

# SPEEK/PPSU-based organic–inorganic membranes: proton conducting electrolytes in anhydrous and wet environments

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Received 9 June 2005; received in revised form 29 September 2005; accepted 2 December 2005

Available online 18 January 2006

## Abstract

A telechelic organic–inorganic polymer (SiPPSU) where  $-\text{SiPh}(\text{OH})_2$  groups are covalently linked to the polymeric chain of polyphenylsulfone (PPSU) was prepared and characterized. The polymer was sulfonated up to a degree of sulfonation (DS) equal to 2 (SiSPPSU), then used to prepare blends with sulfonated polyetheretherketone (SPEEK) having DS = 0.9 in 5 and 10 wt.% concentration. The synthesized polymers and the blends were characterized by ATR/FT-IR spectroscopy. Membranes were prepared with these materials and their proton conductivity was measured using electrochemical impedance spectroscopy (EIS). The formation of the blends substantially altered the physicochemical characteristics of SPEEK: the membrane prepared with the blend at the concentration of 5 wt.% exhibited high and stable conductivity values at 120 °C: both when dry ( $\sigma = 6.1 \times 10^{-3}$  S/cm) and wet conditions ( $\sigma = 6.4 \times 10^{-2}$  S/cm for a 50% water uptake), hence, being suitable for application as electrolyte in intermediate temperature polymer electrolyte membrane fuel cells (PEMFCs).

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**Keywords:** Proton exchange membrane; Blend; Organic–inorganic telechelic polymer; Polyetheretherketone (PEEK); Polyphenylsulfone (PPSU)

## 1. Introduction

The proton-conducting membrane is one of the key components of a fuel cell system. Because of their importance in fuel cells, sulfonated polymer electrolytes have received considerable attention over the last few years [1–3]. For successful performance of such materials it is necessary to obtain the correct balance between the high hydrolytic stability, characteristic of the organic backbone, and the hydrophilic behavior of the sulfonic side chain groups that ensure good proton conductivity [3].

Recently, it has been shown that membranes based on polyetheretherketone (PEEK) show considerable promise as PEEK possesses high thermal stability, good mechanical properties, low cost, and good conductivity when sulfonated [4–6]. Sulfonated polyaromatic membranes must have ion-exchange

capacities at least in the range 1.1–1.4 mequiv./g to meet the requirements needed for PEM [7]. At high degree of sulfonation (DS) sulfonated PEEK (SPEEK) shows large conductivity, but poor mechanical properties [6,7]. It is known that in polyaryletherketone-based systems, such as SPEEK, the absence of significant hydrophilic–hydrophobic separation results in very narrow and poorly connected water channels and large separation between the sulfonic acid groups. As a consequence, dehydration causes a strong decrease in conductivity and poor morphological stability [7,8].

Several approaches have been proposed to attain the correct balance between the hydrophilic and hydrophobic components: among them, the use of inorganic fillers for the development of composite systems, acid or basic doping, and association of polymers [2,9–13].

A different approach that we followed in previous work [14] was to create covalent bonds between the SPEEK polymeric backbone and  $-\text{Si}(\text{OH})_3$  moieties through the preparation of a Class II organic–inorganic hybrid (SiSPEEK). Organic–inorganic hybrids are investigated for a variety of applications, ranging from optics to electronics, to sensors and many

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others [15], since they offer the possibility to combine the properties of the two components in a unique material. The interaction at molecular level allows a much finer tailoring of the material final properties than that obtained in the formation of a composite system [16]. Homogeneous membranes were prepared using SiSPEEK, which did not show excessive water swelling despite the very high DS (0.9) and exhibited high and stable conductivity values ( $\sigma = 10^{-2}$  S/cm at room temperature) [14].

An interesting method to improve polymeric electrolyte performances is to prepare physically cross-linked membranes by blending ionomeric polymers with different mechanical properties [17–19]. The blending technique has the advantage of combining the positive features of each component while being very simple.

