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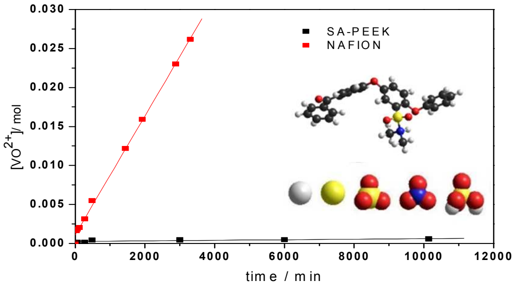

A simple synthesis technique for anionic conducting membranes, based on sulfaminated PEEK with Cl^-, Br^-, NO_3^-, HSO_4^-, $H_2PO_4^-$.

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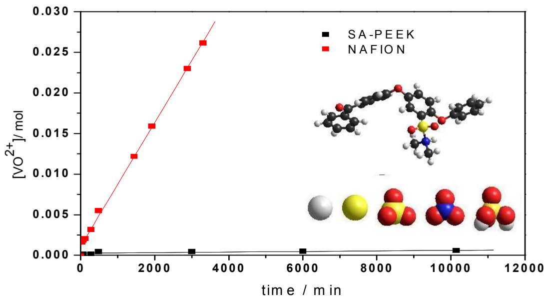

A simple synthesis technique for anionic conducting membranes, based on sulfaminated PEEK with Cl^-, Br^-, NO_3^-, HSO_4^-, $H_2PO_4^-$.

Abstract

A simple synthesis technique for the preparation of anionic conducting membranes is presented. In the first step, poly-ether-ether-ketone (PEEK) reacts with chlorosulfonic acid to chlorosulfonated PEEK, which in a second step is transformed by reaction with a secondary amine, dimethyl- or diethylamine, into sulfaminated PEEK. The sulfaminated PEEK is cast and the membranes are functionalized in a last step by reaction with various aqueous acid solutions, including HCl, HBr, HNO_3, H_2SO_4, and H_3PO_4. The spectroscopic, thermal, mechanical, permeability and electrical properties of the membranes are determined and discussed. The combination of appealing properties, such as high elastic modulus (~1300 MPa), high thermal stability, low cation permeability, respectable anionic conductivity (2-4 mS/cm), and a relatively simple and inexpensive synthesis make these new ionomers very promising for applications especially in acidic media, like in vanadium redox flow batteries.

Keywords: Anion Exchange Membranes; Poly-ether-ether-ketone; Anion conductivity

1. INTRODUCTION

Ionic conducting polymers [1, 2] are a fascinating research field with wide-spread applications, ranging from ultrafiltration or separation membranes, ion exchange resins, to membranes for advanced energy applications [3, 4].

Numerous proton-conducting polymer electrolytes have been developed. The perfluorinated sulfonated polymer Nafion^{TM} was discovered in the 1960's [5]; sulfonated aromatic polymers are alternative, less expensive ionomers [6, 7]. In these nanocomposites, proton transport occurs through percolating hydrated nanometric channels [8]. We have analyzed the proton conductivity of these ionomers, based on the concepts of proton mobility, tortuosity and percolation of proton-conducting channels [9-11].

Anion-conducting membranes have also many high technology applications, including water desalination, alkaline fuel cells or electrolysers (when the anion is hydroxide), or redox flow batteries [12-16]. Few organic moieties can sustain anionic conductivity, mostly ammonium, phosphonium or sulfonium groups [17]. The chemical synthesis of these ionomers generally involves multi-step reactions with sometimes dangerous or toxic reagents [18-20] and the stability, especially in alkaline media, is a matter of concern [21-23]. There is a need for more straightforward and less expensive synthesis methods for anion-conducting ionomers.

In this work, we synthesized anion exchange membranes by sulfamination of Poly-Ether-Ether-Ketone (PEEK). PEEK is a typical example of a fully aromatic polymer with a lot of attractive properties and in order to become anionic conducting a basic functional group must be inserted; the amount of ionogenic groups modifies the ionic conductivity. Sulfonamide moieties are an appropriate choice as basic groups given their thermal and hydrolytic stability. The conductivity is observed in acidic medium and the type of mobile anion can be varied depending on the acid used.

To synthesize sulfaminated PEEK, the polymer is first chlorosulfonated by reaction with $ClSO_3H$ [24, 25]. The chlorosulfonated derivative is very versatile and can be transformed by reaction with a secondary amine, such as dialkylamines, to a sulfaminated polymer. The alkyl groups should be relatively small in order not to obstruct the ionic conduction channels. The chlorosulfonation could also be made by first sulfonating the polymer by reaction with sulfuric acid and then transforming an OH group into Cl by reaction with thionyl chloride. However, the direct use of chlorosulfonic acid is not only more simple, but gives a little amount of cross-linking which improves significantly the mechanical properties of the polymer, as shown previously for SPEEK [26].

The sulfonamide group can in a third step be transformed by reaction with various acids into a dialkyl-ammonium cation fixed on the macromolecular backbone with a mobile counter-anion. The reaction of basic sulfonamide groups with an inorganic acid can be written:

$$R\text{-}SO_2\text{-}NR_2 + HX \longrightarrow R\text{-}SO_2\text{-}NHR_2^+ + X^- \qquad (1)$$

The advantages of this synthesis route are its versatility and the straightforward and inexpensive chemistry.

The anion conductivity of these membranes is observed in a range of low pH values where the reaction 1 is irreversible. Although this can seem a drawback at first sight, there are applications where this apparent disadvantage can be exploited, for example in the all vanadium redox flow battery [27, 28]. This kind of device generally works at high concentration of sulfuric acid and the hydrogenosulfate anion (or another anion in the case of other acids) is the major charge carrier in the separation membrane [29, 30].

