Anion-conducting ionomers: Study of type of functionalizing amine and macromolecular cross-linking

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ABSTRACT

Anion exchange membranes (AEM) were prepared by chloromethylation and amination of polysulfone (PSU) and polyphenylsulfone (PPSU). The reaction pathways were studied by ^{1}H and ^{13}C NMR spectroscopy and *ab-initio* calculations. Various amines were used, including trimethylamine (TMA), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,4-diazabicyclo[2.2.2]octane (DABCO) to study the influence of the molecular volume and the stabilizing effect of a delocalization of the positive ammonium ion charge on a second nitrogen. Furthermore, the effect of a solvothermal cross-linking on the stability of AEM was investigated. The alkaline stability, measured after treatment in 2 M KOH at 60 °C during 168 h, is improved by DBN and polymer reticulation. The ionic conductivity in water reaches values above 10 mS/cm with DABCO. The hydroxide ion mobility depends linearly on the hydration number.

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Introduction

Anion exchange membranes (AEM) are very versatile ion-conducting materials used in several applications, such as alkaline fuel cells [1,2], water electrolysers [3], redox flow batteries [4,5], or electrodialysis devices [6,7]. Many fields can benefit from their application: in alkaline fuel cells, which do not need noble metal catalysts, they reduce problems related to carbonation [8], while in redox flow batteries AEM achieve very low permeability and high selectivity [9].

AEM are formed by a polymeric backbone functionalized with fixed cationic groups and counter anions, generally hydroxide ions that sustain the conductivity. Anion conductivities are lower than proton conductivities, but similar dependencies on humidity and temperature have been reported [10—12].

The stability in severe basic conditions and the reduced conductivity are the main problems of AEM to be solved in order to extend the use of these promising materials. Often the two issues are linked to each other, like in cation exchange membranes: high stability is related to low conductivity and vice versa [13,14].

The AEM stability can be discussed in terms of cationic groups and polymeric backbones. The backbone is responsible for the mechanical properties of membranes [15] and among different polymeric matrixes it was reported that the aromatic polymers polysulfones (PS), can well resist in basic conditions

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[16,17]. Aromatic polymers show many interesting properties: i) the possibility to tailor polymer structures by the use of various monomers or by functionalization; ii) an easy production and recycling of the corresponding membranes, with relatively little environmental pollution problems; iii) a low gas permeability; and iv) a low cost. In addition, PS are soluble in organic solvents, allowing homogeneous solution reactions, and present two activated positions per repeat unit towards electrophilic aromatic substitution, leading to high degrees of functionalization. Based on these considerations, polysulfone (PSU) and polyphenylsulfone (PPSU) seem to be a good choice as base polymers.

However, it was recently reported that trimethylammonium groups attached to PSU can catalyse the degradation of the polymer backbone by OH^- nucleophilic reaction on the quaternary carbon or on the ether junction. It was postulated that the cationic moieties can cause the formation of a dipole moment on the polymer backbone with a positive charge localized on the quaternary carbon or on the ether group facilitating the nucleophilic attack [18].

Regarding the stability of cationic groups, most used are ammonium ions because they show better chemical and thermal stability compared to other cationic groups, such as quaternary phosphonium and tertiary sulfonium ions [2]. However, ammonium groups present also several degradation reactions: bimolecular and unimolecular elimination (E_2 and E_1), bimolecular nucleophilic substitution (S_N2), and ammonium ylide formation [19–21]. E_2 (often called Hofmann elimination) and E_1 can be avoided using ammonium groups without β-hydrogens or, in the case of the Hofmann elimination reaction, using moieties where it is impossible to reach an anti-periplanar conformation; the substitution reaction and the ylide formation are more difficult to circumvent.

While the correlation between conductivity, ion exchange capacity (IEC) and stability seems clear in proton conducting polymers [22–24], this topic has been less studied in anionic membranes. High values of IEC lead to an increase of the water uptake and the conductivity, but also decrease the membrane processability by a microphase separation due to a polymer/polymer immiscibility according to Bauer et al. The formation of cross-linked backbones might help to avoid this phase separation [25]. Furthermore the presence of a covalent bond between the macromolecular chains can also decrease the degradation of the main chain due to the presence of ammonium ions [26]. We have reported the benefits of cross-linked (XL) polymers obtained by in situ reticulation [27–29]: thermal and mechanical stability are improved and also the conductivity [30,31]. The formation of cross-linked AEM (XL-AEM) is explored in this work.

Another option to decrease the degradation of cationic groups due to the S_N2 reaction and the ylide formation is the reduction of the positive charge on the ammonium group by delocalization on different atoms. Furthermore, the performance of AEM may increase if these groups are more basic. To explore this possibility, we used 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,4-diazabicyclo[2.2.2]octane (DABCO) as quaternizing agents. Due to the presence of two nitrogens in these rings, the positive charge can be better stabilized making the polymer degradation more difficult.

This paper explores the influence of various functionalizing amines and of macromolecular cross-linking on the AEM properties and stability.

Material and methods

Materials

Polysulfone (Solvay, PSU, MW = 55,500) polyphenylsulfone (Solvay, PPSU, MW = 46,173), polyetheretherketone (Victrex, PEEK, 450 PF, MW = 38,300), stannic chloride ($SnCl_4$), para-formaldehyde (($CH_2O)_n$), trimethylchlorosilane (Me_3SiCl), trimethylamine (TMA, 4.2 M in EtOH), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,5 diazabicyclo[4.3.0]non-5-ene (DBN) and all other chemicals (Aldrich) were reagent grade and were used as received.