Better electrochemical characteristics are expected if one of the components causes a decrease of the average separation between acidic groups. The proximity of acidic functions might even lead to significant conductivity in anhydrous conditions, where a non-vehicular mechanism is considered to be responsible of proton transfer from a donor to an acceptor site, without the assistance of water molecules acting as carriers [20,21]. Several anhydrous electrolytes have been indeed investigated for applications in fuel cells operating at intermediate temperature (100–200 °C), most of them being based on composite materials or acid–base interactions of two components [22,23].

In this work we have combined in a physical blend SPEEK with elevated DS with a second component to improve its mechanical properties. The starting material chosen for the preparation of such second component was polyphenylsulfone (PPSU), a fully aromatic polymer with good thermal stability and oxidation resistance [24,25]. Several reasons were considered in choosing PPSU: its structural affinity with SPEEK, its solubility in organic solvents that allows to easily carry out functionalization reactions in homogeneous conditions, and the possibility to introduce sulfonic acid groups. Such substitution may add a contribution to the overall conductivity and avoid the inhomogeneity observed when blends between sulfonated and unsulfonated polymers are prepared: van der Waals and dipolar forces between the two polymers were in fact reported to be too weak to lead to blend components compatibility [26].

As for PEEK, the conductivity of PPSU is a function of the degree of sulfonation: conductivity values of about  $10^{-3}$  S/cm have been reported for SPPSU with DS = 0.7, while larger sulfonation degrees lead to water soluble species, preventing possible application in fuel cells [2,27,28].

To obtain proton-conducting membranes with proper mechanical and electrical properties we synthesized a silylated telechelic hybrid polymer by introducing an inorganic network covalently linked to the organic backbone of highly sulfonated PPSU and blend it with SPEEK having DS = 0.9.

## 2. Experimental section

### 2.1. Materials

Polyetheretherketone (Victrex, PEEK, 450 P, MW = 38,300) and polyphenylsulfone (Solvay, PPSU, MW = 46,173) were

used as received. Anhydrous THF was prepared according to literature procedures [30]. All other chemicals (Aldrich) were reagent grade and were used as received.

Sulfonated PEEK was prepared as previously reported [14]. The degree of sulfonation (DS) was evaluated both by  $^1\text{H}$  NMR and by titration, according to published procedures [31]. Both methods gave according results, indicating a DS = 0.9.

### 2.1.1. Synthesis of SiSPPSU: silylation and sulfonation of PPSU

PPSU (5 g, 12.5 mequiv.) was added, in a nitrogen atmosphere, to anhydrous THF (250 mL). The solution was stirred at room temperature for 1 h, then cooled to  $-60^\circ\text{C}$  and kept at this temperature for 1.5 h. An excess of BuLi (2.5 M in hexane, 25 mL, 62.5 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 10 mL, 62.5 mmol) were then added, and the solution was stirred for 2 h at  $-60^\circ\text{C}$ .  $\text{PhSiCl}_3$  (97%, 0.1 mL, 0.625 mmol) was then added and the solution was slowly warmed to room temperature, and then kept at reflux for 2 h. After cooling to RT, the precipitate formed was filtered and washed with water until no chlorides were detected. The product (SiPPSU) was added to concentrated  $\text{H}_2\text{SO}_4$  (500 mL) and the mixture was kept stirring at  $50^\circ\text{C}$  for 5 h, then was then poured in 2 L of ice-cold water obtaining a precipitate that was filtered, washed with water to neutral pH, and dried under vacuum for 5 h.

The degree of sulfonation was determined by Elemental Analysis (C and S content) and was DS = 2. The same method was used to evaluate the Si content, which was  $\% \text{Si} = 0.25 \pm 0.05$  (reproducible over three samples).

