminated EG oligomers interacting with carbonyl functions (Fig. 13c) also provokes the main chain cleavage and to a certain degree the polymer degradation. This may presumably occur in the final stage of curing of the casting mixtures, as substantiated by FTIR observations of new CH fragments in addition to a new C=O bands in the cross-linked membranes. The mechanical properties of the cross-linked membranes, such as flexibility and ability to extremely high swelling (see Table 3, water uptake of samples 78EG3.5; 85GL3.5; 96EG3.0 at 80 °C), suggest that cross-linking may not be purely covalent (Fig. 13d), but include some kind of mixed polar-covalent bonding (Fig. 13c), possibly with a coordination component. So there is certain possibility that chain scission does not occur, and FTIR signal might be caused by such bonding. Unfortunately the solid state reaction occurring in the cross-linked membrane cannot be traced by the liquid phase NMR method and might be only surmised.

The proposed mechanisms of SPEEK cross-linking could be probably further elaborated and developed in more detail in a consecutive study. However, the observations made in this work allow to exclude the previously proposed cross-linking mechanisms exclusively through condensation of sulfonic acid functionalities [26] as well as through terminal hydroxyls of GL or EG molecules [19], and provide a basis for better understanding of the chemistry of sulfonated polymers and specifics of their cross-linking.

5. Conclusion

SPEEK based PEMs, cross-linked using ethylene glycol or glycerol, were found to be stable in hot water and highly proton conductive. The properties and chemical structure of the cross-linked membranes were studied by TGA (MS), liquid phase ^{1}H NMR and FTIR. The obtained results were discussed from the viewpoint of oligomerization of cross-linker molecules, sporadically grafted to sulfonic acid functions. This assumption is mainly based on the results of NMR study, which also revealed, that the products of polyaddition reactions of cross-linker molecules and their derivatives then build up an interpenetrating network which may interact with the neighbouring backbones. FTIR results suggest that the main chain carbonyl functions are involved in this interaction.

An important result of this study was a hypothesis of SO_3H fragmentation and interaction of a hydroxyl radical with the main chain in the course of thermal desulfonation, facilitating polymer degradation. Both organic solvents and cross-linkers provoke easier sulfonate cleavage and there through accelerate SPEEK thermal degradation.

The best mechanical properties (flexibility, little brittleness) were possessed by the membranes with cross-linker/SPEEK mole ratio about three. Lower ratio led to a non-complete cross-linking, while at higher ratio membranes became brittle. This observation corroborates the assumption of various EG oligomers formed in the course of cross-linking. Linked to the sulfonic acid functions they form the structures, favouring improvement of membrane mechanical properties. Presumably average length of those structures should be close to three monomer units in order to ensure a trade off between strength and flexibility of the membranes. Despite the fact that thermal stability of cross-linked membranes is inferior to that of non-cross-linked ones, they are still stable up to temperatures >200 °C which makes this method of membrane cross-linking still promising for FC application.

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