Synthesis of chloromethylated polymers

Chloromethylated-PSU (CMPSU)
a) Reagent ratio PSU:($CH_2O)_n$:Me_3SiCl:$SnCl_4$ = 10:100:100:1. After drying 2 h at 80 °C, PSU (3.78 g, 8.55 mmol) was dissolved in chloroform (410 mL) at RT in a three-neck vessel equipped with a magnetic stirrer under nitrogen flux. The resulting solution was 0.021 M (concentration 2%). After dissolution, paraformaldehyde (2.57 g, 85.5 mmol) and trimethylchlorosilane (10.8 mL, 85.5 mmol) were added. Then $SnCl_4$ (0.1 mL in 20 mL of chloroform) was slowly added to the solution with an addition funnel. The reaction was left under stirring at 55 °C for 240 h. The solution was cooled to RT and then precipitated in ethanol. The product was dried overnight at 60 °C and analysed by ^1H and ^{13}C NMR using $CDCl_3$ as a solvent. The final degree of chloromethylation (DCM) after 240 h was 0.86.

b) Reagent ratio PSU:($CH_2O)_n$:Me_3SiCl:$SnCl_4$ = 5:50:50:1. The initial procedure was the same reported above. After the first addition of the catalyst, the reaction was kept at 55 °C for 24 h. Further 0.1 mL of $SnCl_4$ diluted in 30 mL of chloroform were then added. The solution was kept at reflux for different times in order to obtain different degrees of chloromethylation as reported in Fig. 1. After the precipitation in ethanol, the products were analysed by ^1H and ^{13}C NMR using $CDCl_3$ as a solvent.
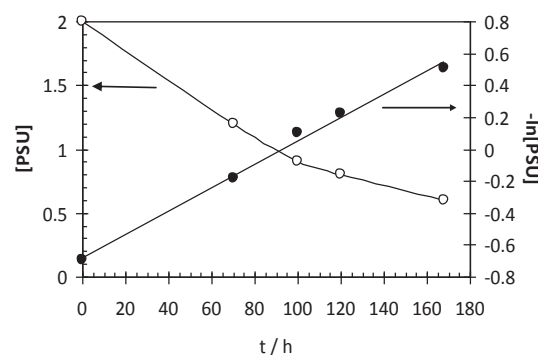

Fig. 1 – Concentration of unreacted PSU and logarithm of PSU concentration versus reaction time.

Chloromethylated PPSU (CMPPSU)

The synthesis of CMPPSU was conducted in a similar way using a concentration 0.021 M of PPSU in $CHCl_3$. After the addition of $SnCl_4$ (initial ratio $PSU:(CH_2O)_n:Me_3SiCl:SnCl_4 = 10:100:100:1$) a precipitate was formed, indicating the presence of a cross-linked polymer with $-CH_2-$ bridges. The synthesis was repeated using a concentration 0.010 M. Under this condition, no precipitation occurred. The reaction was kept under N_2 for 48 h at 55 °C, then further 0.1 mL of $SnCl_4$ diluted in 40 mL was added. A sample taken after 240 h showed a very low conversion of PPSU (<10%). Another 0.1 mL of $SnCl_4$ was then added and the solution was kept at reflux for further 120 h. The final ratio was $PSU:(CH_2O)_n:Me_3SiCl:SnCl_4 = 10:100:100:3$. DCM evaluated by ^1H NMR was 0.25.

Amination of CMPSU

TMA (trimethylamine)-PSU

CMPSU with different DCM (typically 1 mmol) was dissolved in 20 mL DMSO under N_2 at RT. Then 0.48 mL of a 4.2 M solution of trimethylamine in EtOH (2 mmol) was added. The solution was kept under stirring for 72 h at 70 °C then heated under vacuum to remove the excess of amine for 3 h at 85 °C. The solution of TMA-PSU in DMSO (0.05 M) was directly used for the casting procedure. A little quantity was dried and then analysed by ^1H and ^{13}C NMR using DMSO-d_6 as solvent.

DABCO (1,4-diazabicyclo[2.2.2]octane)-PSU

A similar procedure was followed for the synthesis of the DABCO derivative using a ratio between the quantity of chloromethyl groups and DABCO of 1:1.5. After dissolution of the two precursors, the solution was kept under stirring for 96 h at 70 °C then heated under high vacuum to remove the excess of amine at 85 °C for 3 h. The solution of DABCO-PSU in DMSO (0.05 M) was directly used for the casting procedure. A little quantity was dried and analysed by ^1H and ^{13}C NMR using DMSO-d_6 as solvent.

DBN (1,5-Diazabicyclo[4.3.0]non-5-ene)-PSU

Different attempts were made to obtain the product with good yield changing the ratio between the quantity of chloromethyl groups and DBN, the temperature and the reaction time. In sample 7 (see Table 1), the ratio was 1:2, the temperature 70 °C and the time 96 h. After removal of the excess of DBN under vacuum, the solution in DMSO (0.05 M) was directly used for the casting procedure. A little quantity was dried and analysed by ^1H and ^{13}C NMR using DMSO-d_6 as solvent.