### 2.2. Preparation of membranes

Membranes made of SPEEK and SPEEK/SiSPPSU were prepared by solution casting. In a typical procedure, SPEEK (250 mg) was first dissolved in DMA (20 mL) and the appropriate weight of SiSPPSU was then added to the solution. The resulting mixture was stirred for 4 h. The solution was then evaporated to 5 mL, then cast onto a Teflon plate and heated to dryness. After cooling to room temperature, the resulting membranes were peeled off and dried at  $120^\circ\text{C}$  for 10 h, then further dried under vacuum at  $80^\circ\text{C}$  for 8 h for complete solvent removal.

Membranes containing 5 wt.% (sample B1) and 10 wt.% (sample B2) SiSPPSU were prepared, together with a SPEEK reference membrane (sample B0). The thickness of the membranes was about 150  $\mu\text{m}$ . The membranes for wet measurements were activated in 5 M  $\text{H}_2\text{SO}_4$  for 1 h at room temperature, then rinsed with deionized water.

### 2.3. Water uptake

Activated SPEEK and SPEEK/SiSPPSU membranes were dried in vacuum at  $100^\circ\text{C}$ . Disks with a diameter of 6 mm and a thickness of 150  $\mu\text{m}$  were cut from the membranes and weighed. The disks were then soaked in water at room temperature for 1 h and weighed after blotting with absorbent paper. The weight

gain of absorbed water was calculated referring to the weight of the dry sample  $(W_{\text{wet}}/W_{\text{dry}} - 1) \times 100$ .

#### 2.4. Measurements

ATR/FT-IR spectra were collected in the range 4000–550  $\text{cm}^{-1}$ , on a Nicolet 870 E.S.P. with a Golden Gate MK2 Diamond Specac cell. Spectra were recorded positioning the samples on cell platform operating at room temperature (32 scans, 2  $\text{cm}^{-1}$  resolution).

Electrochemical impedance spectroscopy (EIS) measurements were used to evaluate proton conductivity, using a Solartron 1260 coupled with a dielectric interface (Solartron 1296) in the frequency range 10 MHz–10 Hz. The amplitude of the applied voltage signal was 100 mV. The spectra were analyzed using the Zview<sup>®</sup> software. The membranes were placed in a test cell, where they were clamped between two platinum electrodes with a permanent pressure. Membranes for dry measurements were then kept at 25 °C for 16 h and at 150 °C for 16 h prior to electrochemical measurements. The conductivity  $\sigma$  of the samples in the transverse direction was calculated from the impedance data, using the relation  $\sigma = d/RS$ , where  $d$  and  $S$  are the thickness and area of the sample, and the resistance  $R$  was derived from the high frequency intercept with the real axis on a complex impedance plane plot. Values of  $d$  and  $S$  were determined after the measurements. The EIS measurements were performed in air, at ambient RH, in the 20–120 °C temperature range.

### 3. Results and discussion

The species chosen to prepare a blend with highly sulfonated SPEEK was a silylated polymer, where inorganic moieties are covalently bound to the organic backbone of PPSU.

At variance with what previously reported for the preparation of SPEEK based organic–inorganic hybrid [14], in the case of PPSU the formation of C–Si bonds could be carried out as

the first synthetic step, since the polymer is soluble in THF, the solvent of choice for the lithiation reaction. The introduction of –SiPh(OH)<sub>2</sub> residues covalently bound to PPSU was, in fact, achieved by reacting it with butyllithium at low temperature and subsequent reaction with PhSiCl<sub>3</sub> followed by hydrolysis. Being a metalation reaction followed by electrophilic substitution, silylation is expected to occur in the *ortho* position of the aryl sulfone. Post-functionalization was then carried out in concentrated sulfuric acid to bind –SO<sub>3</sub>H groups (DS = 2) and add conducting properties to the polymer.

