

# Sulphonated poly(ether ether ketone) membranes for fuel cell application: Thermal and structural characterisation

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## Abstract

Sulphonated PEEK polymers with a different sulphonation degree (DS) were obtained by varying the sulphonation reaction temperature. Ionomeric membranes were prepared by using different solvents (DMSO, DMAc, DMF and DMAc/DMF mixture). Structural and chemical–physical film characterisations were carried out by X-ray and thermo gravimetric analyses. Membranes obtained from DMF and/or DMAc have a low crystallinity with an amorphous structure, while the DMSO–sPEEK membrane has a more crystalline structure that could inhibit proton conduction. The efficient proton conducting structure for sPEEK chains seems to be the statistical coil. The analysed membranes do not present any ionomer or matrix peak associated with the clustering of sulphonic groups or phase separation due to the statistical distribution of the sulphonic groups on the main PEEK chain. The thermal behaviour was investigated by a differential scanning calorimetry (DSC). From a cooling analysis all the water contained in the membranes was shown to be strongly linked to sulphonic groups and of a non-freezable type. The influence of the casting solvent on the cell performance was studied. The developed membranes were also tested in H<sub>2</sub>/air single cell in the temperature range 80–130 °C. A maximum power density of about 400 mW cm<sup>-2</sup> at 0.5 V was reached at 130 °C.

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## 1. Introduction

The interest of the research, in particular during the last 20 years, was addressed to the improvement of the existent polymer electrolyte membranes for fuel cells and the development of new ones. So far, Nafion<sup>®</sup> membranes have been the most commonly studied and used, for their excellent proton conduction at 80 °C and unsurpassed longevity in fuel cell environment [1–3]. Moreover, structural studies have well defined a crystalline structure for Nafion<sup>®</sup>, with an evident separation between the hydrophobic region of the polymer matrix and the hydrophilic cluster domains of the sulphonic groups [4–6].

Despite the good characteristics of Nafion membranes and the good performance reached in fuel cell operations at the above

considered temperatures, these materials have, nowadays, production costs that are too high, due to the fluorine-chemistry involved in the polymerisation processes.

There are a variety of alternative polymers to Nafion, constituted of polyaromatic backbone, such as polysulphones, polyetherketones, polybenzimidazole, polyphosphazene and others, that differ for the functional groups that promote the proton conduction, but, in any case, the main requirement of these polymers is the temperature stability [1,7].

Furthermore, the characteristics of the membranes obtained by using these polymers depend on the nature of the casting solvent that could influence properties such as conductivity and mechanical strength [8,9]. The polymer microstructure, which is itself sensitive to the molecular weight of the polymer and the membrane forming process (kind of solvent, evaporation rate, evaporation temperature, etc.), strongly influences membrane properties. In this work, particular attention was addressed to the polyether–ketones family, but the existing papers on this kind of polymer are not in agreement because there are

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two different theories on the microstructure. Some SAXS studies [2] demonstrated a water filled channel existence in sulphonated PEEK that are narrower and more highly branched than Nafion. On the contrary, [10] a sulphonated PEEK was investigated and the results were found to be different, because no microstructure in the membrane was highlighted.

Among the existent polymers, a polyether–ether–ketone (PEEK) with a sulphonation degree of about 50% was chosen for our study and investigated in terms of structural, thermal, chemical–physical and electrochemical characterisations, in dependence of the casting solvents used during the membrane preparation. The aim of this work is to establish the real effect of the casting solvent in the structural characteristics of the membranes, the effect of the microstructure on the thermal and mechanical properties and how these parameters could condition the chemical–physical and electrochemical characterisations.

## 2. Experimental

### 2.1. Preparation of sulphonated peek

Three different sulphonated polymers were prepared by using a procedure reported in literature [11,12]. An amount of 5 g of PEEK (Victrex) was dispersed in 96% sulphuric acid maintaining under stirring for 24 h at three different reaction temperatures: 25, 30 and 35 °C. After this reaction time the sulphonated polymers were precipitated in cold water, washed until a neutral pH of rinse water was reached and completely dried.

Functionalised polymers with sulphonation degrees (DS) of 29% (sPEEK/29), 52% (sPEEK/52) and 59% (sPEEK/59) were obtained. The DS was determined by elemental analysis (CHNS-O Carlo Erba CHNS-O Analyzer mod.EA 1108) as the ratio between S/C obtained from the elemental analysis ( $S/C_{\text{exp}}$ ) and the theoretical ( $S/C_{\text{theo}}$ ) calculated by assuming the complete sulphonation of the polymer.

### 2.2. Membranes preparation

For membrane preparation a 6% (w/w) solution was prepared with a solvent and re-concentrated under heat until reaching a suitable density to be stratified. After membrane casting, they were left to dry on a glass plate at 80 °C for 3 h and at room temperature for about 16 h, to remove the solvents, washed in water and treated in HCl 1 M. Dimethylacetamide (DMAc) was used as a solvent for membranes with a different DS. A study of different casting solvents was carried out on sPEEK/52 in order to investigate the membrane properties. The solvents used were: dimethylacetamide, dimethylformamide (DMF), dimethylsulphoxide (DMSO) and a mixture of DMAc/DMF (50%, w/w). Following the above described procedure four membranes were obtained: sPEEK/DMAc, sPEEK/DMF, sPEEK/DMSO and sPEEK/DMAc–DMF with a thickness ranging between 70 and 90  $\mu\text{m}$ .