Synthesis of cross-linked (XL) TMA-PSU and DBN-PSU

PEEK-SO_2Cl (6 mg, 0.016 meq) was dissolved in 2 mL of DMSO and was slowly added to a DMSO solution of TMA-PSU or DBN-PSU (5 mL, 0.05 M) under vigorous stirring at 80 °C. The final composition was 5% in PEEK-SO_2Cl. When higher concentrations of chlorosulfonic PEEK were used, a precipitate occurred with the formation of inhomogeneous membranes, due to the poor miscibility of the polymers.

PEEK-SO_2Cl was synesized starting from sulfonated PEEK [32] (SPEEK) with DS = 0.9. SPEEK (1.8 g, 5 meq) was dissolved in $SOCl_2$ (36 mL, 500 mmol) and dimethylformamide (0.6 mL, 7.8 mmol) at RT and then put at 60 °C under stirring in nitrogen atmosphere for 3 h. The solution was evaporated under vacuum to remove the excess of $SOCl_2$ during 2 h at 60 °C. The residue was washed several times in a solution of tetrahydrofurane/isopropanol 1:2 until pH = 7 and finally dried overnight at 60 °C. The product was analysed by ^1H NMR using DMSO-d_6 as solvent.

Preparation of membranes

Typically 10 mL of a 0.05 M solution in DMSO of various samples was evaporated to 5 mL, cast on a Petri dish or using a home-made doctor-blade type apparatus, then heated to dryness at 100 °C for 24 h. Higher temperatures cannot be used, because the polymer demixes and precipitates; this might be related to some in situ cross-linking by unreacted chloromethylated precursors.

Table 1 – Type of amine used, degree of chloromethylation (DCM), IEC, degree of amination (DAM), water uptake WU, and conductivity σ in KOH and in water at 25 °C before and after the treatment with KOH at 60 °C of anion exchange membranes.

Sample	DCM	IEC/DAM	WU (%)	σ (mS/cm) in KOH 2 M	σ (mS/cm) in H_2O	σ (mS/cm) after treatment in KOH 2 M	σ (mS/cm) after treatment in H_2O
1-TMA	0.76	0.81/0.39	19	16	2.2	17	—
2-TMA	0.86	1.34/0.66	40	30	4.6	—	—
3-TMA	1.10	1.64/0.83	53	58	12	—	—
4-TMA	1.40	1.67/0.84	105	15	2.2	—	—
5-DABCO	0.76	1.10/0.58	33	41	5.3	—	—
6-DABCO	1.40	1.70/1.12	504	63	6.7	—	—
7-DBN	1.40	0.91/0.53[a]	35	8	0.2	38	0.2
8-XL(5%)-TMA as cast	0.76	0.81/0.40[b]	26	17	2.3	—	—
8a-XL(5%)-TMA 120 °C 24 h	0.76	0.81/0.40[b]	17	8	1.0	—	—
9-XL(5%)-TMA as cast	1.10	1.19/0.61[b]	319	12	4.3	—	—
9a-XL(5%)-TMA 120 °C 24 h	1.10	1.19/0.61[b]	32	11	2.2	—	—
10-XL(5%)-DBN 120 °C 24 h	1.40	0.91/0.54[c]	34	6	0.2	17	0.2

[a] Corrected for the presence of TBP.
[b] Corrected for the presence of 5% $PEEKSO_2-$.
[c] Corrected for the presence of TBP and 5% $PEEKSO_2-$.

In the case of DBN-PSU, 20% w/w of tributylphosphate (TBF) was added to the DMSO solution (sample 7 in Table 1).

For the preparation of XL-TMA and XL-DBN (5%) membranes, the DMSO solution was concentrated to about 5 mL, then cast in a Petri dish and heated at 80 °C during 20 h. In the following, these membranes will be called "XL-TMA/DBN (5%) as cast" (samples 8 and 9 in Table 1). The membranes were thermally treated at 120 °C for 24 h (samples 8a, 9a and 10).

Anion exchange with KOH

Typically, membranes were immersed in KOH 2 M for 72 h at room temperature. The exchanged membranes were used directly or after washing in deionized water.

Structural characterization

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded with a Bruker Avance 300 spectrometer operating at 300.13 MHz. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS).

Carbon atom charges were calculated by Mulliken population analysis (MPA) applying a single point *ab-initio* method (6-31G*) on optimized geometries obtained by AM1 semi-empirical calculation using the Gaussian program [33]. Geometric optimizations were terminated when the energy difference among successive iterations was lower than 4.2 J/mol. A 1.5 repeat unit of PSU was chosen as a model compound (see Fig. 2). Enthalpies of formation, ΔH_f, for chloro- and dichloromethyl-PSU were calculated by AM1 semi-empirical calculations on optimized geometries.

Characterization of properties

IEC measurements
The Ionic Exchange Capacity (IEC in milliequivalents per g of dry polymer) of the ionomers was determined by acid-base titration. After the exchange with OH^{-} ions, the membranes were washed in deionized water and dried over P_2O_5 for 72 h.

The samples were weighted and immersed in a 0.1 N HCl solution. The acidic solution was then back-titrated with 0.1 N NaOH. A potentiometric equivalent point detection was used.

Mechanical properties
The mechanical properties were investigated using an ADAMEL Lhomargy DY30 test machine at room temperature at a constant crosshead speed of 5 mm/min with aluminium sample holders as described in Refs. [34,35]. Prior to the measurements, the polymer samples were stabilized at ambient temperature and humidity, which was (50 ± 10)% RH. The measurement time was below 5 min.

