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Synthesis and properties of sulfonated poly(ether ketone ether sulfone) (S-PEKES) via bisphenol S: effect of sulfonation

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Abstract Poly(ether ketone ether sulfone) (PEKES) was synthesized by nucleophilic aromatic substitution polycondensation between bisphenol S and 4,4′-difluorobenzophenone (System A), and between bisphenol S and 4,4′-dichlorobenzophenone (System B). Properties of both post-sulfonated polymers are compared with a commercial PEEK 150XF from Victrex®. The sulfonated polymer samples were characterized by FTIR, ^{1}H-NMR, TGA, and LCR meter, and the degree of sulfonation (DS) was determined. Advantages of the synthesized PEKES is the better solubility of PEKES in H_2SO_4 relative to PEEK 150XF which results in higher sulfonation degrees, and the S-PEKESs backbones contain the aromatic rings, the carbonyl groups (–C=O) and the sulfone groups (–SO_2–), which promote the chain stiffness and thermal stability. The ion exchange capacity (IEC), the water uptake (%), the dielectric permittivity (ε'), and the electrical conductivity increase monotonically with increasing DS.

Keywords Sulfonated poly(ether ketone ether sulfone) · Proton exchange membrane · Degree of sulfonation

Introduction

A proton exchange membrane (PEM) is an electrolyte used in both polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) which allows protons to conduct from the anode to the cathode. It is expected to provide a barrier against electrons, methanol, and gas transporting through the membrane. The currently used PEM is Nafion® which has been produced by Dupont

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since 1960s. It is a perfluorinated polymer with sulfonic acid groups as pendant groups. Nafion has excellent ionic properties, the most important advantage of Nafion[®] is its excellent proton conductivity in the fully hydrated condition. Furthermore, it has good physical, chemical, and mechanical stability. However, the main drawbacks are its high cost, high methanol permeability, and loss of proton conductivity at high temperature [1]. Ideally, PEMs are expected to possess certain characteristics: high proton conductivity, low water and methanol permeability, excellent mechanical property, good thermal and chemical stabilities, high resistance to dehydration, low swelling, high resistance to oxidation, reduction and hydrolysis, and low cost. Furthermore, the polymeric membrane must be an electron insulator to prevent the electron leakage, which leads to low efficiency.

An ultimate aim in PEM development is to find novel materials as alternatives to Nafion[®] that are low cost and can operate at a higher temperature. Presently, existing PEM materials are, for example, Nafion[®] 117 (proton conductivity 90–120 mS cm^{-1} at 80 °C and 34–100% RH), Nafion[®] 115 (41 mS cm^{-1} at 25 °C), sulfonated poly(ether ether ketone) (SPEEK) (0.9 mS cm^{-1} at 20 °C), sulfonated poly(benzimidazole) (SPBI) (10–40 mS cm^{-1} at 130–180 °C), sulfonated poly-(phosphazene) (40 mS cm^{-1} at 25 °C), AMPS asymmetric-based acrylic (42 mS cm^{-1} at 90 °C), poly(vinylidene fluoride) (PVDF) + styrene membrane (resistance 0.454 Ω cm^2), PVDF + SiO$_2$ or SiO$_2$ gel (70 mS cm^{-1} (SiO$_2$) and 200 mS cm^{-1} (gel) at 25 °C), etc. [2].

The poly(arylene ether ketone) family is of particular interest because it is an engineering thermoplastic with excellent thermal and chemical stability, high mechanical strength, good insulating properties, and a relatively low cost compared to Nafion[®]. The poly(ether ketone ether sulfone) (PEKES) and poly(ether ether ketone) (PEEK) are in the poly(arylene ether ketone) family. The sulfonated poly(ether ether ketone) (S-PEEK) has good thermal stability and appropriate proton conductivity at a high degree of sulfonation (DS). Several articles have reported the sulfonation of PEEKs and their properties [3–15]. Synthesized derivatives of poly(ether ketone ether sulfone) have been reported using various starting monomers [16]. S-PEEK-WC were prepared at various DS to compare with the properties of Nafion 117. The proton conductivity strongly increased with DS and temperature and reached 2.5×10^{-2} S cm^{-1} at 115 °C and 100% RH for DS = 0.82. The permeability toward water and methanol vapors of S-PEEK-WC membranes were lower than those of Nafion 117 [17]. Then, S-PEEK-WC was mixed with Zr(SPP) to improve the proton conductivity and the mechanical properties [18]. The tungstophosphoric acid, silicotungstic acid, and phosphomolybdic acid were used as additives in the composite S-PEEK-WC membranes [19].

In this work, two synthesized S-PEKESs were investigated (System A and System B). System A and System B contain 4,4′-difluorobenzophenone and 4,4′-dichlorobenzophenone as the starting monomers, respectively. The synthesis and properties of System B have not been reported so far. In addition, the introduction of sulfone group (–SO$_2$–) into the polymer backbone leads to better solubility of PEKES in H$_2$SO$_4$ relative to that of PEEK 150XF, which results in higher sulfonation degrees. Furthermore, the S-PEKESs backbones contain the aromatic rings, the carbonyl groups (–C=O) and the sulfone groups (–SO$_2$–), which

promote the chain stiffness and thermal stability. The DS was varied by the reaction time. The effect of DS on various properties was investigated and reported here. The synthesized polymers were characterized by Fourier transform infrared spectroscopy (FTIR) and [1]H-Nuclear magnetic resonance spectroscopy (^{1}H-NMR) to determine their chemical characteristics, by TGA to identify the thermal properties, and by an LCR meter to determine the dielectric permittivity to investigate the effect of the DS. Furthermore, the water uptake and the ion exchange capacity (IEC) and the electrical conductivity were investigated and reported here.