### 2.3. MEAs preparation

The membranes were inserted between home-made electrodes to form the membrane-electrode assemblies (MEAs). The procedure for electrodes preparation is based on the spraying technique and described elsewhere [13]. Anodes and cathodes with the same Pt loading (0.5 mg  $\text{cm}^{-2}$ ) in the catalyst layer were prepared, a 30% Pt/Vulcan (E-Tek Inc.) was used as an electro catalyst.

### 2.4. Polymers and membranes characterisations

#### 2.4.1. Polymers and membranes thermal characterisations (TGA and DSC)

Thermo gravimetric analysis (TGA) was performed using a thermo balance Netzsch (mod. STA 409) in air following the variation of the percentage mass loss in weight, in the temperature range between 25 and 1100 °C with a temperature rate of 5 °C  $\text{min}^{-1}$ . Differential TG curves (DTGA) were obtained from the first derivative of TGA data. To obtain the derivative curve, TGA data was first lightly smoothed.

Differential scanning calorimetry (DSC) analysis was performed using a Mettler 822e calorimeter. An amount of 3–5 mg of sample was placed in aluminium pans. Heating scan velocity was 5 °C  $\text{min}^{-1}$  while  $-20$  °C  $\text{min}^{-1}$  was used for the cooling runs.

#### 2.4.2. Polymers and membranes X-ray analyses (WAXS and SAXS)

Wide-angle X-ray diffraction patterns of sPEEK membranes were recorded at the beamline ID15 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. WAXS profiles were recorded using a 2D MAR 345 detector and the WAXS images were recorded over 360°. The X-ray beam energy was 88.5 keV and standard procedures for transmission correction and air background subtraction were used. Small-angle X-ray scattering experiments on both membranes and solutions were performed at the beamline BM26 at the ESRF. Experiments were carried out using a monochromatic 12 keV X-ray beam. The small-angle scattering images were recorded by placing a two-dimensional position sensitive detector at a sample-to-detector distances of 1.5 m. Aluminum standard powder was used to calibrate the angular range for ID15 WAXS experiments while Silver Behenate was used to calibrate the SAXS angular range. The two-dimensional images were radially averaged around the centre of the primary beam in order to obtain the isotropic intensity profiles. The explored  $q$  ranges were, respectively, 0.015–0.3  $\text{\AA}^{-1}$  for SAXS and 0.3–6  $\text{\AA}^{-1}$  for WAXS measurements, where  $q$  is the modulus of the scattering vector and it is equal to  $q[\text{\AA}^{-1}] = \alpha E[\text{keV}]\sin\theta$ , where  $E$  is the energy of the X-ray beam,  $\theta$  the half of the scattering angle and  $\alpha$  is a constant of the value 1.014. For solution scattering experiments sPEEK 1% (w/w) solutions were filled in a glass capillary with 10  $\mu\text{m}$  thick walls. After absorption difference correction scattering from the empty capillary was subtracted to obtain SAXS data presented in the paper.

### 2.4.3. IEC and water uptake measurements

The obtained films were characterised in terms of ion exchange capacity (IEC  $\text{meq g}^{-1}$ ) and water uptake (w.u.%) measurements.

IEC and w.u. parameters were calculated by acid–base titration (using an automatic titrator Metrohm Mod. 751GPD Titrino) and water retention measurements.

The sample was desiccated for 2 h at  $80^\circ\text{C}$  in an oven under vacuum, in order to obtain the dry mass ( $m_{\text{dry}}$ ), then it was immersed in water at room temperature for 24 h, in order to obtain the wet mass ( $m_{\text{wet}}$ ) and the water uptake was calculated as the percentage difference between the wet and dry mass. The desiccated sample was immersed in a NaCl 1 M solution until the pH value was stabilised and then titrated with a NaOH 0.01N solution to calculate the IEC.

### 2.4.4. Electrochemical characterisation

Fuel cell tests were carried out in a commercial  $5\text{ cm}^2$  single cell (Globe-Tech) in a range of temperatures between  $80$  and  $130^\circ\text{C}$ , with humidified  $\text{H}_2$  and air at 3 absolute bar. The gas fluxes were fixed at 1.5 and 2 times the stoichiometry at a current density of  $1\text{ A cm}^{-2}$  for hydrogen and air, respectively.

## 3. Results and discussion

At first, a thermo gravimetric analysis was carried out on the polymers to point out the occurring processes on the sulphonated polymer. In Fig. 1 the thermo gravimetric analysis and the differential thermo gravimetric analysis for 52% sulphonated PEEK (sPEEK/52) powder are reported. After the sulphonation reaction, a significant water loss, of about 10% (w/w), was recorded, which corresponds to the water loss from the room conditions to the dry state. At about  $280^\circ\text{C}$  the loss of sulphonic groups starts while the degradation process of the sulphonated polymer starts at around  $350^\circ\text{C}$  and it is complete at about  $650^\circ\text{C}$ .

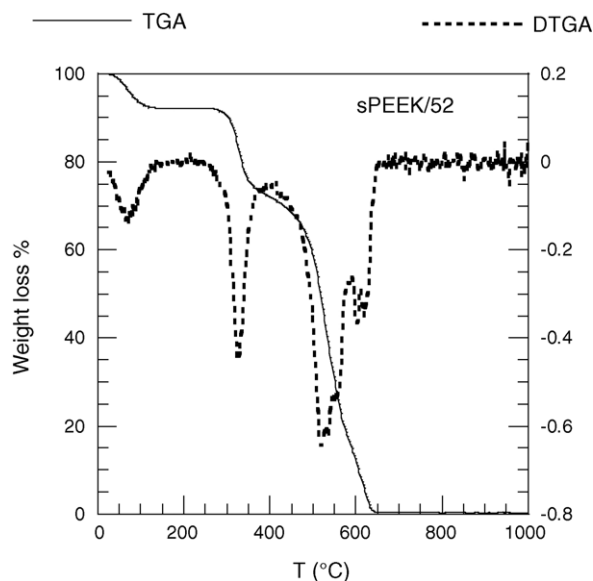


Fig. 1. Thermal analysis (TGA and DTGA) of sPEEK/52.