Water uptake measurements and ionic conductivity
The water uptake was measured by full immersion in deionized water at 25 °C: polymer samples were weighed before and after immersion times of 24 h. The dry weight was obtained after keeping the sample 72 h over P_2O_5.

The anionic conductivity was determined at 25 °C by through-plane measurements with stainless steel electrodes using a Swagelok cell. The samples were previously immersed in 2 M KOH or in water for 24 h. The impedance spectrometer (EG&G M6310) was operated between 100 kHz and 50 Hz with an a.c. voltage amplitude of 20 mV. The membrane resistance was obtained from the high frequency intersection of the impedance arc with the real axis of the Nyquist plot. For tests of the stability in hydroxide solutions, the membranes were immersed in 2 M KOH solution at 60 °C during 168 h and the conductivity measured before and after the immersion in water for 24 h.

Results and discussion

Synthesis of chloromethyl derivatives

The synthesis of an aromatic AEM *via* the chloromethyl derivative can be carried out with different reagents [36,37], sometimes dangerous or toxic. Our friendly method uses
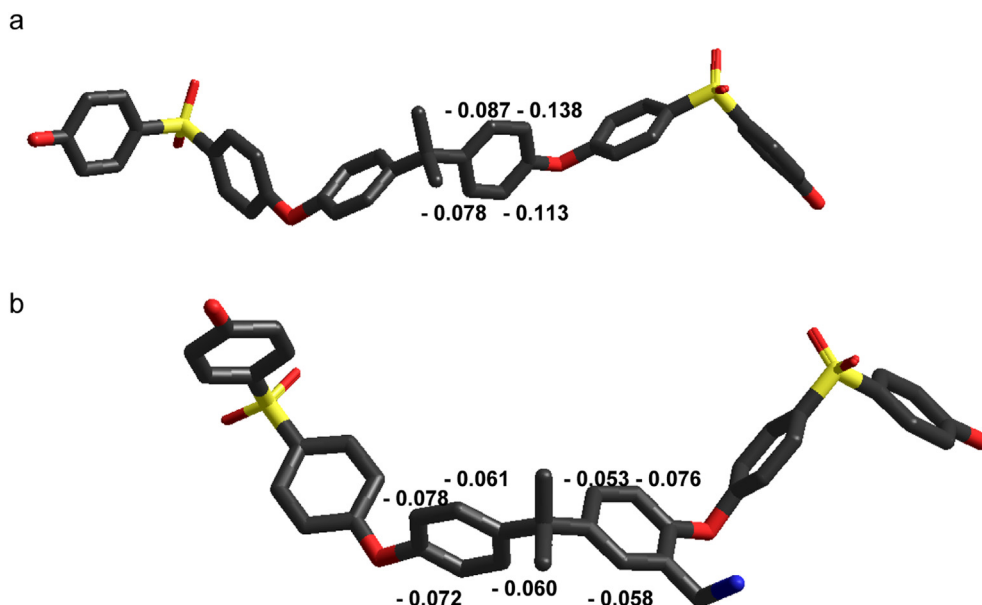

Fig. 2 – Ab-initio calculation of carbon atomic charges by Mulliken population analysis.

paraformaldehyde, SnCl$_4$ and chlorotrimethylsilane as reagents.

The mechanism was already clarified [38,39], but different conditions and times were reported. In this study, we modified the synthesis conditions for chloromethyl-PSU (CMPSU) and chloromethyl-PPSU (CMPPSU) reported by Daly et al. [40] changing the time and the reagent ratio to obtain chloromethyl derivatives with five different DCM. Fig. 1 shows the concentration of unsubstituted PSU *vs* the reaction time; the time dependence indicates a pseudo-first order reaction kinetics. High degrees of chloromethylation are thus difficult to obtain and a larger quantity of catalyst must be added. The amount of catalyst and the PSU concentration must be balanced in order to avoid the formation of XL derivative, due to the Friedel–Crafts alkylation reaction between the CH$_2$Cl derivative and unsubstituted PSU. The formation of a precipitate due to cross-linking was observed before, but was not explained.

Two activated positions can be recognized for the introduction of the chloromethyl moiety by electrophilic aromatic substitution in PSU and PPSU polymers. For the CMPSU derivative, the substitution in *ortho* to the ether linkage or in *ortho* to the carbon dimethyl groups are both possible; sometimes these two products are described indifferently in the literature.

Ab-initio calculations on optimized geometry of PSU (see experimental) were used to determine the carbon atom charge, which was calculated by Mulliken population analysis. Atomic charges are not quantum mechanical observables and methods for their calculation are necessarily arbitrary; only the variation within a series should be considered [41]. The results, shown in Fig. 2a, indicate that the favourite position for the introduction of the first CH$_2$Cl group is in *ortho* to the ether linkage where the atomic charge is lower. There is instead no evident favourite position for the attack of the second group, as shown by the value of the carbon atomic charge in Fig. 2b. The second CH$_2$Cl moiety can enter in the same aromatic ring or in the adjacent one. The ΔH_f values do not give a clear answer, because the difference ($\Delta(\Delta H_f)$) between the two products is less than 8 kJ/mol. The obtained values are reported in Table 2.