Experimental

Starting materials

Bisphenol S or 4,4′-sulfonyldiphenol, 4,4′-dichlorobenzophenone, and 4,4′-difluorobenzophenone (98–99%, Aldrich) were used as the monomers. Concentrated sulfuric acid (Merck, 98 wt%), sodium chloride (Univar, 99.9%), and sodium hydroxide (Univar, 97%) were used as received. Potassium carbonate (Riedel-de-Haen, 98–100%) and dimethyl sulfoxide (Riedel-de-Haen, 99.5%), and toluene (Fisher-Scientific 99.99%) were used as received. PEEK 150XF was purchased from Victrex®.
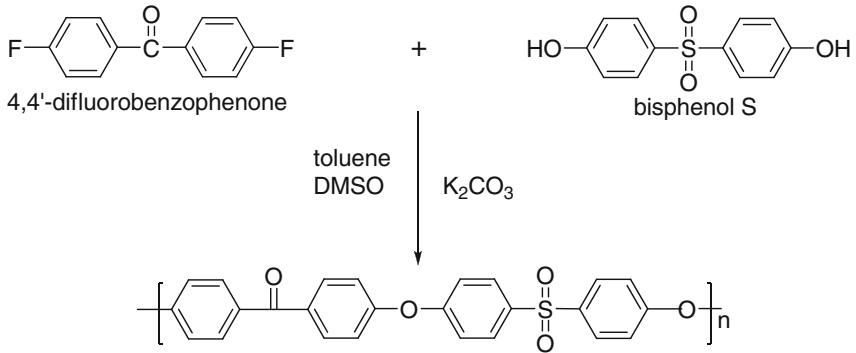
Synthesis of poly(ether ketone ether sulfone)

As shown in Scheme 1, the poly(ether ketone ether sulfone)s were synthesized via the nucleophilic aromatic substitution reaction by using these monomers: 4,4′-difluorobenzophenone (System A), 4,4′-dichlorobezophenone (System B), and bisphenol S [20]. The amount of each monomer was fixed at 20 mmol and mixed with 24 mmol potassium carbonate in 40 mL DMSO and 45 mL toluene, in a 250-mL three necked round bottom flask equipped with a Dean-Stark trap, a reflux condenser, a nitrogen inlet, and a thermostat. The mixture was refluxed for 3 h at 150 °C, and then the excess toluene was distilled off. Toluene was used to eliminate the water which was a product in the reaction, and the solution was heated at 175 °C for 20 h. The reaction mixture was then cooled to room temperature and poured into a mixture of methanol and distilled water (ratio 1:1). The crude product was then washed with water to remove any inorganic salt. The polymer was filtered and dried in a vacuum oven at 80 °C for 48 h [16]. The chemical structure of PEEK 150XF (System C) is shown in Fig. 1.
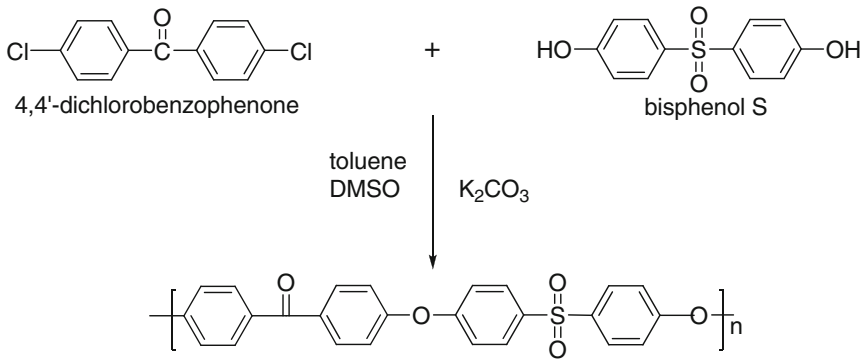
Post-sulfonation reaction

The synthesized PEKES and PEEK 150XF powder were dried in a vacuum oven at 100 °C overnight. Then, 5.0 g of the polymer was dissolved in 50 mL concentrated sulfuric acid (98%), which was kept under a molecular sieve 4 A for 24 h, and vigorously stirred at 25 ± 2 °C for durations of 12, 24, 36, 48, 60, 72, and 84 h. Then, the solution was gradually precipitated into ice-cold water under mechanical

System A

4,4'-difluorobenzophenone   +   bisphenol S

toluene
DMSO K_2CO_3

System B

4,4'-dichlorobenzophenone   +   bisphenol S

toluene
DMSO K_2CO_3

Scheme 1 Condensation polymerization of the PEKES

Fig. 1 Chemical structure of PEEK 150XF from Victrex®
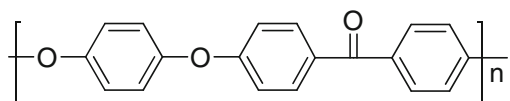
stirring. The polymer suspension was left overnight. Then, the precipitate was filtered, washed several times with distilled water until neutral a pH was obtained, and dried under vacuum at 60 °C for 24 h [3]. The chemical structures of S-PEKES-A, B, and S-PEEK 150XF are shown in Scheme 2 and Fig. 2.

Membrane preparation

Membranes were prepared by dissolving 1.0 g of polymer in 30 mL dimethyl sulfoxide (DMSO) with vigorous stirring for 12–18 h until the polymer solutions were homogeneous. Each solutions was cast on a petridish; it was kept at room temperature for 12 h, followed by drying at 80 °C for 2 days under a vacuum.

Scheme 2 Post-sulfonation
of PEKES Systems A and B
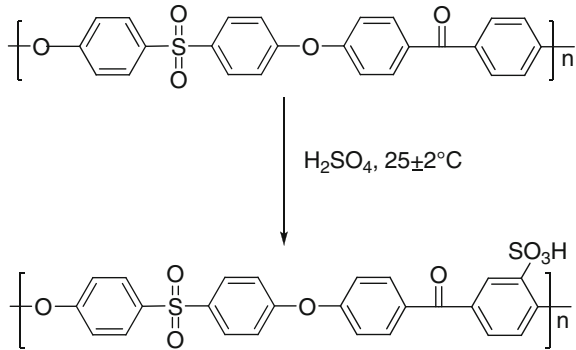
Fig. 2 Post-sulfonation
of PEEK 150XF
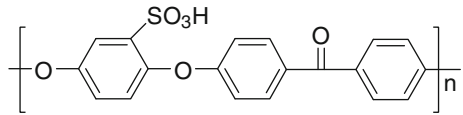
Polymer characterization

Fourier transform infrared spectroscopy

The FTIR spectra of the polymers were recorded using a Thermo Nicolet/Nexus 670 FTIR spectrometer using spectronic-grade KBr as the background. The operation conditions were: absorption mode with 32 scans at a resolution of ± 4 cm^{-1} covering the wavenumber range of 4,000–400 cm^{-1}.

^{1}H-Nuclear magnetic resonance spectroscopy

The ^{1}H-NMR spectra of the polymer were obtained from a nuclear magnetic resonance spectrometer (JNM-A500) using CD_3COCD_3 as the solvent. Tetramethylsilane (TMS) was used as the internal standard.

Thermal behavior

A thermogravimetric analyzer (TGA) (PerkinElmer/TGA7) was used to investigate the thermal stability of the polymers. Between 5.0 and 10.0 mg samples were heated from 50–800 °C at a rate of 10 °C/min under N_2 atmosphere [14].