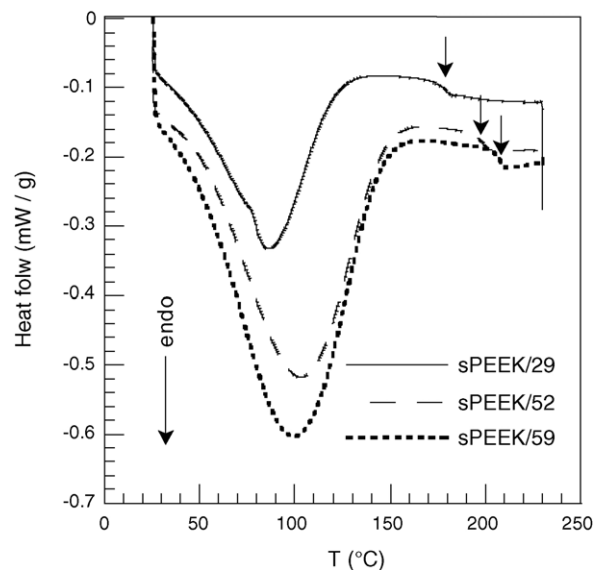


Fig. 2. DSC first scans of sPEEK powders at different sulphonation degrees.

As a consequence of the above, the differential scanning calorimetry was performed in a temperature range between  $25$  and  $230^\circ\text{C}$ , before the desulphonation process. Fig. 2 reports the first scan DSC thermo grams ranging from  $25$  to  $230^\circ\text{C}$  for the three sulphonated PEEK powders at different sulphonation degrees. The polymers were kept for several days at room temperature and humidity before performing the measurement.

In all the reported thermograms we can clearly distinguish two signals: a large endothermic peak centred at around  $100^\circ\text{C}$  and a glass transition at temperatures higher than  $170^\circ\text{C}$ . The large endothermic peaks are related to the water loss, because the water amount is associated to the sulphonic groups, the peak intensity increases with the increase of sulphonation degree. For the 52 and 59% DS polymers this signal is centred at  $100^\circ\text{C}$ , while for the 29% polymer the peak occurs at lower temperatures ( $86^\circ\text{C}$ ). Furthermore the transition starts immediately with heating and is really broad from  $25^\circ\text{C}$  up to  $145^\circ\text{C}$  for sPEEK/29 and  $170^\circ\text{C}$  for sPEEK/52 and sPEEK/59. This means that the distribution of water inside the ionomeric material is very complicated and leads to the possibility of the existence of another transition at a temperature just lower than  $100^\circ\text{C}$ . This very broad transition was seen for a lot of ionomers and its attribution is still under debate [14–17]. Details for such a transition are discussed below. At higher temperatures it is possible to see a second transition for each analysed sample. This transition has a clear relaxation behaviour and is the glass transition of the polymeric material. The position of the glass transition shifts upwards with the increase of the sulphonation level. This behaviour was accurately studied for acid form sPEEK from Zaidi et al. [2] and its sodium salt from Bailly et al. [18]. In fact, the introduction of sulphonic groups in the phenyl rings between the two ether oxygens leads to a more rigid material. The sulphonic groups can increase the rigidity of the polymer because they act as physical intra and inter-chain bridges forming strong hydrogen bonding with other sulphonic groups or with the ketone CO groups of the polymer backbone. These

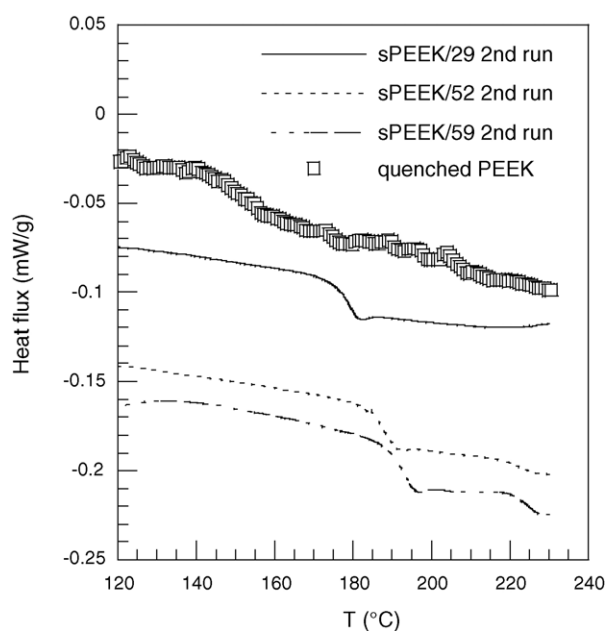


Fig. 3. sPEEK second DSC runs for  $T_g$  dependence with a sulphonation degree evaluation.

intermolecular forces make the internal rotation of sulphonated phenyl rings difficult compared to the unsulphonated PEEK. As a consequence, the  $T_g$  values increase with the introduction and the increase of sulphonic groups. In order to extract correct values for  $T_g$  and  $\Delta c_p$ , a second heating DSC scan was carried out (see Fig. 3). In this way during the first heating, residue volatile solvent traces are eliminated and data is more reproducible. For comparison, data obtained from bare PEEK Victrex® is reported. These results agree with the w.u.% and IEC values measured on the membranes prepared with the three different polymers as reported in Table 1. In fact, both water retention and IEC are directly related to DS and they increase by increasing the sulphonation.