Scheme 1a shows the synthesis of CMPSU compound with a DCM = 2. For simplicity the two CH$_2$Cl groups are located in different rings. The first step is an electrophilic aromatic substitution that uses an activated formaldehyde, generated in the presence of stannic chloride, which reacts with chlorotrimethylsilane to form the trimethylsilyl ether of chlorohydrin [42]. SnCl$_4$ acts as a homogeneous Lewis acid catalyst for the formation of the chloromethylating agent. The main advantage of this procedure is that the electrophilic agent is generated in situ and easily decomposed by ethanol during the precipitation step.

The chloromethylation of PPSU was obtained with a long reaction time in very dilute conditions to avoid the precipitation of the cross-linked polymer [39,40]. Even careful control of the reaction conditions did not afford a considerable amount of chloromethylation. The ^{1}H NMR spectrum (Fig. 3) shows a peak at 4.7 ppm due to the CH$_2$Cl moiety. The series of peaks of low intensity in the aromatic region, ascribed to the functionalized PPSU, indicate the low conversion of the polymer. PPSU is more reactive versus electrophilic aromatic substitution so that the chloromethylated PPSU can more easily react to form the cross-linked polymer. This means that more diluted conditions must be applied, leading probably to lower reaction rates.

Synthesis of aminated PSU

In Table 1 are reported the IEC and the water uptake of different samples of AEM quaternized with trimethylamine (samples 1–4). The IEC indicate an incomplete amination reaction with about 80% conversion rate, possibly due to second-order kinetics. However, the formation of highly aminated products might also be limited by the Manning condensation, because the distance between adjacent ammonium groups must be higher than 0.7 nm [43]. The casting temperature must be limited, because the polymer demixes and precipitates at temperature above 100 °C, which might be related to some in situ cross-linking by unreacted chloromethylated precursors.

Two other cyclic amines were explored as quaternizing agent. DABCO is a strong base (pKa = 8.8). Bauer et al., in 1990 reported a high alkaline stability for AEM functionalized with DABCO groups, due to the impossibility to reach an anti-periplanar conformation essential to have the Hofmann elimination. The S$_N$2 degradation reaction was also decreased by the interaction between the two nitrogens [25]. Due to the presence of two nucleophilic sites in the DABCO structure, it is possible during the quaternization reaction to obtain cross-linked membranes reducing the IEC, because the mass of the repeat unit is higher. However, when an equimolar ratio (or more) of CH$_2$Cl derivative and DABCO is used, it is possible to avoid the cross-linking reaction. Membranes were prepared with two different IEC.

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN), a bicyclic amidine, is a very strong base (pK$_a$ = 13.5) [44,45] that can help to increase the conductivity of AEM. However, it is also a bulky compound and it is expected to have a low reactivity in the S$_N$2 amination reaction due to steric hindrance. Table 1 (sample 7) shows that the conversion is around 38%, although the synthesis of DBN-PSU was conducted increasing the reaction time and the temperature.

It was shown by IR analysis that in protonated DBN, the positive charge is delocalized owing to the interaction with the π-electrons of the double bonds and the lone pair of the second N atom [44]. The delocalization is possible only if the reaction site is the nitrogen N$_1$ as shown in Scheme 1b. One can reasonably assume that the delocalization of the positive

Table 2 – Enthalpies of formation, ΔH_f, for chloro- and dichloromethyl-PSU calculated by AM1 semi-empirical calculations on optimized geometries.	
Compound	ΔH_f (kJ/mol)
PSUCH$_2$Cl (CH$_2$Cl ortho to ether linkage)	−514
PSUCH$_2$Cl (CH$_2$Cl ortho to C(CH$_3$)$_2$ linkage)	−485
PSU(CH$_2$Cl)$_2$(different rings both ortho to ether linkage)	−574
PSU(CH$_2$Cl)$_2$ (same rings both ortho to ether linkage)	−566

a)