Degree of sulfonation by titration

DS represents the number of sulfonic acid groups per repeating unit in the polymer chain, titration method was used to quantitatively determine sulfonic acid concentration in the polymer. Before each titration, the polymer membrane was acidified with an excess 0.1 M HCl solution at 80 °C for 6 h.Then the polymer was dissolved in DMF, the obtained solution was titrated with 0.01 M NaOH, the

titrations were repeated three times and the DS was obtained [14]. The DS values of all polymers will be compared with that of Nafion® 117 membrane.

Ion exchange capacity by titration

The IEC indicates the number of milliequivalents of ions in 1 g of dry polymer (meq./g). The membrane was acidified with an excess 0.1 M HCl solution at 80 °C. Then it was dried and a known amount of this dry polymer, around 0.4–1.0 g, was immersed in 100 mL of a 1.0 M NaCl solution at 50–60 °C for 24 h with continuous stirring. Thus, the proton released due to the exchange reaction with sodium ions were titrated against 0.01 M NaOH, using phenolphthalein as the indicator, and the IEC was obtained [21]. The titrations were repeated three times to obtain consistent IEC values. The IEC was determined from

$$\text{IEC (meq./g)} = \frac{X \times N_{\text{NaOH}}}{\text{weight (polymer)}}, \tag{1}$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH. Then, IEC of all polymers are compared with that of Nafion® 117 membrane.

Water uptake

The post-sulfonated polymer membranes were dried in an oven at 100 °C for 24 h. The polymer membranes were soaked in de-ionized water at 25 °C for 24 h, removed from the water, quickly dry-wiped by an absorbent paper to remove any surface moisture, and immediately weighed to determine their wet masses (M_{wet}). The polymer membranes were then dried at 100 °C for 24 h and weighed again to determine their dry masses (M_{dry}). The membranes with same DS were prepared and the water uptake were measured in triplicate. Then, the water uptake values of all polymers are to be compared with that of Nafion® 117 membrane. The water uptake was calculated by using the following equation [22]:

$$\text{Water uptake (\%)} = \frac{(M_{\text{wet}} - M_{\text{dry}})}{M_{\text{dry}}} \times 100\%, \tag{2}$$

Dielectric permittivity (ε')

The dielectric permittivity (ε') values were measured by an LCR meter (HP, model 4284A) connected to a rheometer (Rheometric Scientific, ARES) with a 25 mm parallel plate fixture. The thickness of the specimens was typically 1 mm and the diameter was 25 mm. The top and bottom side of the specimens were coated with a silver adhesive to improve the electrical contact between the specimens and the electrodes. The measurements were carried at 300 K (27 °C). The AC voltage applied was 1 V. The dielectric permittivity was measured at frequencies between 20 and 800,000 Hz.

The dielectric constant (ε) is calculated from the ratio between the dielectric permittivities of the material (ε') and the free space (ε_0), which is 8.86 pF/m [23].

Electrical conductivity (σ'_{DC})

Electrical conductivities were measured, according to the previous work presented elsewhere [24], by a meter which consists of two-probes making contact on the surfaces of pellet samples. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage and the resultant current in the linear Ohmic regime were converted to the electrical conductivity using equation as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t}, \tag{3}$$

where σ is specific conductivity (S/cm), ρ is specific resistivity (Ω cm), R_s is sheet resistance (Ω/sq), t is the thickness of sample pellet (cm), V is the applied voltage (voltage drop) (V), I is the measured current (A), and K is the geometric correction factor of the two-point probe meter.

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials, silicon wafer chips (SiO_2), where specific resistivity values were known. In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated as follows:

$$K = \frac{\rho}{Rt} = \frac{I\rho}{Vt}, \tag{4}$$

where K is the geometric correction factor, ρ is the known resistivity of standard silicon wafer (Ω cm), t is the film thickness (cm), R is the film resistance (Ω), and I is the measured current (A).

Results and discussion

Synthesis of sulfonated poly(ether ketone ether sulfone) (S-PEKES)

The FTIR characteristic peaks of poly(ether ketone ether sulfone) of Systems A and B, identifying their functional groups, are shown in Figs. 3, 4, respectively. The peaks at around 1,585 and 1,655 cm^{-1} represent the stretching of the carbonyl group [4]. The peaks at 1,242 and 1,149 cm^{-1} represent the stretching of the sulfone group [4].

Figures 3, 4 show the FTIR spectra of PEKES-A, post-S-PEKES-A, PEKES-B, and post-S-PEKES-B, respectively; the absorption band at 1,243 cm^{-1} can be assigned to the asymmetric stretching of the sulfone group, the bands at 1,013, 1,070, and 1,030 cm^{-1} represent the symmetric stretching of the $-SO_2-$ of the sulfonic acid group [20]. These FTIR spectra confirm the sulfonation of the synthesized polymer.

For the FTIR spectra of the PEEK 150XF and post-S-PEEK 150XF, the absorption band at 1,243 cm^{-1} can be assigned to the asymmetric stretching of the sulfone group, the band at 1,030 cm^{-1} represents the symmetric stretching of the $-SO_2-$ of the sulfonic acid group [17]. These FTIR spectra confirm the sulfonation of the polymer.
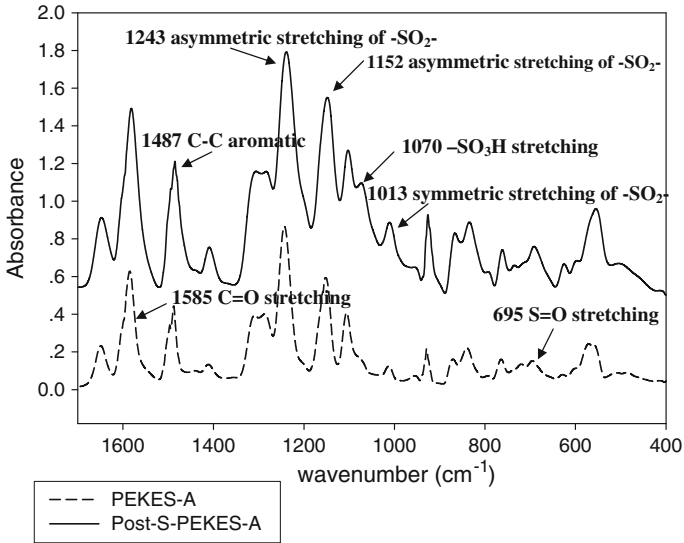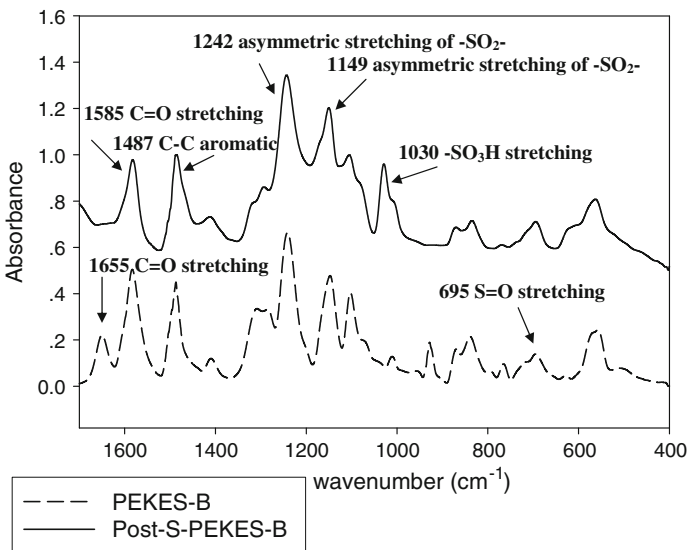
Fig. 3 FTIR of the PEKES-A and post-S-PEKES-A