Also the  $\Delta c_p$  values increase in accordance with this trend. Furthermore, as shown in Fig. 4 for sPEEK/59, when the second DSC heating run is performed immediately following the cooling from the first scan, a second new transition appears at around 95 °C. This transition below the  $T_g$  is not observed in quenched PEEK 450PF and so it is probably due to the introduction of the sulphonic group on the PEEK backbone.

The trend with increasing DS of this transition is similar to the main glass transition, namely its position and intensity increase by increasing the DS. The same transition will be found and discussed later in the paper for all the studied sPEEK membranes. In addition, in Fig. 4, hysteresis in the sPEEK/52  $T_g$

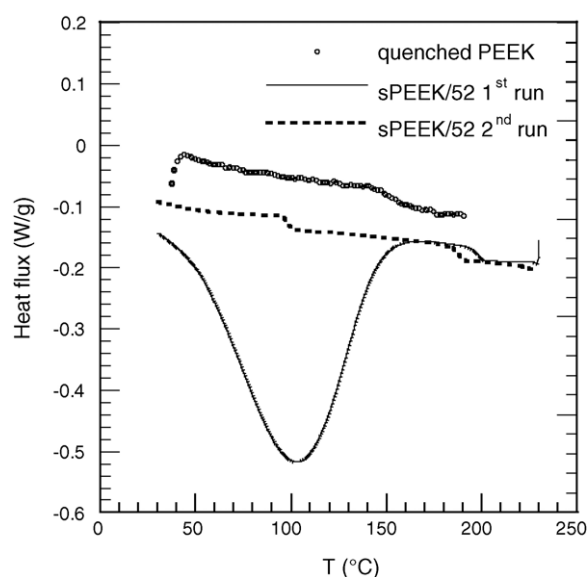


Fig. 4. First and second heating DSC run on sPEEK/52 compared with the DSC scan on amorphous PEEK.

position between the first and second DSC heating runs can be pointed out. However, the associated  $\Delta T_g$  and  $\Delta c_p$  do not change between the two runs. Changes in  $T_g$  position are probably due to a structural re-organisation subsequent to the thermal treatment during the first heating run. This evidence clearly shows how thermal treatments have an influence on the ionomer structure and behaviour. This influence on sPEEK membranes was shown to have a strong effect also on the electrochemical fuel cell performance as reported by [3]. As will be shown further in the paper, also different membranes preparation procedures (i.e. changes in solvent casting) may have some influence on structure and thermal and electrochemical behaviour.

A preliminary electrochemical single cell test at 80 °C was carried out on the membranes prepared with the three different polymers to help us in the choice of the best DS to use for a study on the influence of different casting solvents. Fig. 5 shows a comparison between the polarisation curves for sPEEK/52 (membrane 16A) and sPEEK/59 (membrane 9A) is shown. The 6A membrane was not considered for the very low DS. As we can see, the less sulphonated membrane has a better performance and overall a higher OCV. We think that a high sulphonation level renders the membrane more soluble, taking into account that the polarisation curves were recorded after 1 day of conditioning at 80 °C. For this reason the sPEEK/52 was selected as the best compromise between the electrochemical performance and stability.

Table 1

Glass transition parameters of sulphonated PEEK powders at different sulphonation degrees as extracted from the DSC analysis and chemical–physical data of the developed membranes

Polymer	DS (%)	Onset $T_g$ (°C)	$T_g$ (°C)	$\Delta c_p$ (J g <sup>-1</sup> K <sup>-1</sup> )	Membrane	Thickness (μm)	IEC (meq g <sup>-1</sup> )	w.u. (%)
PEEK450	0	144	151	0.11	–	–	–	–
sPEEK/29	29	176	178	0.25	6A	60	1.1	15
sPEEK/52	52	184	187	0.29	16A	70	1.6	32
sPEEK/59	59	188	192	0.32	9A	70	1.9	37

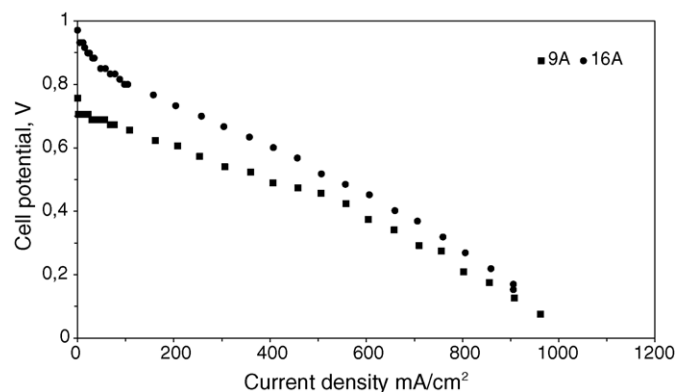


Fig. 5. Comparison between the polarisation curves for sPEEK/52 (membrane 16A) and sPEEK/59 (membrane 9A) after 1 day of conditioning at 80 °C.

Four membranes using different casting solvents and named sPEEK/DMAc, sPEEK/DMF, sPEEK/DMSO and sPEEK DMAc/DMF according to the solvent used, were prepared and a DSC analysis was performed.