In this work, we report the synthesis and we study the properties of sulfaminated poly-ether-ether-ketone ionomers, made by this reaction sequence, using dimethylamine or diethylamine and various aqueous acidic solutions. The water uptake of the membranes was determined at 25°C. NMR and FTIR spectroscopic analysis were applied to study the composition and structure of the ionomers, thermogravimetry to investigate their thermal stability, tensile stress-strain tests to determine the mechanical properties, such as elastic modulus and tensile strength, and impedance spectroscopy to determine the ionic conductivity at 25°C. Given the potential application in all vanadium redox flow batteries, the membrane permeability to vanadium ions was also measured.

2. EXPERIMENTAL

Polymer Synthesis.

Poly-ether-ether-ketone (PEEK) was obtained from Victrex (450 P, MW = 38300). Chlorosulfonic acid (HSO_3Cl, Fluka ≥98%), sodium acetate (Aldrich, anhydrous 98%), dimethylamine (2M in THF, Aldrich), diethylamine (>99%, Aldrich) and all other chemicals were used as received.

Chlorosulfonation of PEEK. PEEK (5 g, 17.3 meq) was dried at 80 °C overnight and then added in nitrogen atmosphere to $ClSO_3H$ (30 ml). The mixture was stirred 5 h at 50 °C obtaining a viscous orange solution. The solution was then cooled to RT and anhydrous CH_2Cl_2 was added, giving a white precipitate. The mixture was stirred for 10 min, then the solvent was rapidly removed under nitrogen, and fresh anhydrous CH_2Cl_2 was added. The procedure was repeated until neutral pH. Under these conditions, the chlorosulfonation degree was 0.9 with a degree of cross-linking (DXL) of 0.1, as deduced from ^{1}H NMR spectroscopy reported in Figure 1a.

Synthesis of sulfaminated PEEK (SA-PEEK). The chlorosulfonated polymer (1,5 g, 3.87 meq), CH_3COONa (0.64 g, 7.74 meq) and the selected amine in the ratio 1:3 (11.6 meq) were added under stirring to 75 mL dichloroethane at RT; after dissolution the reaction vessel was kept at 50°C for one day. The solution was then precipitated by adding methanol and after filtration washed several times with acetonitrile. The product was dried overnight at 80°C. The sulfamination degree (*DSA*) after reaction was 0.9 as determined by ^{1}H NMR spectroscopy.

The ionic exchange capacity (*IEC, in mol/Kg*) of the polymer can be calculated according to:

$$IEC = \frac{DSA}{288 + DSA \times M(SO_2NR_2)} \qquad (2)$$

$M(SO_2NR_2)$ is the mass of the sulfonamide group, which depends on the amine used (dimethyl- or diethylamine). The *IEC* values were for dimethylamine IEC = 2.34 mol/kg, for diethylamine IEC = 2.20 mol/kg.

The SA-PEEK membranes were cast using N-Methylpyrrolidone (NMP) as casting solvent and a home-made doctor-blade type equipment. After dissolution of 250 mg polymer in 8 mL NMP, the solvent was evaporated during a heat treatment at 120°C for 24 h. The membrane thickness was determined using a micrometer.

In the final step, the cast membranes were immersed into 2M solutions of various acids: HCl, HBr, H_2SO_4, HNO_3, and H_3PO_4 during 24 h. After the reaction, the membranes were immersed in high purity water (ρ = 18 MΩ.cm) for 24 h to remove any excess of unreacted acid. The repeat units of SA-PEEK derivatized with dimethylamine and HCl or diethylamine and HBr are shown as examples in Scheme 1.

Scheme 1

Structural Characterization

^{1}H NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at 300.13 MHz. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS). DMSO-d_6 was used as solvent.

FTIR spectra were recorded in transmission mode from 4000 to 400 cm^{-1} with a Bruker Equinox 55 spectrometer. The membrane thickness was (25 ± 5) µm. A background spectrum was run and sample spectra were normalized against the background spectrum.

Thermal, Mechanical, Permeability and Electrical Characterization

The thermal stability and degradation of SA-PEEK membranes were investigated between 30 and 500 °C by high resolution thermogravimetric analysis using a platinum sample holder (TGA Q500, TA Instruments) with a heating rate of 5 K/min under air flux (60 mL/min).

The mechanical properties were measured at ambient temperature and relative humidity using an Adamel-Lhomargy tensile test machine (M250-2.5 CT, France). Samples were cut into pieces with 5 mm width and 25 mm length. The constant crosshead speed was 5 mm/min.

The water uptake *WU* was determined at 25°C. The acid form membranes were immersed in pure water during 24 h and weighed rapidly in a closed vessel (m_{wet}). The dry weight (m_{dry}) was determined in a closed vessel after drying 72 h over P_2O_5. WU and the hydration number λ were calculated according to the equations:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \qquad (3)$$

$$\lambda = \frac{WU \cdot 10}{IEC \cdot M(H_2O)} \qquad (4)$$

The vanadium permeability was determined in a home-made membrane-separated cell (exposed membrane area 0,64 cm^2) by filling 1,5 M $VOSO_4$ in 3 M H_2SO_4 solution into one reservoir and vanadium-blank solution with equivalent ionic strength (1,5 M $MgSO_4$ in 3 M H_2SO_4) into another reservoir according to the standard procedure reported in the literature [31, 32]. The amount of the vanadium permeated was detected by UV−Vis spectroscopy using a Varian Cary 300 Scan UV-Visible Spectrophotometer.