Fig. 4 FTIR of the PEKES-B and post-S-PEKES-B

[1]H-nuclear magnetic resonance spectroscopy

The ^{1}H-NMR spectra (500 MHz, CD_3COCD_3) of both post-S-PEKES-A and B are shown in Fig. 5, consisting of the peaks $\delta_{H1,4,5}$ at around 7.15–1.35 ppm, $\delta_{H6,7,8}$ at around 7.80–7.95 ppm, and $\delta_{H2,3,9}$ at around 8.00–8.10 ppm. Peaks H1–H9
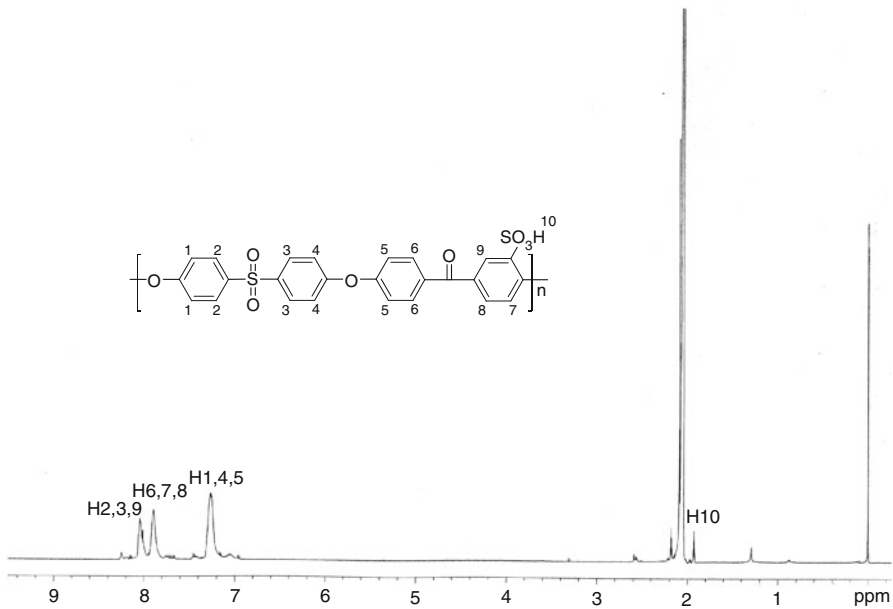
Fig. 5 Chemical structures of S-PEKES-A and S-PEKES-B

represent the hydrogen atom on the benzene ring of the post-sulfonated polymers; these peaks are broad and overlap because the peak of each proton present is near to each other. δ_{H10} is around 2.0, representing the hydrogen atom of sulfonic acid group, however, the peaks of sulfonic acid group are hindered by the peak of proton residue in CD_3COCD_3 which is evidently sharp at 2.1 ppm [4].

Thermogravimetric analysis (TGA)

Figure 6 shows the thermograms of PEKES-A, S-PEKES-A (DS = 0.67 ± 0.01), PEKES-B, and S-PEKES-B (DS is 0.66 ± 0.04). The first step weight loss of PEKES-A starts at around 380–390 °C, representing the splitting-off of the sulfonic acid group. For S-PEKES-A, its thermogram shows the first weight loss starting at 250 °C. The second step weight loss occurs at 450 °C, representing the degradation temperatures of both PEKES-A and S-PEKES-A. The first step weight loss of S-PEKES-B starts at around 300 °C representing the splitting-off of the sulfonic acid group. The second step weight loss of S-PEKES-B occurs at 470–500 °C, corresponding to the PEKES main chain decomposition. The PEKES-B and S-PEKES-B are completely degraded and no char remains [4].

The thermograms of poly(ether ether ketone) System C (PEEK 150XF) and S-PEEK 150XF show the first step weight losses starting around 290 °C due to the splitting-off of the sulfonic acid group. The second step weight loss occurs at 580 °C corresponding to the main PEEK chain decomposition [4].

In summary, all sulfonated polymers are thermally stable within the temperature range 25–120 °C.
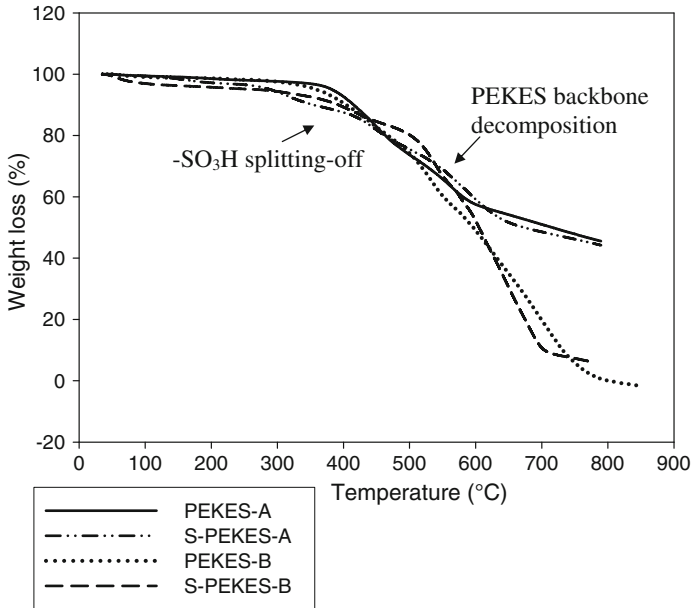
Fig. 6 Thermograms of PEKES-A, S-PEKES-A, PEKES-B, and S-PEKES-B