In Figs. 6 and 7 the first and second DSC runs performed on the membranes are reported.

Three main features can be pointed out observing Figs. 6 and 7. As already highlighted for sPEEK powder samples, a large endothermic transition is observed in all the studied membranes. Such a transition is reported for many of ionomers and its position depends on the ionomer type, on the cation type ( $H^+$ ,  $Na^+$ , etc.), on the thermal treatment of the membrane and as shown in Fig. 2, on the water content [19,14]. For H-Nafion this transition is usually reported at 115 °C and for ethylene-methacrylic acid (EMAA) it is at 58 °C [20,14]. Even if this transition is at the centre of many studies, its assignment is still under debate [14–17]. However, because of its dependence on the cation type it is fairly referred to as “ionic cluster” transition, related to material contained in an ion rich phase. Tadano et al.

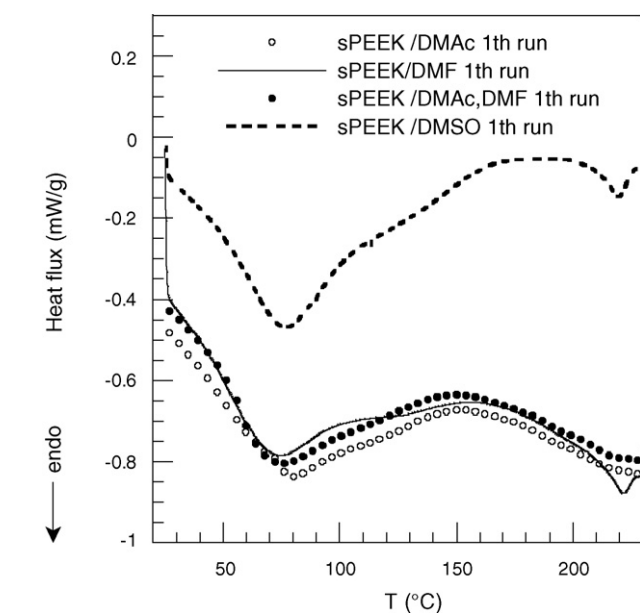


Fig. 6. DSC first heating for sPEEK membranes cast with different solvents.

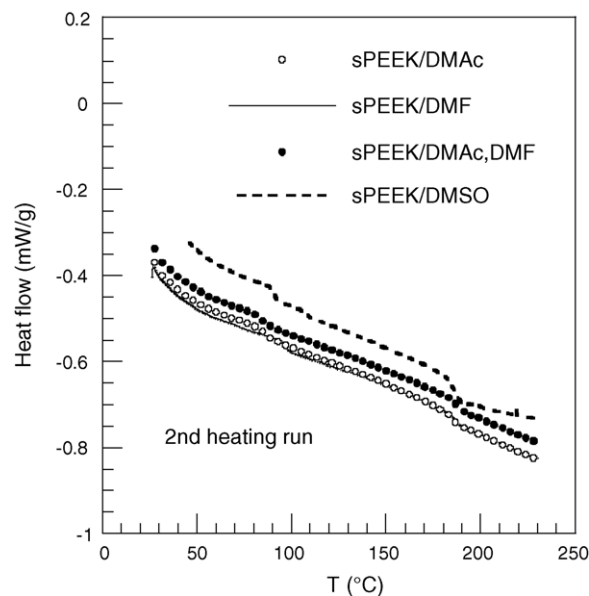


Fig. 7. DSC second heating for sPEEK membranes cast with different solvents.

[21] explained this transition as an “ionic crystallite transition” in ethylene-methacrylic acid copolymer ionomers related to an order–disorder transition inside ionic domains. Both annealing at room temperature and water absorption effects may largely affect this transition. On the other hand, Goddard, Grady and Cooper had some doubts on the “ionic cluster” transition. They showed by means of EXAFS studies that the endothermic peak has a complex structure and contains contributions from the energy change associated with water vaporization along with the energy change associated with water leaving the immediate coordination environment of ions [17].

For sulphonated PEEK, no detailed studies on such a thermal transition are present in literature. The endothermic peaks of Fig. 6 are centred between 75 and 80 °C with a hump centred at 120–130 °C. The second DSC scan (Fig. 7), collected following a cooling at  $-20\text{ °C min}^{-1}$ , showed no more evidence of this endothermic peak, even if a new anomalous transition has been found and will be discussed later. According to the order–disorder “theory” of Tadano et al. [21], annealing at room temperature of a polymer in a controlled humid environment or in an anhydrous atmosphere could in time lead to a recovery of the endothermic transition. Thus, the dry sPEEK/DMF, DMAc membrane was kept under a  $N_2$  flux at 22 °C immediately after the second heating scan. The result is reported in Fig. 8. As shown, there is a partial recovery of the endothermic peak.

In order to discern a little more the composition of this endothermic peak for sPEEK, we heated the room humidity equilibrated membranes up to 80 °C under nitrogen flux. After the annealing of membranes for 3 h at this temperature, the sample was cooled at  $-20\text{ °C min}^{-1}$  and a DSC scan ranging from 25 to 230 °C was immediately recorded. The resulting DSC trace is reported in Fig. 9. We can clearly see that the large endothermic peak is suppressed and the new transition appears at about 75 °C. The glass transition of material is visible at 188 °C and the melting of small semicrystallite entities is visible at 214 °C.