The ionic permeability *P* can be calculated from the equation [31]:

$$\frac{dc}{dt} = \frac{A \cdot P}{V \cdot L}\left(C_A - C_B(t)\right) \qquad (5)$$

Where C_A and $C_B(t)$ are the vanadium concentrations in the reference cell and in the measurement cell at time t, respectively. V is the volume of the reference cell; A and L are the area and thickness of the membrane.

The ionic conductivity was measured by impedance spectrometry (EG&G model 6310) in a Swagelok cell with stainless steel electrodes; the ac voltage amplitude was 20 mV and the frequency range 10^{-1}-10^{5} s^{-1}. All measurements were made at 25 °C in fully humidified conditions. The area specific resistance was measured in 2 M acid solution (corresponding to the acidic operating conditions in most redox flow batteries). The intrinsic ionic conductivity was determined after 24 h washing with high purity water to remove any excess of unreacted acid and during 30 days, including several washing steps, to check the membrane stability. The through-plane conductivity σ was calculated according to the equation:

$$\sigma = \frac{d}{R \cdot A} \tag{6}$$

R is the membrane resistance, d its thickness, which was in the range (25 ± 5) µm, and A the electrode area, which was 0.264 cm^2.

3. RESULTS AND DISCUSSION

Scheme 2 shows the reaction pathways for the synthesis of SA-PEEK. The sulfamination of fully aromatic polymers, such as poly-ether-ether-ketone (PEEK), can be realized in two steps. In the first step the chlorosulfonic acid is used as chloro sulfonating agent, this is an electrophilic aromatic substitution. The sulfonic acid derivative is the only product when chlorosulfonic acid is used in equimolar ratio [24, 33]. In an excess of reagent, sulfonic acid is converted into sulfonyl chloride with the formation of sulfuric acid. The reversibility of this reaction was demonstrated for different aromatic substrates [34], but it was also shown that the reaction is driven to completion when the ratio of reagent to substrate is 5:1 [33].

A little quantity of the chlorosulfonic moieties can react again in the reaction media to give a cross-link side-reaction, as shown in the Scheme 2, via the formation of sulfone bridges; no degradation of the polymeric chain was observed. The formation of cross-links occurs by reaction of the sulfonic acid derivative with aromatic rings (PEEK) under the influence of the chlorosulfonic reagent via the formation of the anhydride [26].

Scheme 2

Figure 1a shows the ^{1}H NMR spectrum of the chlorosulfonated PEEK. Four groups of signals are present in the figure: A corresponds to 4 protons in ortho-position to the carbonyl group of PEEK that remain unchanged during the reaction and are taken as reference (4H per repeat unit); B' indicates the proton in ortho-position to the chlorosulfonyl moiety that is shifted downfield compared with the position of the other two protons in the hydroquinone ring [35]; C indicates a proton in ortho-position to a cross-linking SO_2 group; B refers to the other hydrogens in the aromatic rings. The degree of chlorosulfonation can be evaluated from the integration of B' protons [36]: DS = 0.9.

In the region ascribed to aromatic moieties some peculiarity can be observed with respect to the spectrum reported for PEEK sulfonated in concentrated sulfuric acid [35]. In particular, the splitting of the signal at about 7.5 ppm can be rationalized by taking into account the possible existence of different conformations as observed already in the spectrum of chlorosulfonated PEEK. The cross-linking reaction produces, in fact, asymmetry in the unit next to the cross-linked one, as previously demonstrated [26].

Figure 1.

The occurrence of cross-linking is demonstrated by the presence of the signal at about 8.2 ppm (C) characteristic of a hydrogen atom in ortho-position to a SO_2 group [37, 38]. The extent of cross-linking was evaluated by the relative intensities of resonances at 8.2 ppm (C) and 7.8 ppm (A): DXL = 0.1.

In the second step, the chlorosulfonated product can react with dialkylamines in the presence of sodium acetate to yield the final product: a sulfaminated polymer (SA-PEEK). This is a S_N2 reaction, performed with excess alkyl-amine.

Scheme 2 shows the reaction pathways for the synthesis of SA-PEEK.

Figure 1b shows the ^{1}H NMR spectrum of N,N-dimethyl-PEEK sulfonamide. Typical signals of methyl groups (6 hydrogen atoms) linked to nitrogen are present at 2.8 ppm (D). The relative intensity of signals A:D is 4:5.6, indicating a complete amination reaction (DSA = 0.9). It was shown that the proton affinity of nitrogen in sulfonamides is higher than that of oxygen, so that the protonation occurs on the N atom [39, 40].

The asymmetry of protons in *ortho* to the $-SO_2N(CH_3)_2$ groups resulted enhanced by the substitution of a chlorine atom in the chlorosulfonate derivative with bulky methyl groups in the sulfonamide derivative.

The FTIR spectra of SA-PEEK, collected directly on membrane samples, before and after immersion in various acids, at room temperature are presented in Figure 2a and 2b, respectively.

Figure 2

All spectra are dominated by PEEK absorptions [41, 42]. The main peaks are summarized in Table 1; very strong bands due to the asym. stretching of diphenyl ether groups and the asym. stretching of Ph-CO-Ph groups are observed in the region around 1250 cm^{-1}.

In Figure 2a, peaks due to asymmetric and symmetric stretching of CH_3 groups linked to nitrogen atoms are visible at 3075 and 2950 cm^{-1} respectively [43]. The absorbance of water present in the membrane can be observed around 3500 cm^{-1}. The absorbance at 930 cm^{-1} (Figure 2b) is characteristic of the stretching of S-N bonds [44, 45], confirming the presence of sulfonamide moieties. Changes after immersion in acid are observed at low wavenumbers below 400 cm^{-1}; in general, the infrared bands for inorganic groups are broader, fewer in number and appear at lower wavenumbers than those observed for organic moieties. The spectra do not change even after 30 days immersion time in water showing the stability of the sulfammonium groups under these conditions; probably interactions with adjacent macromolecular chains lead to some further stabilization.