Degree of sulfonation

The sulfonation processes were carried out at room temperature (25 ± 2 °C). The DS of all sulfonated polymer systems increase almost linearly with increasing sulfonation time between 12 and 84 h, as shown in Fig. 7. The highest DS belongs to S-PEKES-B with DS values varying between 0.15 ± 0.01 and 0.66 ± 0.04. S-PEKES-A has DS values slightly lower than those of S-PEKES-B, with the DS values varying between 0.13 ± 0.02 and 0.67 ± 0.01. Therefore, the maximum DS values for S-PEKES-A and S-PEKES-B are nearly the same within experimental errors. DS values of S-PEEK 150XF varies from 0.10 ± 0.02 to 0.52 ± 0.02 for sulfonation times between 12 and 84 h, respectively; they are lower. This suggests that the sulfonic groups can attach themselves to the PEKES-B and PEKES-A backbones more strongly than that of PEEK 150XF due to the better solubility of the former two systems in H_2SO_4 than that of PEEK 150XF, resulting in higher sulfonation degrees. The DS of Nafion® 117 is 1.0 ± 0.02. Xing et al. [15] used a commercial PEEK from Victrex® for sulfonation. They varied the sulfonation time (60, 110, 140, 160, 190, and 240 h) at 22 °C and measured the DS by using the ^{1}H-NMR technique. The DS values were 0.48, 0.64, 0.66, 0.67, 0.79, and 0.78, respectively. In the present study, both S-PEKES-A and S-PEKES-B have higher DS values than that of Xing's at 60 h sulfonation time (DS for S-PEKES-A is 0.50 ± 0.01 and S-PEKES-B is 0.51 ± 0.02). In the work of Li et al. [8], the S-PEEK was synthesized by using a non-sulfonated monomer and a sulfonated monomer. DS was controlled by adjusting the ratio between these two monomers. At the ratios of non-sulfonated and sulfonated monomers of 2:8, 4:6, 5:5, and 6:4,
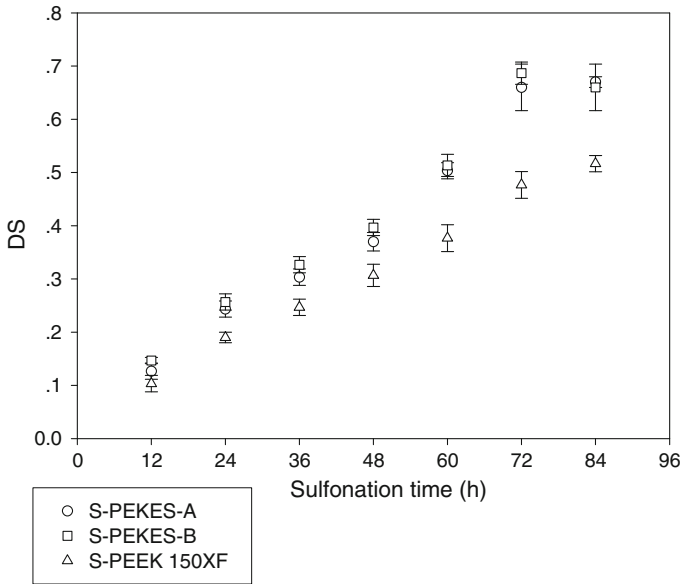
Fig. 7 Degrees of sulfonation of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF

the DS values were 0.4, 0.8, 1.0, and 1.2, respectively. The directly sulfonated monomers lead to precisely controlled amounts of sulfonic acid groups attaching to the polymer backbone. However, there remains a possibility that one repeating unit could be attached by more than one groups of the sulfonic acid.

Ion exchange capacity

Figure 8 shows IEC values of all S-PEEK systems versus the DS. The data suggest that the successful attachment of the sulfonic group onto the PEEK backbone. The IEC value of S-PEEK-A varies between 0.56 ± 0.05 and 1.34 ± 0.04 meq./g, corresponding to DS values between 0.13 ± 0.02 and 0.67 ± 0.01, respectively. The IEC value of S-PEEK-B varies between 0.61 ± 0.04 and 1.36 ± 0.04 meq./g, corresponding to DS values between 0.15 ± 0.01 and 0.66 ± 0.04, respectively. The IEC value of S-PEEK 150XF varies between 0.26 ± 0.06 and 1.01 ± 0.02 meq./g, corresponding to the DS values between 0.10 ± 0.02 and $0.52 \pm 0.0.02$, respectively. The IEC values of S-PEEK-A and S-PEEK-B are thus comparable, but the IEC values of S-PEEK 150XF are evidently lower than those of the first two systems. The IEC value of Nafion® 117 is 0.95 ± 0.04, corresponding to the DS of 1.0 ± 0.01. However, this IEC value Nafion® 117 is lower than those of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF which have DS values above 0.5.

In the work of Li et al. [8], the DS values of 0.4, 0.8, 1.0, and 1.2 were obtained corresponding to the IEC values of 0.712, 1.312, 1.421, and 1.521 meq./g, respectively; they are lower than those S-PEEK-A and S-PEEK-B. Vetter et al. [22] used a commercial PEEK from Victrex® for sulfonation at 40 °C; for the
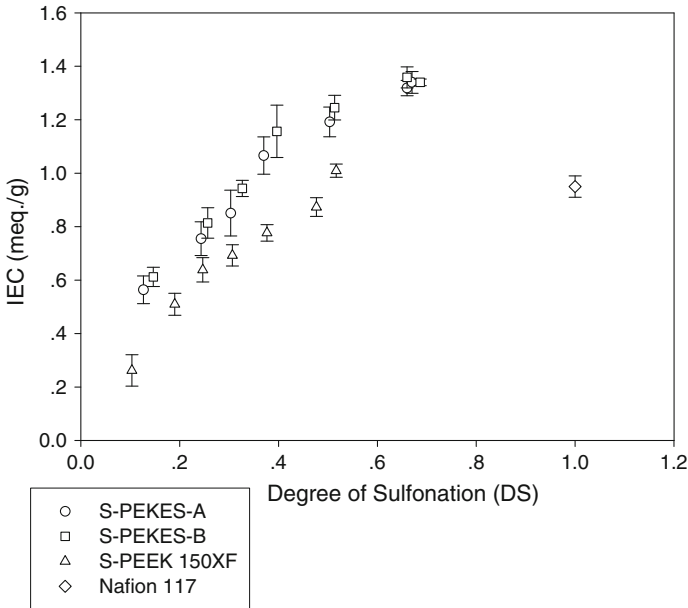
Fig. 8 Ion exchange capacity (IEC) of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF

sulfonation times of 48, 72, 96, 120, and 168 h, the DS values were 38, 43, 48, 50, and 58%, corresponding to the IEC values of 1.139, 1.167, 1.286, 1.371, and 1.601 meq./g, respectively—values which are comparable to those obtained in our work.