b)
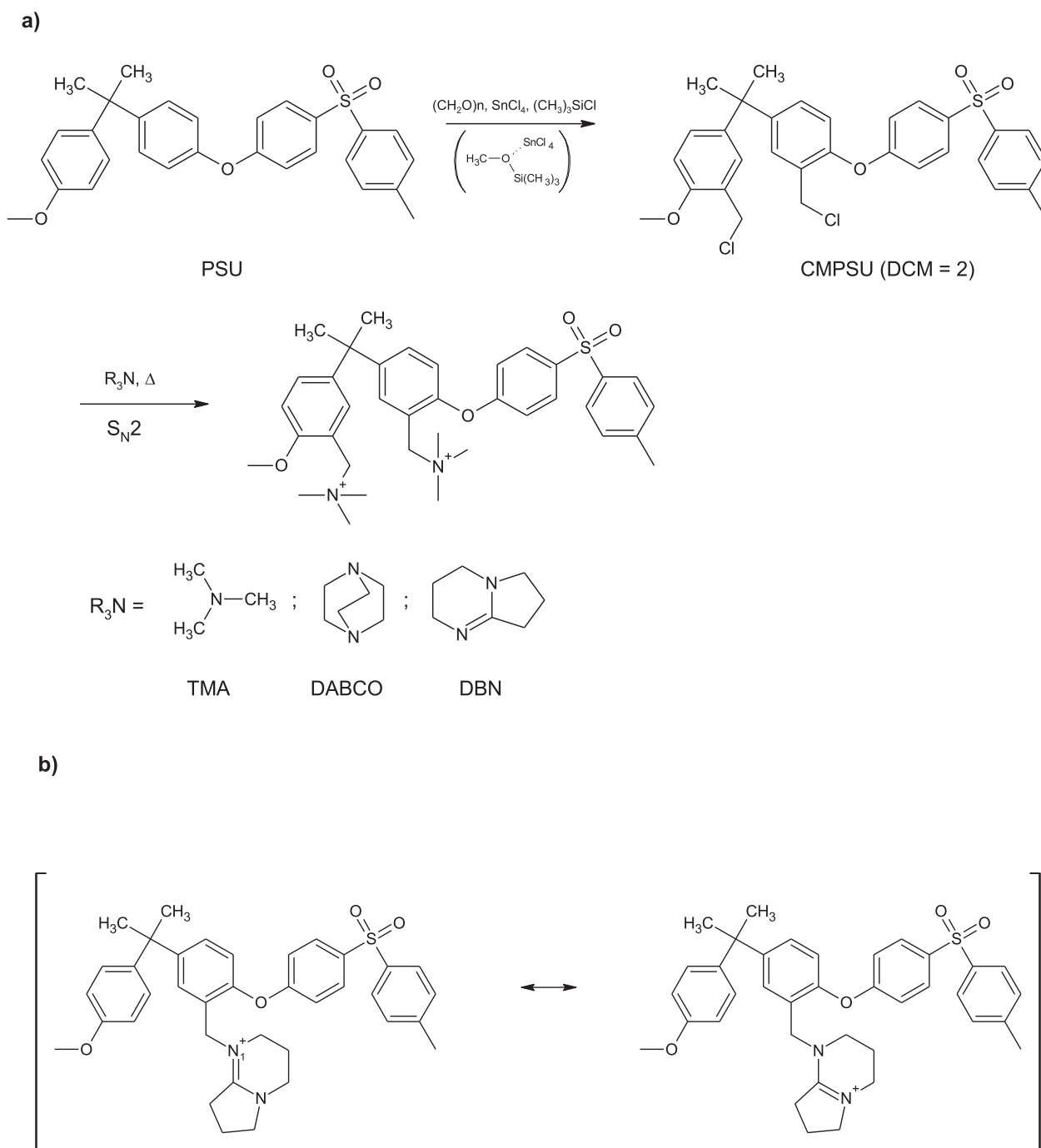
Scheme 1 — a) Reaction pathways for the synthesis of chloromethylated and of aminated PSU; b) delocalization of the positive charge in DBN-PSU.

charge is an important factor also for DBN-PSU. The delocalization can help to prevent the S_N2 degradation reaction, the ylide formation and the polymer degradation. This consideration can balance the lower reactivity.

Probably due to the steric hindrance and to the reduced hydrophilicity of DBN, the membranes were very brittle and difficult to use. A certain amount of TBF (20% w/w) used as plasticizer, improved the processability. The ^1H NMR spectra of DBN and DBN-PSU are shown in Fig. 4a and b respectively. From the comparison of the two spectra, the shift of the protons of DBN in α-position to N atoms at 3.6 ppm is consistent with protons in α to ammonium ions. The equivalence of protons 1, 3, 4 in spectrum 4b also indicate the presence of a delocalized charge, as shown in Scheme 1b. The signal at 4.6 ppm is ascribed to the CH_2-N^+ moiety. The ratio between the area of signals at 7.9, 4.6, and 3.6 ppm gives a conversion around 65%. A different value of conversion is instead obtained by titration (38%) as shown in Table 1. The conversion obtained by NMR analysis is often higher than that obtained by titration. In this specific
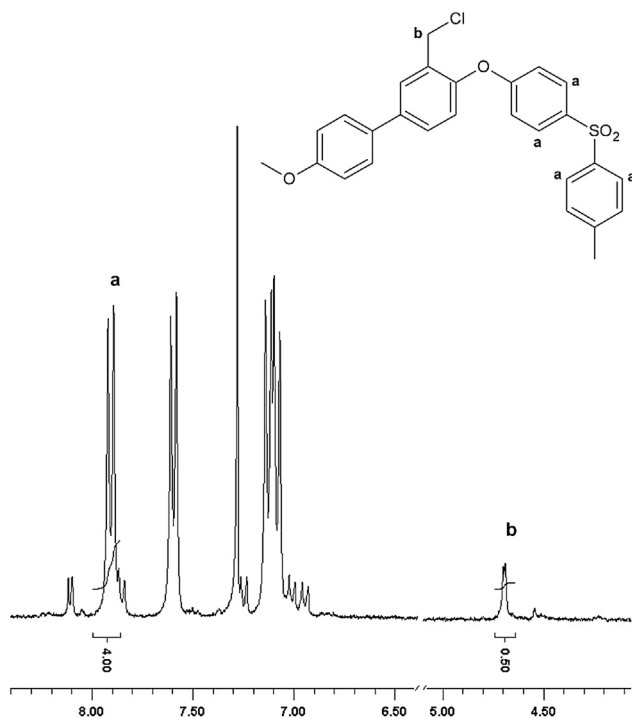
Fig. 3 – ¹H NMR spectrum of chloromethylated PPSU (DCM = 0.25).

example, one should also consider the error due to the presence of TBF in the membranes, although the value for DAM was corrected.