Actually, it is well known that the hydrolysis reaction of sulfonamide derivatives is very slow and occurs at high temperature [46]. For further control of the absence of decomposition, NMR spectra were recorded after 30 days immersion in water and no changes were observed.

Figure 3 presents a typical thermogravimetric curve of SA-PEEK.

Figure 3

The small mass loss above 150 °C can be attributed to evaporation of the casting solvent N-methylpyrrolidone, as confirmed by FTIR spectroscopy before and after thermal treatment, whereas the sulfonamide groups decompose around 300 °C, as observed in similar ionomers

[47]. The main chain decomposition is observed as usual for aromatic polymers above 400°C [48, 49]. The thermal stability is thus fully sufficient even for higher temperature operation.

Typical tensile test curves of SA-PEEK before and after reaction with the various acids are presented in Figure 4; the curves are quite similar for all acid-treated samples. The average mechanical properties are reported in Table 2. SA-PEEK shows high a tensile strength, in line with data of related sulfonated aromatic polymers, a very high elastic modulus, indicating strong interactions among the macromolecular chains, and a low elongation at break [50, 51].

Figure 4.

The sulfaminated polymers exhibit thus a glassy behavior with brittle facture. The mechanical properties of SA-PEEK with diethylamine and dimethylamine are very similar. The addition of acid provokes a slight decrease of mechanical strength and modulus, but they remain high. The acid addition has overall a slight plasticizing effect on the membrane [52]. All membranes treated in acid present a sightly lower elastic modulus than the initial one. As the measurements are made in ambient humidity, this result reflects probably the higher water uptake in the acidified material (Table 2), which reduces the Van der Waals forces between macromolecular chains, as previously shown for SPEEK [51].

Figure 5 shows the typical linear time dependence of the permeated $VOSO_4$ concentration through a SA-PEEK membrane. The vanadium permeability determined for dimethyl- and diethylamine SA-PEEK functionalized with H_2SO_4 is $1.3x10^{-9}$ and $5x10^{-10}$ cm^2/min, respectively. These values are 3 orders of magnitude lower than those of Nafion measured by us under similar conditions ($1.4x10^{-6}$ cm^2/min in good agreement with the literature [53]) and comparable to those of other anion exchange membranes [53]. This behavior is consistent with cation blocking due to Donnan exclusion. The smaller value for the diethyl-derivative might be related to the larger volume of the ethyl group.

Figure 5.

The conductivity of pristine SA-PEEK without any addition of acids is similar to aromatic polymers without ionic groups, such as poly-phenyl-oxide [54] (~10^{-4} S/cm, due to partial electronic conductivity related to some conjugation), and one order of magnitude below the conductivity of the acid-doped ionomers (Tables 2 and 3). The ammonium cations can be considered immobile, being fixed to the macromolecular chain. The large conductivity increase after addition of acid can be attributed to anionic conduction.

The area specific resistance (ASR) observed in 2 M acid solution is between 0.2 and 0.6 $\Omega.cm^2$, competitive with the best literature data for anion-conducting membranes. These are the conditions encountered in real redox flow batteries, which generally operate in highly acidic solutions [28-30, 55, 56].

The conductivity data after 30 days in water reported in Table 2 are shown to confirm that the membranes do also conduct in absence of excess acid. One can recognize no significant difference between the two derivatives with dimethylamine or diethylamine, but some scatter of the data.

The influence of ions, especially anions, on the physical behavior of polymers is a subject of study since 1888 when the Hofmeister series was discovered [57]. Recent studies show that the effect of anions depends mainly on the direct interaction between the ion and the macromolecule as well as interactions with water molecules. These interactions play an important role by modifying the anion mobility.

Tables 2 and 3.

Overall, the ionic conductivity is competitive with other anion-conducting ionomers [58-60].

4. CONCLUSION

A new simple method for preparing anion-conducting hydrated polymers was designed. Fully aromatic PEEK polymer was first chlorosulfonated by reaction with $ClSO_3H$, then reacted with dimethyl- or diethylamine to give sulfaminated PEEK (SA-PEEK). Finally, cast SA-PEEK membranes were functionalized by immersion in 2M solutions of various acids. The thermal and mechanical resistances are adequate for use as membranes in various applications. The ionic conductivity is competitive with other anion-conducting ionomers. The cation permeability is orders of magnitude lower than that of Nafion^{TM}, due to Donnan exclusion. The described straightforward and inexpensive synthesis method can therefore be a good choice for the production of various anion-conducting membranes, intended for applications operating in acidic or neutral media such as ultrafiltration membranes for water purification and cation-blocking separators, for instance for vanadium redox flow batteries.

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CAPTIONS

Scheme 1. Repeat unit of SA-PEEK: a) functionalized using dimethylamine and HCl, b) functionalized using diethylamine and HBr. For clarity the portion containing the sulfone bridge is not shown.

Scheme 2. Synthetic routes for the preparation of SA-PEEK.

Figure 1. ^{1}H NMR spectra of: a) chlorosulfonated PEEK and b) SA-PEEK

Figure 2. FTIR spectra of SA-PEEK: a) derivatized with dimethylamine, b) derivatized with diethylamine and various acids after 24h in water. Following the arrow: — as cast; — HCl; — HNO_3; — H_3PO_4; — H_2SO_4; — HBr

Figure 3. High-resolution thermogravimetric curve of SA-PEEK functionalized with dimethylamine and HCl in air with heating rate of 3 K/min.

Figure 4. Typical tensile test curves for SA-PEEK (dimethylamine derivative) and SA-PEEK with various acids at 25 °C in ambient humidity.