Water uptake (%)

Water uptake (%) values of the three sulfonated polymer systems are shown in Fig. 9. The water uptake (%) values of PEKES-A, PEKES-B, and PEEK 150XF at the zero sulfonation time are $1.43 \pm 0.25\%$, $1.61 \pm 0.31\%$, and $1.26 \pm 0.10\%$, respectively. The water uptake (%) value of S-PEKES-B is the highest. For DS values between 0.13 ± 0.02 and 0.67 ± 0.01, the water uptake (%) value of S-PEKES-A varies between 11.13 ± 2.20 and $44.59 \pm 0.87\%$, respectively. The water uptake (%) value of S-PEKES-B varies between $13.39 \pm 1.12\%$ and $47.45 \pm 0.73\%$, corresponding to DS values between 0.15 ± 0.01 and 0.66 ± 0.04, respectively. The water uptake (%) value and S-PEEK 150XF varies between $5.30 \pm 1.35\%$ and $35.63 \pm 1.43\%$, corresponding to DS values between 0.10 ± 0.02 and 0.52 ± 0.02, respectively. This result suggests that the increase in DS leads to the ease of water absorption, as the sulfonic acid group can be easily solvated by water. The water uptake (%) of all polymers can be compared with Nafion® 117 which possesses the water uptake (%) value at around $39.07 \pm 2.35\%$, corresponding to DS 1.0 ± 0.01.
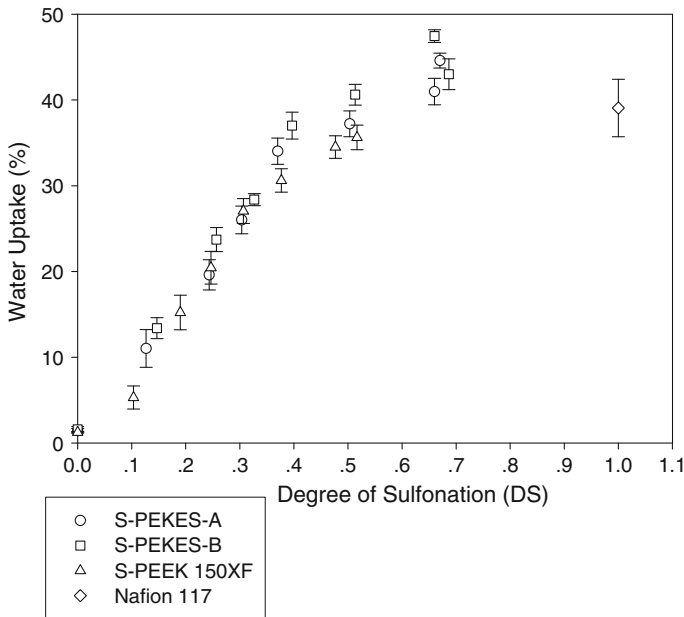
Fig. 9 Water uptake (%) of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF

In the work of Li et al. [8], for the DS values of 0.4, 0.8, 1.0, and 1.2, the water uptake values were 13, 37, 45, and 54%, respectively. Xing et al. [15] determined the water uptakes of sulfonated commercial PEEK at DS values of to 0.48, 0.64, 0.66, 0.67, and 0.79; to be 5, 12, 19, 19, and 23%, respectively (which are lower than the S-PEKES-A and S-PEKES-B when compared at the same DS).

Dielectric permittivity (ε') and electrical conductivity (σ'_{DC})

Dielectric permittivity (ε') values of S-PEKES-A, S-PEKES-B, and S-PEEK 150XF are shown in Figs. 10, 11. The ε' values of all 48 h sulfonated polymers are shown in Fig. 10; ε' values of all systems are nearly independent of frequency. ε' of S-PEKES-A has a value of around 29.18×10^{-12} F/m at a frequency of 20 Hz and ε' of S-PEKES-B has a value of around 29.17×10^{-12} F/m at same frequency. The S-PEEK 150XF ε' has the lowest value, about 21.74×10^{-12} F/m at a frequency of 20 Hz. This is because S-PEKES-A and S-PEKES-B have higher DS than S-PEEK 150XF and they contain a greater amount of sulfonic acid pendant groups—more than S-PEEK 150XF. The sulfonic group is of high polarity and can increase the polarizability of the polymer backbone. In spite of the fact that the S-PEKESs backbones contain the aromatic ring, the carbonyl group (–C=O) and the sulfone group (–SO$_2$–) are capable of reinforcing the chain stiffness and can obstruct the polarization.

Figure 11 shows ε' values of 12, 48, and 84 h S-PEKES-B. The DS increases with increasing sulfonation time because the PEKES backbones are more likely to
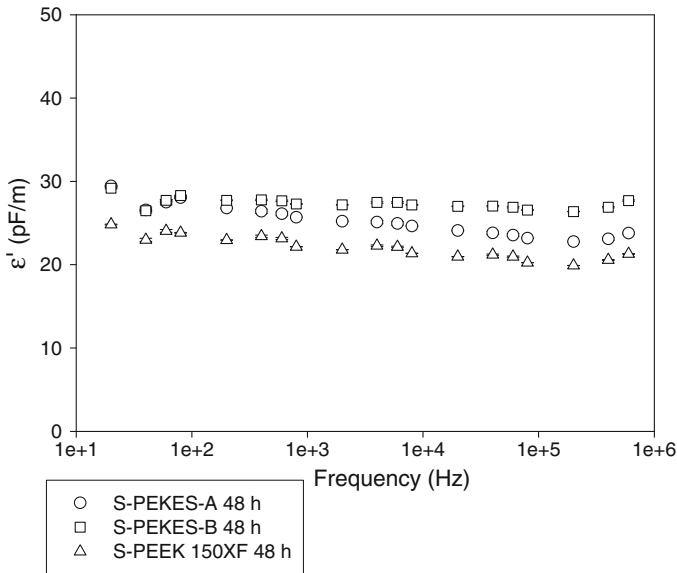
Fig. 10 Frequency dependence of the dielectric permittivities of sulfonated polymer systems (48 h sulfonation time) at room temperature ($T \sim 27$ °C). All samples were in the dry solid state

be attached to by the sulfonic groups. The ε' of the 84 h sulfonation S-PEKES-B, which has the highest DS of all the S-PEKES systems, is frequency dependent; and it decreases from 51×10^{-12} to 33×10^{-12} F/m as frequency is varied from 20 to 800,000 Hz. This result is due to the presence of the high polar sulfonic acid groups, which can induce high interfacial polarization at low frequencies. However, the interfacial polarization decreases with increasing frequency.