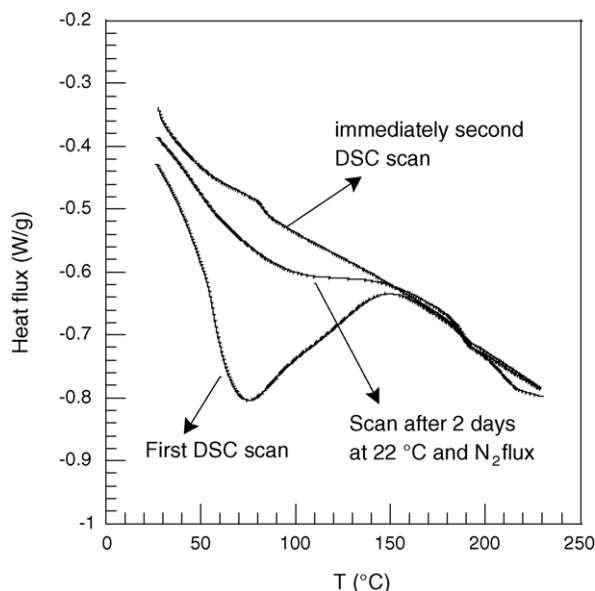


Fig. 8. Room temperature annealing experiment on a sPEEK DMAc/DMF membrane. Nitrogen was used as annealing atmosphere.

Furthermore a residual endothermic peak is still visible at 123 °C. From thermo gravimetric analysis it's evident that the water molecule loss process starts immediately from 30 °C and stops up to 150 °C, this endotherm can be associated to the evaporation of water molecules strongly incorporated in the membrane. The fact that this residual water vaporizes at  $T$  greater than 100 °C suggests the existence of a strong interaction between water molecules and sulphonic groups. Some authors [22,23] have reported that the overall strength of hydrogen bonding between water molecules is lower within Nafion than within pure water and it decreases with dehydration. At low hydration levels,  $\text{H}_2\text{O}-\text{H}_2\text{O}$  bonds are replaced with more energetic  $\text{SO}_3\text{H}-\text{H}_2\text{O}$  bonds. The fact that this interaction energy is greater

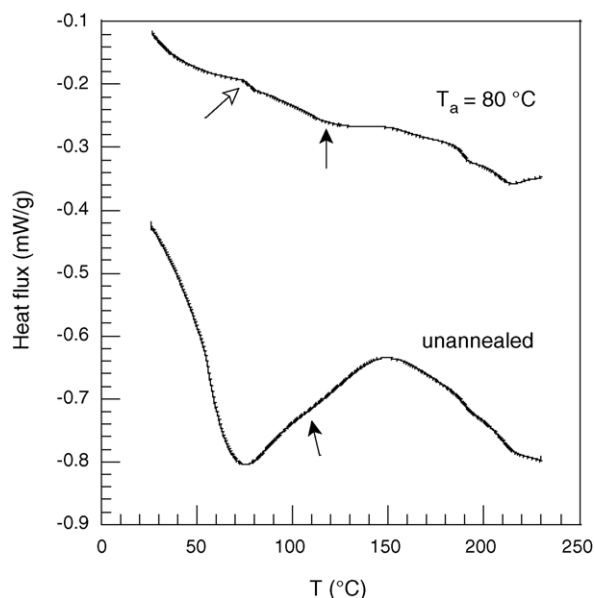


Fig. 9. Variation of DSC thermo gram for a sPEEK DMAc/DMF membrane annealed at 80 °C for 3 h under nitrogen atmosphere.

Table 2

Swelling properties and the  $n$  variation of membranes prepared by using a mixture of solvents at different temperatures

Membrane	$T$ (°C)	w.u.%
sPEEK DMAc/DMF	Room	31
	60	35
	80	53
	100	717

than that for pure water would account for the elevated temperature of water vaporization. Annealing for 3 h at 80 °C was also sufficient to vaporize loosely bound water molecules and to suppress the transition due to the ionic phase.

The main glass transition of the material,  $T_g$ , is masked in the first run by a higher temperature endothermic transition. After cooling and following a second DSC scan the two endothermic peaks are suppressed and the glass transition is clearly visible for all the membranes at around 185 °C. The value of this main  $T_g$  is equal for all the membranes obtained by casting from different solvents and corresponds to sPEEK/52  $T_g$  powder. Its position in the “masked state” during the first DSC run and in the second scan is almost the same. These two sets of evidence show that no solvent effect is found on the  $T_g$  of the material. Furthermore, a second transition appears in the second scan at about 70–80 °C. This transition was rarely reported in literature and it is found for all the four studied membranes in Fig. 4. To the present state of knowledge it is impossible to assign a meaning to this transition and we defined it as  $T_X$ . The position of  $T_X$  changes with the casting solvent used in the membrane preparation process. The large endothermic peak in the first scan probably hides this transition. However, its shape seems similar to a relaxation process that occurs immediately after the order–disorder transition as shown by the empty arrow in Fig. 9. It could be interesting to note, as the value of  $T_X$  is very close to the swelling critical temperature of about 80 °C. By swelling the sPEEK membrane in hot water above 80 °C, an irreversible swelling occurs as found by Kreuer [24] and as seen in Table 2, where water uptake data measured as a function of the swelling temperature for the sPEEK–DMAc/DMF membrane is reported.

Since the proton conductivity is directly related to the water content in the PEM such a temperature is also a critical temperature above which the cell performance has to improve. Therefore,  $T_X$  transition could be interestingly related to the occurrence of irreversible swelling and to a lesser resistance to hot water compared to other ionomers like Nafion.