Figure 5. Permeation curve of $VOSO_4$ through Nafion and a dimethyl SA-PEEK membrane (thickness: 197 and 28 μm, respectively) at 25 °C.

Table 1. Main infrared bands for sulfaminated PEEK.

Table 2. Mechanical properties (elastic modulus E, maximum tensile strength TS_{max}, elongation at break ε), and ionic conductivity in water at 25 °C of SA-PEEK (dimethylamine IEC = 2.34 mol/kg, diethylamine IEC = 2.20 mol/kg) and SA-PEEK doped with various acids.

Table 3. Water uptake *WU*, hydration number λ, area specific resistance (ASR) in 2 M acid and ionic conductivity in water at 25°C for SA-PEEK doped with various acids.

Table 1. Main infrared bands for sulfaminated PEEK.

Band / cm^{-1}	**Vibration**
3075	(m) asym. stretching of CH_3 groups linked to nitrogen atoms
2950	(m) sym. stretching of CH_3 groups linked to nitrogen atoms
1650	(m) sym. stretching of C=O group
1598	(s) skeletal in-plane vibration of phenyl rings
1473	(s) skeletal in-plane vibration of phenyl rings
1250	(s) asym. stretching of diphenyl ether groups
1225	(vs) asym. stretching of Ph-CO-Ph
1186	(m) asym. stretching of diphenyl ether groups
1120	(m) in-plane bending of aromatic hydrogens
1085	(m) asym. stretching of SO_2-
1026	(m) sym. stretching of SO_2-
930	(w) stretching of S-N bonds
865	(w) out-of-plane bending of aromatic hydrogens

Table 2. Mechanical properties (elastic modulus E, maximum tensile strength TS_{max}, elongation at break ε), and ionic conductivity in water at 25 °C of SA-PEEK (dimethylamine IEC = 2.34 mol/kg, diethylamine IEC = 2.20 mol/kg) and SA-PEEK doped with various acids.

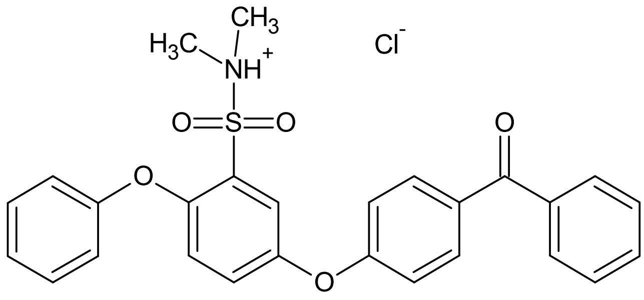
Membrane	*E* / *MPa*	TS_{max} / *Mpa*	*ε* / *%*	*σ/* *mS/cm*
Dimethylamine	1460 ± 130	53 ± 8	6 ± 1	0.5±1.0
+ HCl	1290 ± 70	50 ± 3	7 ± 3	3.1±1.0
+ HBr	1460 ± 150	44 ± 10	4 ±2	3.9±1.0
+ H_2SO_4	1080 ± 70	48 ± 10	7 ± 4	2.6 ± 1.0
+ HNO_3	1270 ± 70	41 ± 5	4 ± 2	2.0±1.0
+ H_3PO_4	1060 ± 70	35 ± 5	4 ± 2	2.5±1.0
Diethylamine	1550 ± 280	51 ± 15	4 ± 1	0.2±0.6
+ HCl	1340 ± 180	43 ± 9	6 ± 1	2.9±1.0

Table 3. Water uptake *WU*, hydration number λ, area specific resistance (ASR) in 2 M acid and ionic conductivity σ in water at 25°C for SA-PEEK doped with various acids.

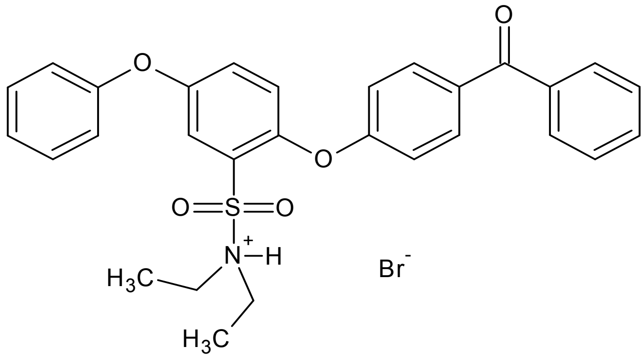
	Dimethylamine				Diethylamine			
Anion	*WU* / %	λ	*ASR (2 M HX)/* $\Omega\ cm^2$	σ *(H_2O)/ mS/cm*	*WU* / %	λ	*ASR (2 M HX)/* $\Omega\ cm^2$	σ *(H_2O)/ mS/cm*
Cl^-	26 ± 1	6	0.6	3.1±1.0	25 ± 3	6	0.4	2.9±1.0
Br^-	34 ± 5	8	0.2	3.9±1.0	26 ± 6	6	0.3	2.7±0.7
HSO_4^-	29 ± 6	7	0.2	2.6±1.0	27 ± 4	7	0.2	3.3±0.6
NO_3^-	26 ± 9	6	0.2	2.0±1.0	30 ± 7	8	0.2	2.8±1.0
$H_2PO_4^-$	25 ± 1	6	0.2	2.5±1.0	26 ± 2	6	0.2	2.6±0.8

Scheme 1. Repeat unit of SA-PEEK: a) functionalized using dimethylamine and HCl, b) functionalized using diethylamine and HBr. For clarity the portion containing the sulfone bridge is not shown.