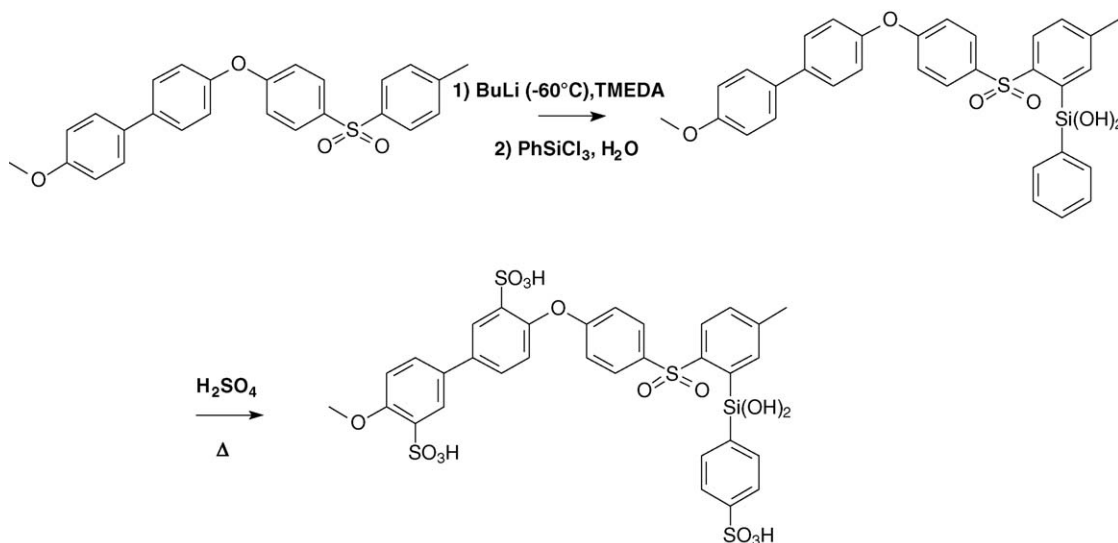
Sulfonation is known to occur at the position shown in Scheme 1, but further sulfonation on the silicon bound phenyl ring external to the polymeric chain cannot be excluded.

The product, SiSPPSU, was characterized by elemental analysis, which showed the presence of 0.25% Si. This value corresponds to the stoichiometric ratio used for the synthesis, 1:0.05 monomeric unit:silicon, demonstrating the high efficiency of the preparative procedure.

The very low solubility and poor plastic properties of SiSPPSU in the solvents conventionally used for membrane casting (DMSO, DMF, DMA, NMP, etc.) prevented its electrochemical characterization. Despite the high DS it is, however, insoluble in water. To achieve the required mechanical properties it was then mixed with high DS SPEEK. The two polymers have a similar chemical structure, so that both  $\pi$ – $\pi$  and electrostatic interactions are expected to occur in the blend formation easing homogeneous dispersion.

Membranes containing 5 and 10 wt.% SiSPPSU in SPEEK (samples B1 and B2, respectively) were successfully cast from DMA together with a SPEEK reference membrane (sample B0). Miscibility of the two polymers was indicated by the homogeneity of the casting solutions and by the transparency of the resulting membranes.

ATR/FT-IR spectroscopy was used to characterize the synthesized polymers and membranes. Fig. 1 shows the ATR/FT-IR spectra of PPSU, SiPPSU, and SiSPPSU (traces a, b and c, respectively). All spectra are dominated by PPSU absorptions.



Scheme 1.