During the DSC, the glass transition clearly visible in the first scan of powder samples now appears to be masked by a new endothermic transition that occurs at temperatures higher than 210 °C. This signal is small and sharp and is well defined in sPEEK/DMF and sPEEK/DMSO samples. In sPEEK/DMAc and DMAc/DMF this transition is less defined but still visible and centred at lower temperatures. In order to try to assign this transition, we could consider the used sulphonation method. Indeed, the direct sulphuric acid method cannot be used to produce random copolymers completely. This is

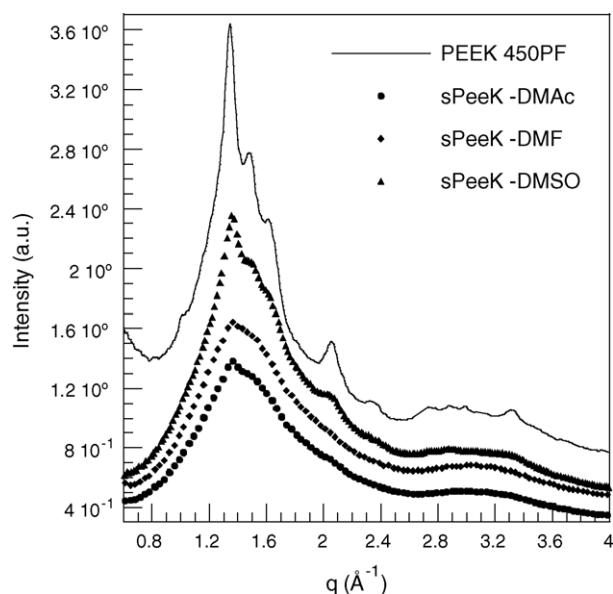


Fig. 10. WAXS spectra for Victrex PEEK 450PF as received and for the three sPEEK membranes.

because the sulphonation reaction begins immediately when the PEEK powder is immersed in concentrated  $\text{H}_2\text{SO}_4$ , in a heterogeneous environment prior to complete polymer dissolution. This leads to a block copolymer of ion rich and ion poor segments with some short segments of unsulphonated PEEK. Under certain conditions the short PEEK segments may form (or segments really poor in ion content) small crystallites. This hypothesis is confirmed by the WAXS analysis (Fig. 10). While the membranes obtained by casting from DMF and DMAc present no semicrystalline diffraction peaks, the sPEEK/DMSO membrane possesses a semicrystalline structure. The different chemical–physical properties of the DMSO casting solvent compared to DMF and DMAc, especially the dielectric constant (Table 3), may induce an aggregation of crystallisable segments during the casting process.

This may be a consequence of a lower solubility of the polymer at a high concentration in DMSO compared to DMF and DMAc. For comparison with as-received PEEK powder diffraction pattern, the unit cell of the semicrystalline entities in sPEEK/DMSO seems to be very close to that of bare PEEK. This evidence confirms the above hypothesis on the existence of short unsulphonated PEEK segments. Furthermore, there is the possibility to form a low portion of semicrystalline materials during the heating. Bailly et al. [18] showed that the melting of PEEK crystalline material occurs at lower temperatures as the sulphonation level increases.

Table 3  
Solvent chemical–physical constants

Solvents	Density	Boiling point (°C)	Dielectric constant (25 °C)	Dipole moment $\times 10^{30}$
DMAc	0.937	166	37.78	12.41
DMF	0.944	152.3	37	12.88
DMSO	1.101	189	46.68	13

Thus this high temperature endothermic transition can be related to the melting of small semicrystalline entities performed in the membranes during the casting process (sPEEK/DMSO) or during the dynamic annealing in the first DSC scan. The melting temperatures and the enthalpy of fusion are reported in Table 1.

Once the crystallites are molten at the end of the first heating run, during cooling no crystallization process is seen and in the second re-heating scan the melting peak is suppressed. This means that the melting of small semicrystalline entities is an irreversible process, i.e. during membrane preparation or alternatively in partially hydrated state (w.u.% at room humidity is about 10%) ions are solvated, crystallization can be induced and a melting peak is found. At the end of the first DSC scan, in the dry melted polymer state, physical cross-linking occurs and would prevent or inhibit crystallization. It could be interesting to note that in the membranes cast using DMAc, the melting peak is smaller and centred at lower temperatures.

In order to investigate the morphology of H-sPEEK proton conducting membranes, a preliminary SAXS analysis was performed. A large number of studies were carried out using SAXS and SANS to observe ion clustering in ionomers. For aliphatic backbone (flexible chain) ionomers, phase separation between aliphatic hydrophobic and hydrophilic ionic parts occurs at a nano-scale level forming ion clustering [25]. However, there are some ionomers like Udel polysulphone that do not present ionic clusters [26]. In the case of sulphonated polyaromatic membranes, Kreuer [4] reported ion clustering in 60% sPEEK similar to Nafion films, a weak ionomer peak at 2.6 nm is reported by Bailly for Na-sPEEK with DS above 30% and no ionomer peak is reported for H-sPEEK and H-sPEEK by Prado et al. [10].