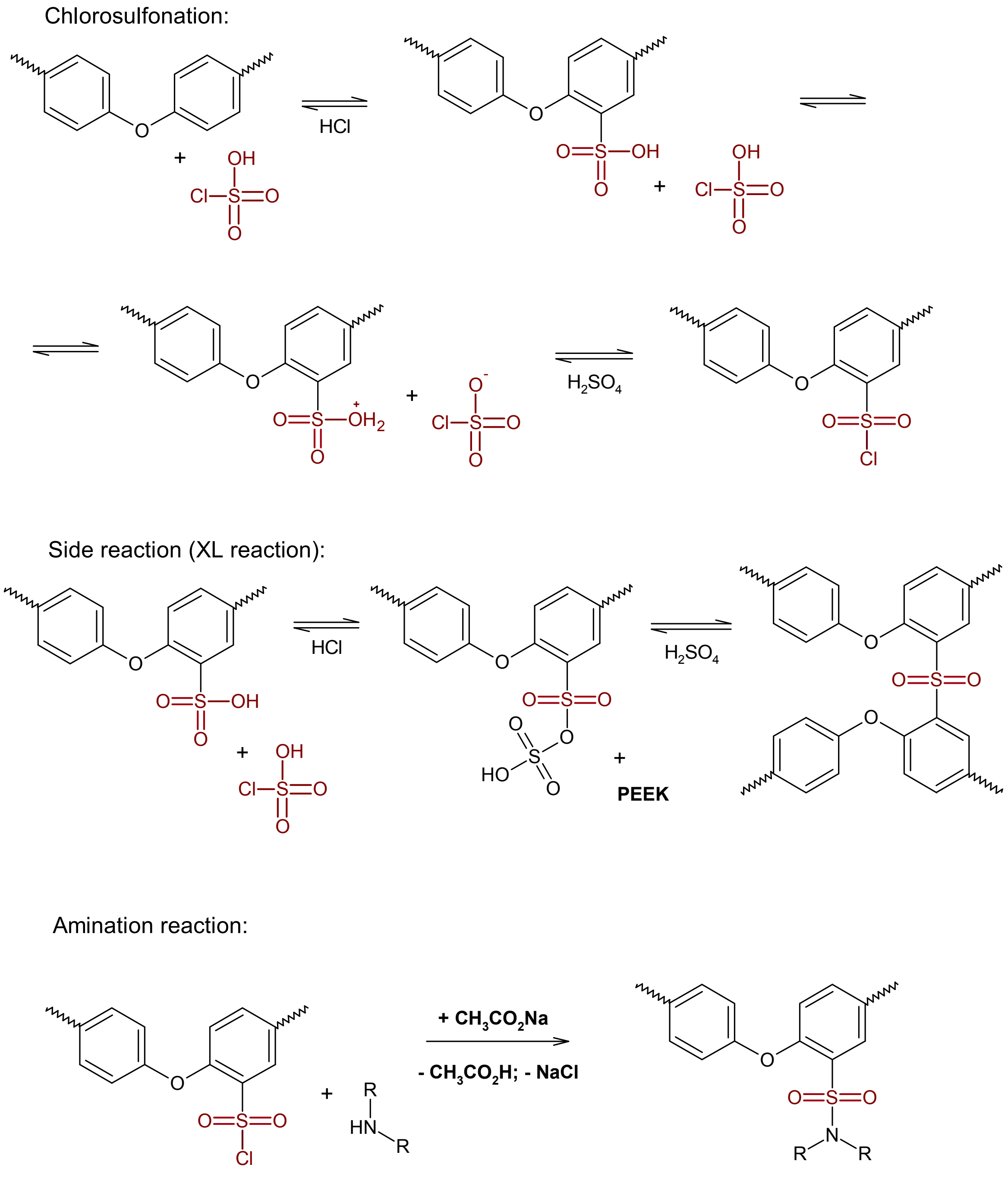
a) SA-PEEK-Me-Cl



b) SA-PEEK-Et-Br



Scheme 2. Synthetic routes for the preparation of SA-PEEK.