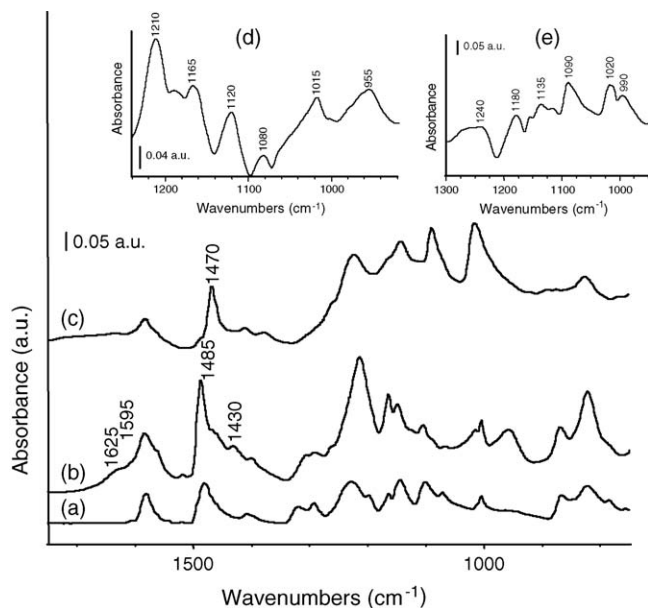


Fig. 1. ATR/FT-IR spectra of (a) PPSU, (b) SiPPSU, (c) SiSPPSU, (d) and (e) subtraction results with (d) = (b) – 1(a) and (e) = (c) – 1(b).

Subtraction of the spectrum of PPSU from that of SiPPSU is shown Fig. 1d to highlight the signals characteristic of silicon-phenyl bonds. Numerous studies directed towards the identification of frequencies apt to characterize the silicon-phenyl bond have been reported [32–34]. Most authors concentrated their attention on bands at 1430 and 1100  $\text{cm}^{-1}$ . However, the first absorption is atypical normal band of mono-substituted aromatics, while the 1100  $\text{cm}^{-1}$  band is the most sensitive to silicon substitution [35]. Such band can be clearly observed in the subtraction spectra (Fig. 1d) at 1120  $\text{cm}^{-1}$ . The absorption is attributed to an in-plane deformation of the ring with some contribution from the Si–C stretch [35]. Furthermore, in the spectrum of SiPPSU (Fig. 1b), the presence of two components, 1625 and 1595  $\text{cm}^{-1}$ , typical of arylsilicon compounds, confirmed the occurrence of silylation as shown in Scheme 1. The latter absorption is shifted at higher wavenumbers, with respect to the values reported for mono-substituted arylsilicon species, indicating of the presence of di-substituted and unsymmetrically tri-substituted rings [36]. The presence of 1:4- and 1:2:4-substituted phenyl rings was also demonstrated by the occurrence in the subtraction spectrum (Fig. 1d), of absorptions at 1210 and 1080  $\text{cm}^{-1}$ , together with a weak broad signal centered at 1015  $\text{cm}^{-1}$  [35]. Although rather weak, the additional band at 1165  $\text{cm}^{-1}$  supports the presence of 1:2:4-substituted species. The band related to vibrations of the Si–OH groups is observed at about 950  $\text{cm}^{-1}$  [32].

Fig. 1e shows the spectrum obtained subtracting the spectrum of SiPPSU from that of SiSPPSU. Bands due to aromatic sulfonic groups are clearly observed at 1020  $\text{cm}^{-1}$  ( $\nu_{\text{sym}} -\text{SO}_3\text{H}$ ), 1180  $\text{cm}^{-1}$  ( $\nu_{\text{as}} -\text{SO}_3\text{H}$ ), and 990  $\text{cm}^{-1}$  ( $\delta -\text{SO}_3\text{H}$ ) [37]. New signals, characteristics of 1:2:4-substituted aromatic compounds, are present at 1240, 1090 and 1135  $\text{cm}^{-1}$ . The shift of the 1479  $\text{cm}^{-1}$  signal of SiPPSU, typical of ring stretching vibra-

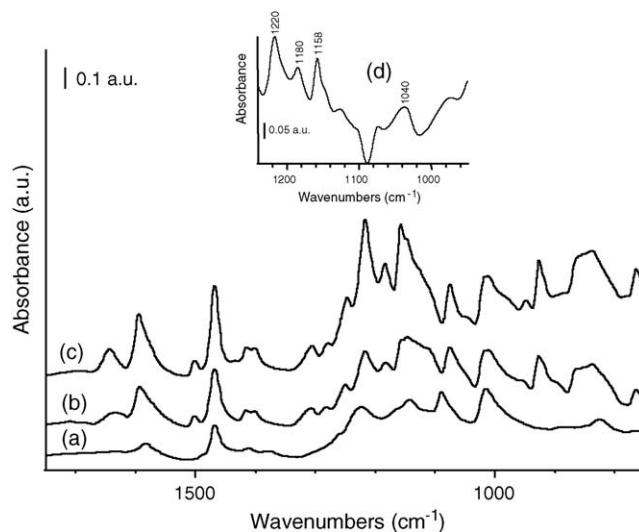


Fig. 2. ATR/FT-IR spectra of (a) SiSPPSU, (b) SPEEK, (c) B1 and (d) subtraction result (d) = (c) – 1(b).