Table 1 shows the ε' values at lowest frequency (20 Hz) of all sulfonated polymer systems of 0, 12, 48, and 84 h sulfonation times. The ε' shows the same tendency for all sulfonated polymer systems, in which ε' increases monotonically with increasing DS. Furthermore, the dielectric permittivities of S-PEKES-A and S-PEKES-B are comparable in magnitude but are higher than those of the commercial S-PEEK 150XF.

In the work of Gasa et al. [25], the ε of sulfonated poly(ether ketone ketone) (SPEKK), with IEC equal to 2.01 meq./g, was strongly frequency dependent in which the ε value decreased with increasing frequency. The ε value decreased from 6.8 to 2.7 in the frequency range of 10–10,000 Hz. In our work, the ε values at 20 Hz of the 12 h sulfonated polymers, all systems, are between 2.5 and 3.3, the ε values of all 48 h sulfonated polymers are between 2.8 and 3.3. The ε values of the 84 h S-PEKES-A is around 3.3, and the ε value of the 84 h S-PEEK 150XF is around 2.8. The ε value of the 84 h S-PEKES-B decreases from 5.8 to 3.5 in the frequency range of 10–100,000 Hz. All ε values are smaller than the values of SPEKK in Gasa's work since our IEC values are <2.01 meq./g.

The electrical conductivities (σ'_{DC}) of all polymer systems increase with increasing the DS as shown in Table 1. σ'_{DC} of S-PEKES-A varies between
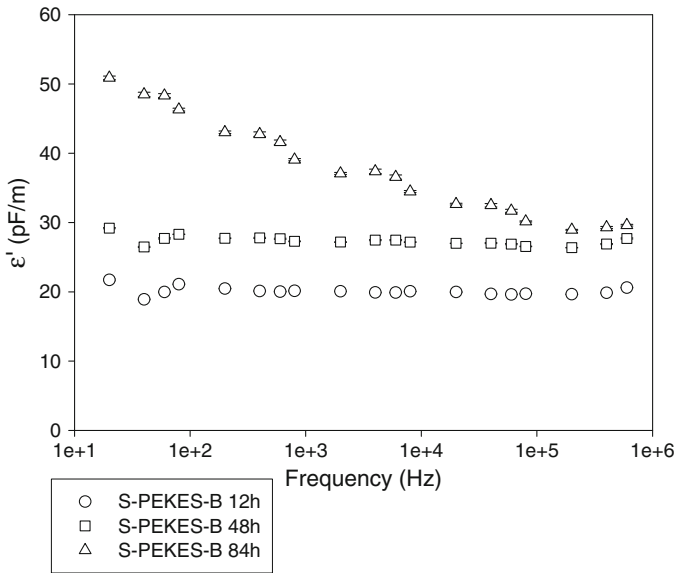
Fig. 11 Frequency dependence of the dielectric permittivities of S-PEKES-B (12, 48, and 84 h sulfonation) at room temperature ($\sim 27\ ^\circ$C). All samples were in the dry solid state

Table 1 The ε' and σ'_{DC} of all sulfonated polymer systems (0, 12, 48, and 84 h sulfonation) at a frequency of 20 Hz and at room temperature ($\sim 27\ ^\circ$C)

Polymer systems	Sulfonation time (h)	Degree of sulfonation (DS)	ε' (pF/m) at 20 Hz	ε at 20 Hz	σ'_{DC} (S/cm)
S-PEKES-A	0	0.00	18.45 ± 0.07	$2.08 \pm 8.15E{-}03$	$1.37E{-}05 \pm 8.58E{-}08$
	12	0.13	27.41 ± 0.15	3.09 ± 0.01	$4.64E{-}05 \pm 1.79E{-}07$
	48	0.37	29.18 ± 0.08	3.29 ± 0.01	$1.24E{-}03 \pm 1.87E{-}05$
	84	0.67	29.44 ± 0.05	3.32 ± 0.02	$4.29E{-}03 \pm 3.37E{-}04$
S-PEKES-B	0	0.00	18.91 ± 0.09	2.13 ± 0.01	$3.89E{-}05 \pm 2.69E{-}07$
	12	0.15	29.17 ± 0.08	$3.29 \pm 6.75E{-}03$	$4.30E{-}05 \pm 7.73E{-}07$
	48	0.40	29.44 ± 0.05	$3.32 \pm 6.05E{-}03$	$1.16E{-}03 \pm 1.51E{-}05$
	84	0.66	50.89 ± 0.24	5.74 ± 0.03	$3.61E{-}03 \pm 7.91E{-}05$
S-PEEK 150XF	0	0.00	17.24 ± 0.08	1.94 ± 0.01	$2.62E{-}05 \pm 1.82E{-}07$
	12	0.10	21.74 ± 0.10	2.45 ± 0.01	$2.67E{-}05 \pm 1.59E{-}07$
	48	0.31	24.82 ± 0.04	$2.80 \pm 5.00E{-}03$	$3.07E{-}05 \pm 9.55E{-}08$
	84	0.52	24.44 ± 0.12	2.76 ± 0.01	$3.22E{-}05 \pm 2.92E{-}07$

All samples are solids in the dry state

1.37×10^{-5} and 4.29×10^{-3} S/cm corresponding to DS values between 0.00 and 0.67. S-PEKES-B σ'_{DC} varies between 3.89×10^{-5} and 3.61×10^{-3} S/cm with DS values between 0.00 and 0.66. σ'_{DC} of S-PEEK 150XF varies between 2.62×10^{-5} and 3.22×10^{-5} S/cm with DS between 0.00 and 0.52. In the work of

Roeder et al. [26], the blended S-PEEK/PANI membrane was prepared, their electrical conductivity was in the order of 10^{-6} S/cm. In their study in 2006 [27], they reported that the mixed conductive membranes of PANI/SPEEK obtained from an initial composition of 80 wt% SPEEK had an electrical conductivity of 1×10^{-5} S/cm; after a second doping with 1 mol/L HCl, it increased to 4.9×10^{-5} S/cm which is comparable to that in present study.