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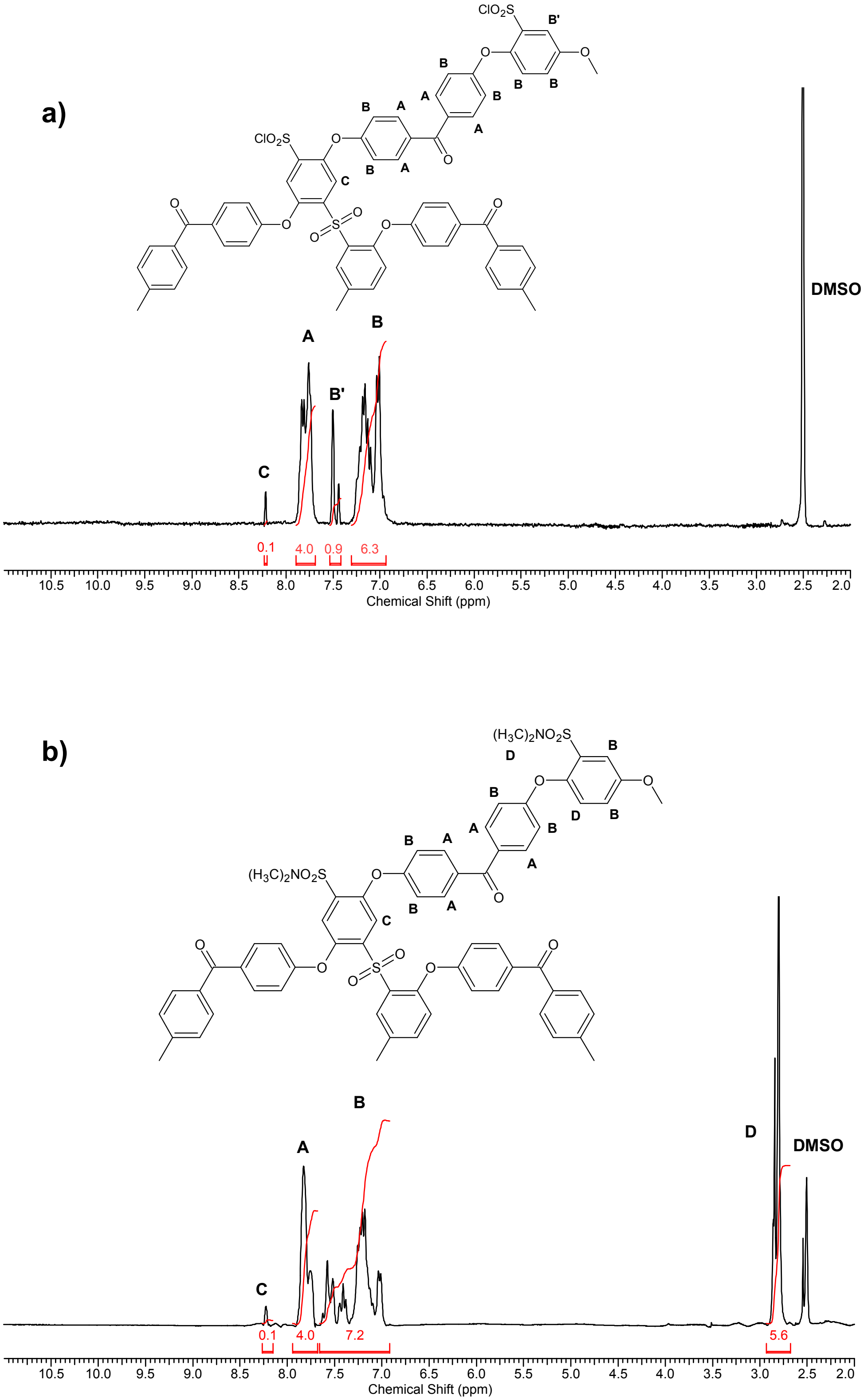

Figure 2. FTIR spectra of SA-PEEK: a) derivatized with dimethylamine, b) derivatized with diethylamine and various acids after 24h in water. Following the arrow: — as cast; — HCl; — HNO_3; — H_3PO_4; — H_2SO_4; — HBr

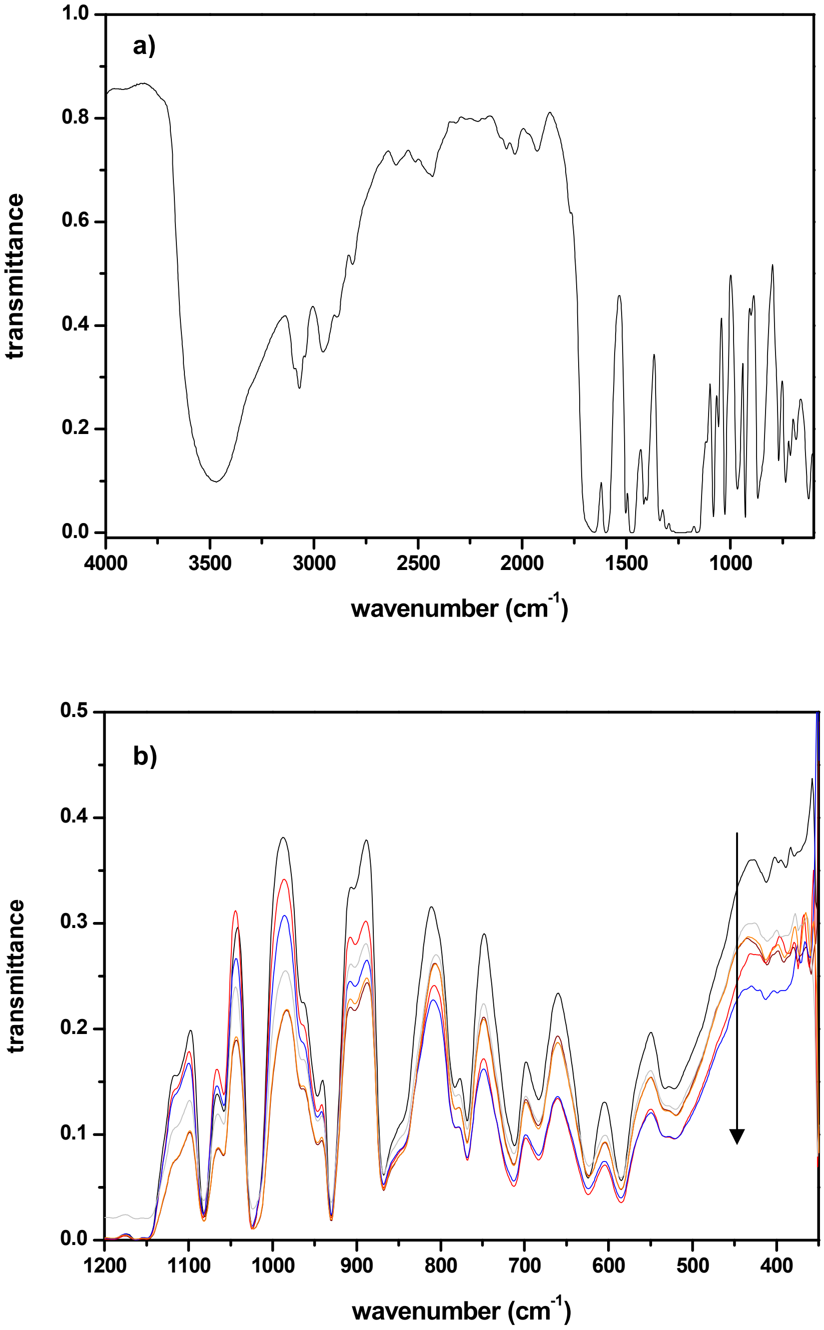

Figure 3. High-resolution thermogravimetric curve of SA-PEEK functionalized with dimethylamine and HCl in air with heating rate of 3 K/min.