tions of *para*-substituted compounds, to 1485  $\text{cm}^{-1}$  further supports the occurring of sulfonation as shown in Scheme 1.

Fig. 2 shows the ATR/FT-IR spectrum of membrane B1 (Fig. 2c) compared with the spectra of SPEEK (Fig. 2b) and SiSPPSU (Fig. 2a). In the difference spectrum, shown in Fig. 2d, the presence only of the asymmetrical stretching vibration of the sulfonic acid group at 1180  $\text{cm}^{-1}$ , together with the bands at 1158 and 1040  $\text{cm}^{-1}$ , due to the PPSU– $\text{SO}_2$  groups and absent in the spectra of the parent compounds, is indicative of interaction the two blend components, probably via H-bonding. The presence of the 1220  $\text{cm}^{-1}$  absorption, characteristic of 1:2:4-trisubstituted benzene rings, confirmed the occurring of  $\pi$ – $\pi$  interactions between the two polymers.

The electrochemical characterization of samples B0, B1 and B2 was carried out by EIS. Fig. 3 shows the Arrhenius plots for the three dry samples and for wet membrane B1. All systems showed a linear Arrhenius behavior between 20 and 120  $^{\circ}\text{C}$ .

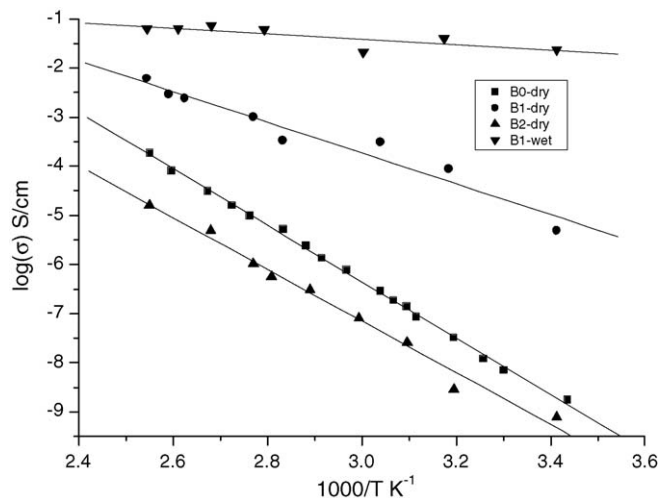


Fig. 3. Arrhenius plots of dry B0, B1, B2, and wet B1 samples.

A comparison of the data relative to the three dry membranes showed that while the formation of the 5 wt.% blend caused an increase in conductivity, opposite behavior was observed for sample B2. Even in the absence of water, which is known to assist proton conduction in sulfonated polymers, conductivity as high as  $6.1 \times 10^{-3}$  S/cm was obtained for sample B1 at  $T = 120^\circ\text{C}$ , over one order of magnitude higher than the value recorded for pure SPEEK at the same temperature. Data were reproducible over temperature cycles, and no weight loss was observed for all the dry membranes after the electrochemical measurements, thus, indicating the absence of degradation processes.