Cross-linked (XL) AEM

Scheme 2 shows the formation of the cross-linked polymer. We already reported the formation of XL *via* sulfone bridges during the annealing of sulfonated membranes. This is an electrophilic aromatic substitution that occurs in the solid phase in the presence of the casting solvent DMSO at a temperature in the range 150–180 °C [46,47]. An analogous reaction can be performed on the chlorosulfonic derivative instead of the sulfonated polymer. Due to the high reactivity of the chlorosulfonic moieties, the formation of XL is expected to occur at a lower temperature. Samples with different degrees of chloromethylation were mixed with 5% of chlorosulfonated PEEK and treated at 80 °C for 24 h (membranes "as cast", see experimental). The membranes were then thermally treated at 120 °C during 24 h. From the data shown in Table 1, it is evident that the XL reaction occurs also at 120 °C, where the quaternary groups are stable (see below): the water uptake decreases while the IEC remains the same (corrected for the percentage of the second component). The method of formation of XL at low temperature during the casting procedure appears general and very versatile.
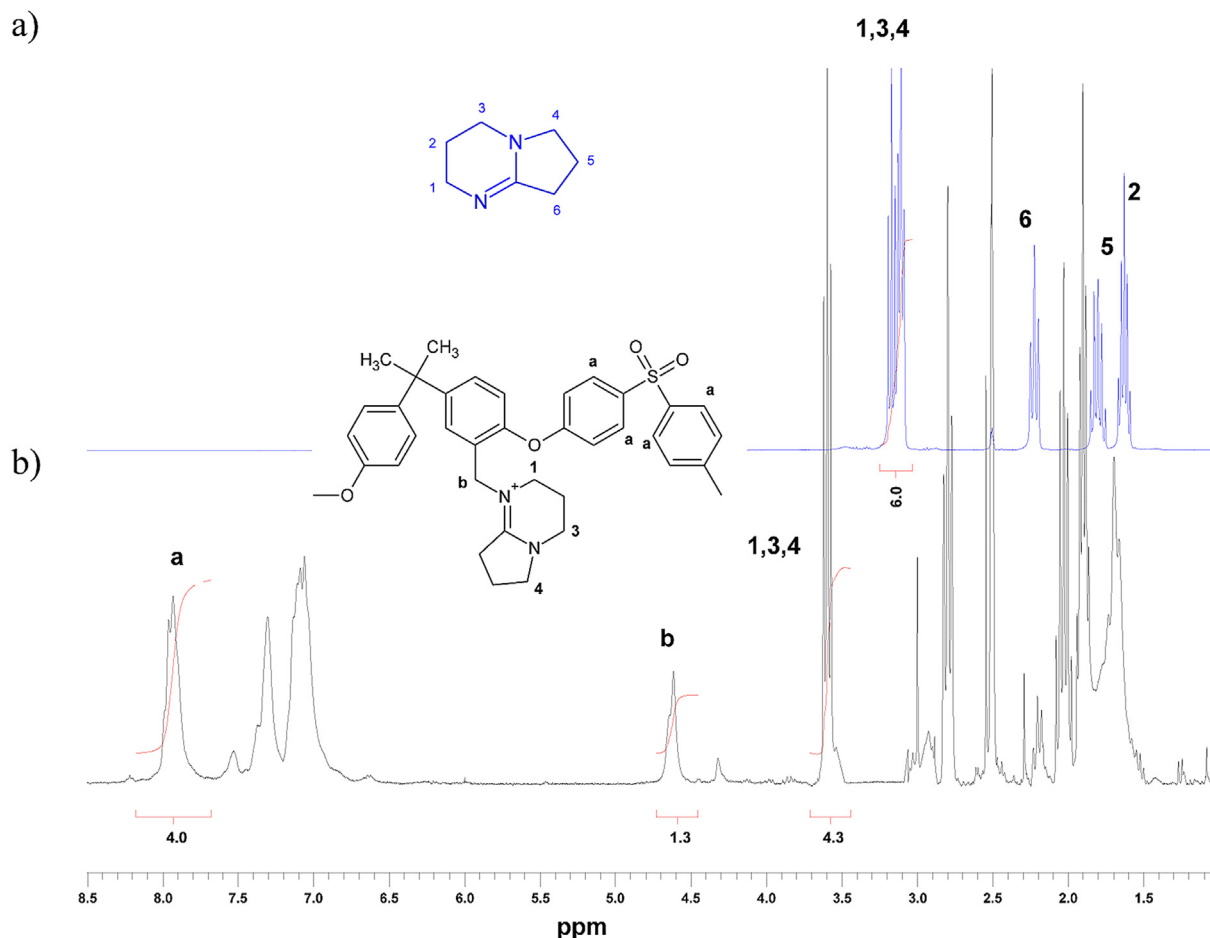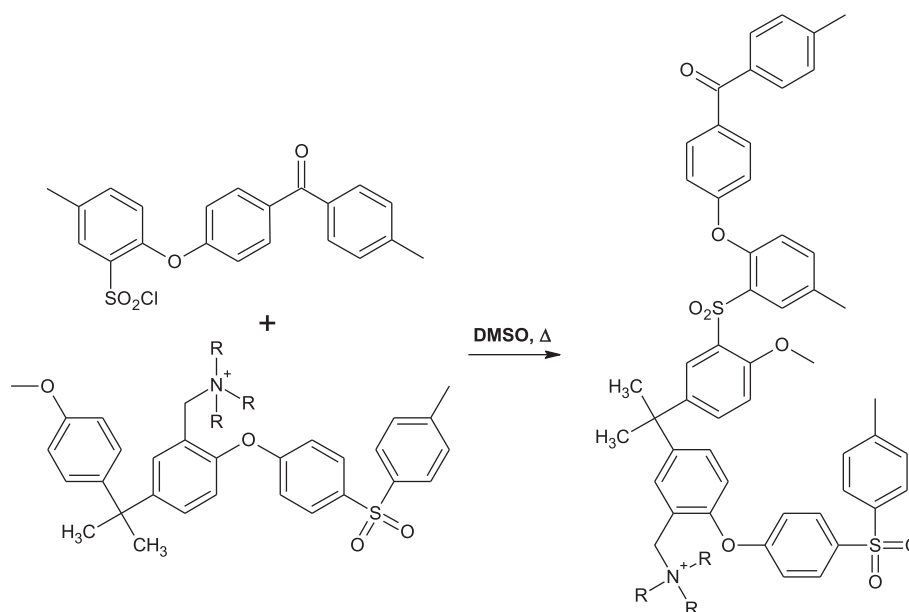