Conclusions

The S-PEKESs derived from bisphenol S were successfully synthesized and chemically characterized by FTIR and ^{1}H-NMR, confirming the structures. The thermal properties, DS, IEC, and the water uptake of the synthesized S-PEKESs were compared with the commercial S-PEEK 150XF. The data show that the synthesized S-PEKESs have a higher degradation temperature, higher DS, IEC, and water uptake values than those of the commercial one DS, IEC, and water uptake of all polymers were compared with those of Nafion® 117. Furthermore, the dielectric permittivities of synthesized S-PEKES-A (12, 48, and 84 h) and S-PEKES-B (12 and 48 h), and commercial S-PEEK 150XF (12, 48, and 84 h) are independent of frequency and they increase with DS value. The dielectric permittivity of the 84 h S-PEKES-B decreases with increasing frequency due to the high polarity of the sulfonic acid groups. The water uptake, dielectric permittivity, and electrical conductivity values increase monotonically with increasing DS.

References

1. Carette L, Friedrich KA, Stimming U (2001) Fuel cells—fundamentals and applications. Fuel Cells 1:5–39
2. Neburchilov V, Martin J, Wang H, Zhang J (2000) A review of polymer electrolyte membranes for direct methanol fuel cells. J Power Sources 169:221–238
3. Li L, Zhang J, Wang Y (2003) Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell. J Membr Sci 226:159–167
4. Gil M, Ji X, Li X, Na H, Hampsey JE, Lu Y (2004) Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications. J Membr Sci 234:75–81
5. Huang RYM, Shao P, Burns CM, Feng X (2001) Sulfonation of poly(ether ether ketone) (PEEK): kinetic study and characterization. J Appl Polym Sci 82:2651–2660
6. Javaid ZSM (2005) Preparation and characterization of composite membranes using blends of SPEEK/PBI with boron phosphate. Electrochim Acta 50:4771–4777
7. Kaliaguine S, Mikhailenko SD, Wang KP, Xing P, Robertson G, Guiver M (2003) Properties of SPEEK based PEMs for fuel cell application. Catal Today 82:213–222
8. Li X, Wang Z, Lu H, Zhao C, Na H, Zhao C (2005) Electrochemical properties of sulphonated PEEK used ion exchange membranes. J Membr Sci 254:147–155
9. Li X, Zhao C, Lu H, Wang Z, Jiang W, Na H (2005) Preparation of a new type of ion-exchange membrane based on sulfonated poly(ether ether ketone ketone)s. J Appl Polym Sci 98:2481–2486

10. Mikhailenko SD, Robertson GP, Guova MD, Kaliaguine S (2006) Properties of PEMs based on cross-linked sulfonated poly(ether ether ketone). J Membr Sci 285:306–316
11. Mikhailenko SD, Wang K, Kaliaguine S, Xing P, Robertson GP, Guiver MD (2004) Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK). J Membr Sci 223:93–99
12. Reyna-Valencia A, Kaliaguine S, Bousmina M (2006) Structural and mechanical characterization of poly(ether ether ketone) (PEEK) and sulfonated PEEK films: effects of thermal history, sulfonation, and preparation conditions. J Appl Polym Sci 99:756–774
13. Wang F, Li J, Chen T, Xu J (2003) Synthesis of poly(ether ether ketone) with high content of sodium sulfonate groups and its membrane characteristics. Polymer 40:795–799
14. Wang Z, Ni H, Zhao C, Li X, Fu T, Na H (2006) Investigation of sulfonated poly(ether ether ketone sulfone/Heteropolyacid composite membranes for high temperature fuel cell applications. J Polym Sci Polym Phys 44:1967–1978
15. Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Wang K, Kaliaguine S (2004) Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. J Membr Sci 229:95–106
16. Rao VL, Sabeena PU, Ninan KN (1998) Synthesis properties of polyetherketone and polyetherketonesulfone copolymers. Eur Polym J 34:567–570
17. Drioli E, Regina A, Casciola M, Oliveti A, Trotta F, Massari (2004) Sulfonated PEEK-WC membranes for possible fuel cell applications. J Membr Sci 228:139–148
18. Regina A, Fontananova E, Drioli E, Casciola M, Spanappa M, Trotta F (2006) Preparation and characterization of sulfonated PEEK-WC membranes for fuel cell applications: a comparison between polymeric and composite membranes. J Power Sources 160:139–147
19. Fontananova E, Regina A, Drioli E, Trotta F (2006) Improving of the performances of sulfonated PEEK-WC membranes by introducing heteropolyacids in the polymeric matrix. Desalination 200:658–659
20. Xiao G, Sun G, Yan D (2002) Synthesis and characterization of novel sulfonated poly(arylene ether ketone)s derived from 4,4′-sulfonyldiphenol. Polym Bull 48:309–315
21. Li X, Lui C, Lu H, Zhao C, Wang Z, Xing W, Na H (2005) Preparation and characterization of sulfonated poly(ether ether ketone ketone) proton exchange membranes for fuel cell application. J Membr Sci 255:149–155
22. Vetter S, Ruffmann B, Buder I, Nunes SP (2005) Proton conductive membranes of sulfonated poly(ether ketone ketone). J Membr Sci 260:181–186
23. Mariani E, Eckstein J, Rubinova E (1967) Permittivity, dielectric loss and dc conductivity of NaNO$_3$ crystals grown by epitaxy. J Phys B 17:552–558
24. Kunanuruksapong R, Sirivat A (2007) Poly(p-phenylene) and acrylic elastomer blends for electroactive application. Mater Sci Eng A 454–455:453–460
25. Gasa JV, Weiss RA, Shaw MT (2008) Structured polymer electrolyte blends based on sulfonated polyetherketonerketone (SPEKK) and a poly(ether imide) (PEI). J Membr Sci 320:215–223
26. Roeder J, Silva H, Nunes SP, Pires ATN (2005) Mixed conductive blends of SPEEK/PANI. Solid State Ion 176:1411–1417
27. Roede J, Zucolotto V, Shishatsky S, Bertolino JR, Nunes SP, Pires ATN (2006) Mixed conductive membrane: aniline polymerization in an acid SPEEK matrix. J Membr Sci 279:70–75