The larger conductivity of sample B1 is consistent with the much lower value of the activation energy determined for the proton transfer process. The  $E_a$  values, calculated from linear fit of the Arrhenius plots relative to the three samples, resulted in fact to be similar for samples B0 and B2 (1.14 and 1.01 eV, respectively), while a much lower value was determined for sample B1 ( $E_a = 0.62$  eV). In comparing activation energy values for different polymeric electrolytes, different effects must be taken into account, most important being the relative acidity of sulfonic acid groups, their number, and proximity [23,38]. Given the structural similarity of SPEEK and SiSPPSU, the difference in acid strength can be considered negligible. The differences in the nominal ion content in the three samples are also negligible: the number of sulfonic groups per mg of electrolyte (calculated considering the degree of sulfonation of the two polymers and their stoichiometric ratio in the blends) is  $2.25 \times 10^{-3}$ ,  $2.31 \times 10^{-3}$ , and  $2.37 \times 10^{-3}$  for B0, B1 and B2, respectively.

The observed differences in activation energy and conductivity for the three samples may thus be ascribed to the proximity of sulfonic groups available for proton transfer. In anhydrous conditions proton transfer occurs via  $\text{H}^+$  hopping from one sulfonic group to another, so that all the  $-\text{SO}_3\text{H}$  substituents appear to contribute to conductivity in sample B1. Up to the limit of 5 wt.% concentration, the large number of  $-\text{SO}_3\text{H}$  groups present in DS = 2 SiSPPSU positively contributes to SPEEK conductivity making available at close distance extra sites for proton hopping. Above such concentration, the interactions between sulfonic groups become predominant and negatively affect electrochemical performance.

A decrease in the differences between the three samples was observed with increasing temperature, probably because of the higher mobility of the polymer chain.

We have then studied the electrochemical performances of wet membranes: the water uptake procedure is a treatment harsher than the one that the electrolytes undergo in FC operating conditions, and thus it might represent a preliminary selection factor for the utilization of the materials [6].

Numerous studies have been reported in the literature on the physico-chemical properties of SPEEK: data obtained by different authors are not always coherent but it appears quite clear that membrane preparation and activation procedures play an important role in the electrical performance [16]. Water uptake is another important parameter, conduction being enhanced by the presence of water. However, excessive water uptake may lead to excessive swelling and mechanical degradation. Careful control of water uptake is critical for reducing swelling and

degradation of the mechanical properties. Treating SPEEK with water for over 1 h at RT caused dissolution of the sample. This observation set the limiting condition for water treatments. The swelling in water of the blends was thus determined by measuring the weight difference of the swollen and dry membranes after immersion in water for 1 h at RT.

The formation of the blends modified the water absorption characteristics of SPEEK. The number of mol of water absorbed per mol of acid group ( $\lambda$ ) was thus determined and resulted in  $\lambda = 17$  for sample B0,  $\lambda = 12$  for B1,  $\lambda = 5$  for B2. The very low water uptake of sample B2 supports the hypothesis of the segregation of sulfonic groups in this blend and the electrochemical performance of the hydrated membrane resulted almost identical to that of the dry sample.

The hydrated B1 membrane showed high and stable conductivity values up to  $6.4 \times 10^{-2}$  S/cm at  $120^\circ\text{C}$ , thus, demonstrating that the material is suitable to be used as a polymeric electrolyte in PEMFCs operating at intermediate temperatures.

#### 4. Conclusions

To select proper materials as electrolytes for PEMFC applications, solubility and conducting properties must be modulated and this can be done with the preparation of polymer blends. In this work an organic–inorganic telechelic polymer (SiSPPSU) where  $-\text{SiPh}(\text{OH})_2$  moieties are covalently bound to the main chain of highly sulfonated (DS = 2) polyphenylsulfone has been synthesized and characterized and used to prepare blends with SPEEK having DS = 0.9.

The formation of the blend led to membranes with controlled water uptake, negligible swelling and high conductivity values even when dry up to  $120^\circ\text{C}$ . At the composition SiSPPSU:SPEEK = 5:95 w/w, a synergic effect has been observed of the mechanical properties of the SiSPPSU and the conducting properties of SPEEK because of the very high density of sulfonic groups that ease proton transfer.

#### Acknowledgements

Thanks are due to Ms. Cadia D'Ottavi for her valuable technical assistance. This work has been supported by MIUR (FISR Project Development of composite protonic membranes and innovative electrode configuration for PEFCs).

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