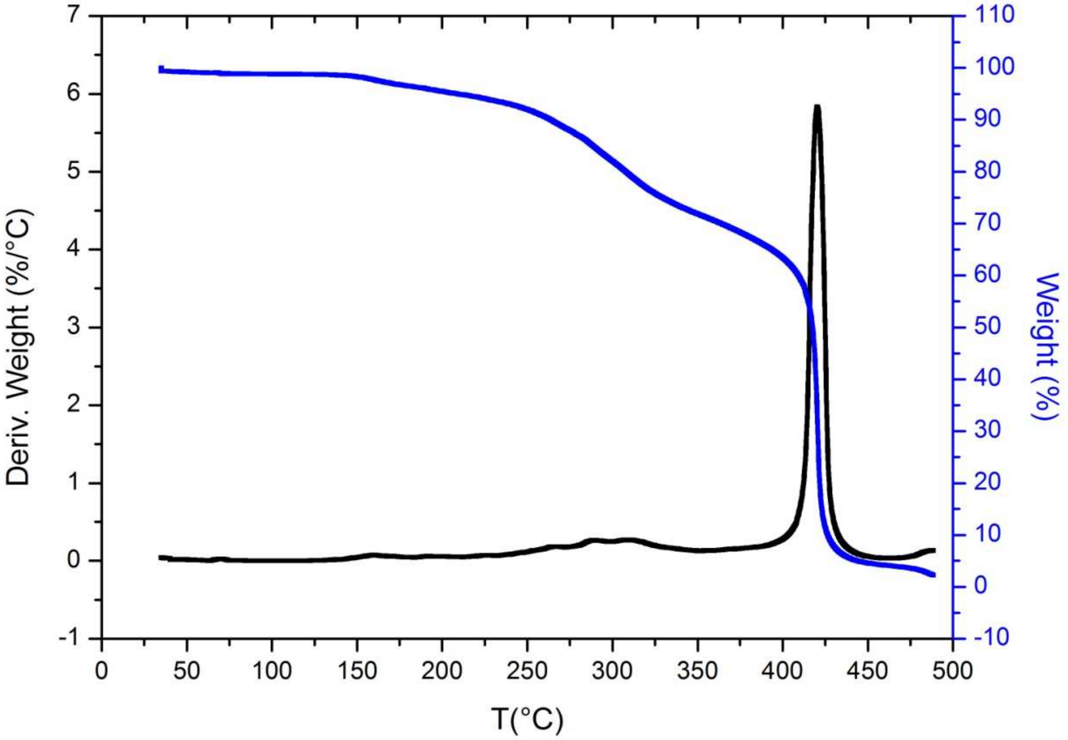

Figure 4. Typical tensile test curves for SA-PEEK (dimethylamine derivative) and SA-PEEK with various acids at 25 °C in ambient humidity.

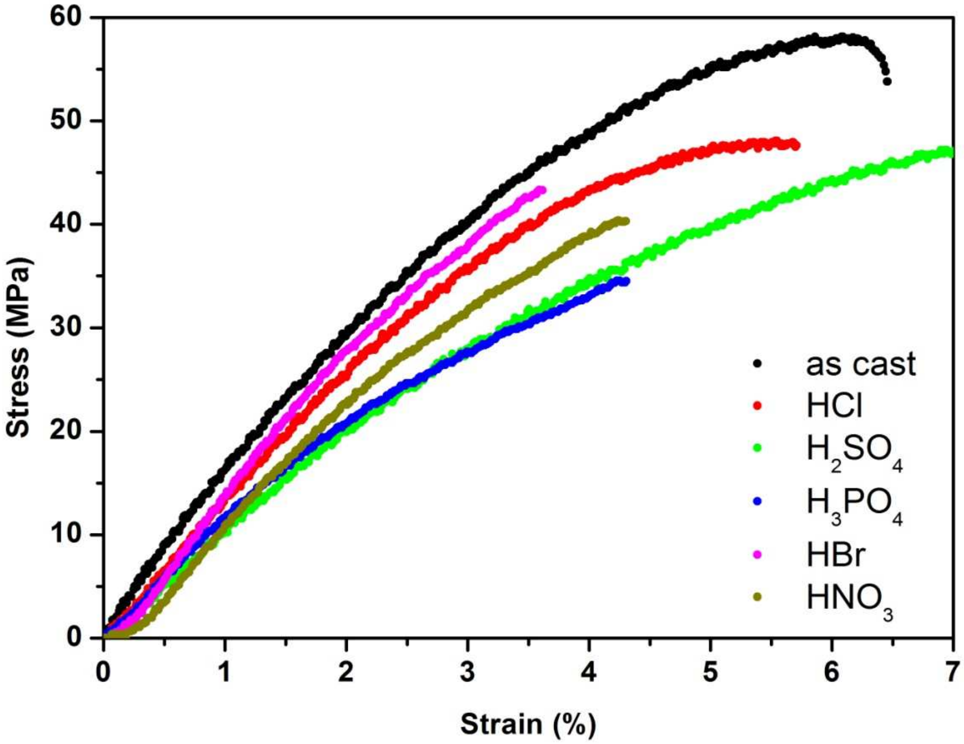

Figure 5. Permeation curve of $VOSO_4$ through Nafion and a dimethyl SA-PEEK membrane (thickness: 197 and 28 μm, respectively) at 25 °C.