In our preliminary SAXS data on 52% sPEEK membranes at room humidity (water volume fraction of about 0.10) no evidence of clear SAXS peaks for bare and recast Nafion membranes is seen like those well described in literature and found in one of our previous work. Only after 24 h swelling in water at room temperature a very weak and large peak can be found with a correlation distance of about 3 nm. The absence of a well defined matrix peak, related to self-aggregation of polymer chains in supramolecular structures can be pointed out by solution SAXS data. SAXS data for a 1% sPEEK DMAc solution proved the existence of random Gaussian coils without any aggregation behaviour. SAXS data recorded at ESRF BM26 beamline is shown in Fig. 11. The experimental data was fitted using theoretical equation for a Gaussian coil as calculated by Debye [27] with a radius of gyration of 3.5 nm. In contrast, for Nafion the formation of cylindrical aggregates in a solution also at low concentrations was reported and is related to the matrix peak found in SAXS experiments on Nafion membranes [28].

The membranes prepared with different casting solvents were tested in a electrochemical single cell. In Fig. 12 the comparison at 100 °C is reported, showing that the sPEEK membrane prepared using DMSO as a casting solvent has the poorest performance, due to its structural characteristics that inhibit the proton conductivity. This could be confirmation that the semicrystalline

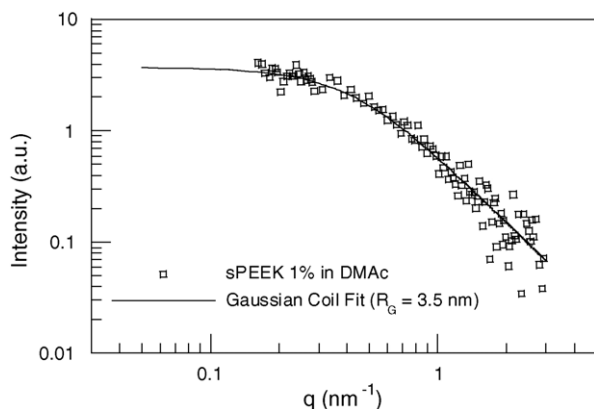


Fig. 11. SAXS data for a 1% DMAc solution of sPEEK. The solid line is the theoretical intensity for a random coil with radius of gyration of 3.5 nm (Debye equation).

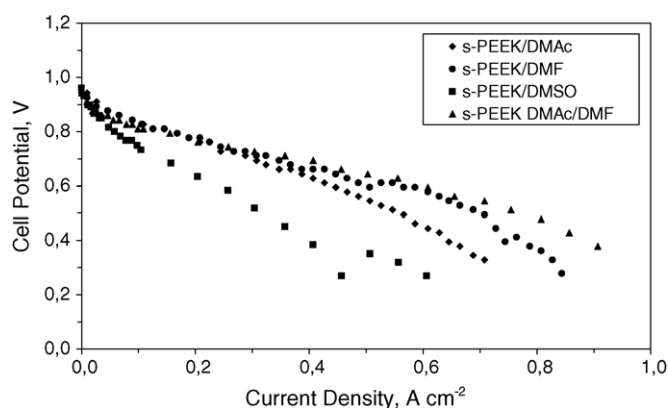


Fig. 12. Polarisation curves of sPEEK at 100 °C ( $P = 3$  absolute bar) in humidified  $H_2$ /air.

structure found for DMSO is attributable to short unsulphonated PEEK segments.

Moreover, sPEEK DMAc/DMF shows a better performance and it was tested at a higher temperature. Fig. 13 reports the power density at 130 °C compared to commercial N112, reaching a maximum power density of about  $400 \text{ mW cm}^{-2}$  at 0.5 V.

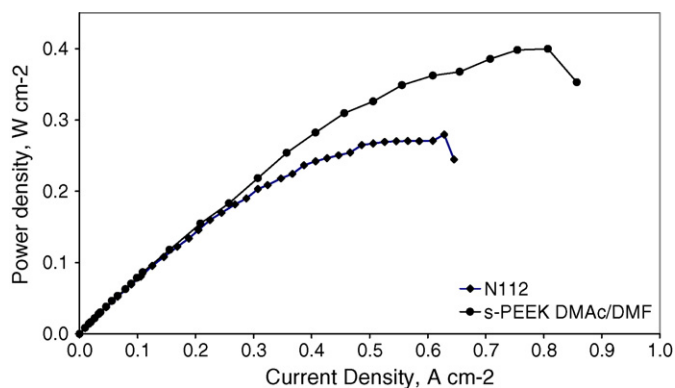


Fig. 13. Comparison of power density at 130 °C in  $H_2$ /air for sPEEK DMAc/DMF and N112.

#### 4. Conclusions

Direct sulphonation of PEEK polymer produces a copolymer with ion rich and ion poor regions. From thermo gravimetric analyses it was found that for both polymers and membranes,  $T_g$  and  $\Delta c_p$  values increase with the introduction of sulphonic groups and by increasing the DS. Membranes with a different sulphonation degree and different casting solvents were developed in order to investigate the chemical–physical and electrochemical properties.

WAXS and SAXS data suggests a very low crystalline structure with sulphonic groups randomly distributed inside the polymer matrix. Water is homogeneously located in the membrane and strongly coordinated to the sulphonic groups (non-freezable water). When DMSO is used as a solvent casting, it induces ion poor segment crystallisation due to the lower solubility of a polymer at high solvent concentrations, during the casting process. Membranes prepared by using DMAc and/or DMF can be considered to possess an amorphous structure, and maintain the chemical–physical properties unaltered compared to the sulphonated polymer powders.

All membranes were tested in humidified  $H_2$ /air single cell at 100 °C and the DMSO membrane has a poorer performance than the others. A sPEEK DMAc/DMF membrane was also tested at 130 °C, reaching a maximum power density of about  $400 \text{ mW cm}^{-2}$  at 0.5 V against a  $270 \text{ mW cm}^{-2}$  at the same potential for N112.

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