Fig. 4 – ¹H NMR spectra of a) DBN and b) DBN–PSU.

Scheme 2 – Cross-link reaction of aminated PSU and chlorosulfonated PEEK.

Mechanical properties, hydration and ionic conductivity

In the last years, the research on AEM is growing and some papers in the literature discuss their physical and chemical properties, including water uptake, conductivity, etc. However, like in proton exchange membranes, the properties and performances depend strongly on the history of ionomeric membranes – casting solvent, treatment and measurement conditions, equilibration times – leading to scattered literature data, which are difficult to compare [48].

Fig. 5 shows typical tensile stress–strain curves for TMA-PSU (hydroxide form) with two different degrees of amination. These curves are representative of rigid polymers with an elastic modulus around 1 GPa, a tensile strength in the order of 30 MPa, and a low elongation at break of
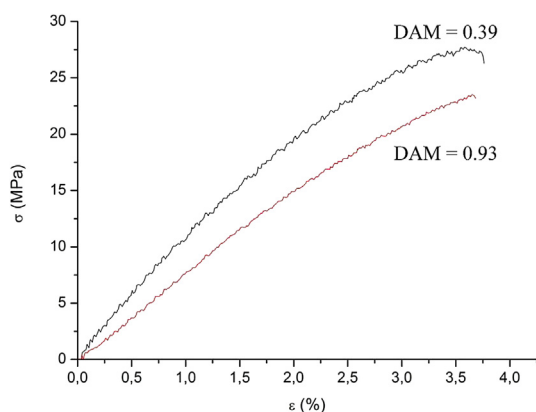

Fig. 5 – Typical tensile stress–strain curves of TMA-PSU derivatives in hydroxide form (blue: DAM = 0.39, red: DAM = 0.93) obtained at 25 °C and ambient humidity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

approximately 5%. The presence of a large amount of ionic groups, the quaternary ammonium ions, and the original stiffness of the PSU backbone lead to these properties, which are similar to those of highly sulfonated aromatic polymers [29,30,35,47,49]. The sample with higher DAM shows slightly lower mechanical performances, possibly due to a larger amount of water that has a plasticizing effect.

The water uptake follows a general trend for all studied AEM: the quantity of water increases with increasing degree of amination, approximately linearly for low DAM and then very strongly when DAM reaches and surpasses 1 (Table 1), so that some AEM with high IEC dissolve in water. The hydration remains however lower than in sulfonic acid derivatives with similar IEC [28], showing a lower hydrophilicity of AEM, probably related to the lower solvation of large hydroxide anions than of protons.

The ionic conductivity in water at 25 °C is also strongly dependent on the amination degree and derivatives of various amines show similar dependence vs DAM (Table 1). Many literature data can be found for TMA-PSU membranes. Apparently the results are different when the amination reaction is carried out on the preformed membrane of chloromethylated-PSU or directly in homogeneous solution. For membranes of TMA-PSU obtained in solution, cast in DMAc/water at 50 °C for 24 h and then heated under vacuum at 50 °C for 24 h, water uptake values of 90% and 140% were reported for an IEC of 1.7 and 1.8, respectively [50]. In general, the ionic conductivity increased linearly with the IEC and was on the order of 10 mS/cm at room temperature [8]. For membranes cast from DMSO and dried at 60 °C for 12 h, followed by 80 °C under vacuum for 4 h, a conductivity of 18 mS/cm was found for a sample with an IEC = 1.23 meq/g (WU = 50%), while the conductivity was 40 mS/cm for an IEC = 1.75 meq/g (WU = 123%) [51]. When the quaternization reaction was conducted on the preformed membrane cast using DMF at 70 °C and then dried at 120 °C for 1 h, a conductivity around

5 mS/cm was obtained at 24 °C [52]. PSU-TMA obtained with the same amination procedure, cast at 65 °C for 16 h and then further dried in vacuum at 80 °C for 10 h, showed a conductivity of 12 mS/cm for a WU around 25% and an IEC of 1.05 meq/g, while when the IEC was 1.18 meq/g and the WU 250%, the conductivity was 22 mS/cm. DABCO-PSU membranes with an IEC of 1.2 meq/g showed an area specific resistance of 1.05 Ωcm^2 [25]. We report in Table 1 also the ionic conductivity observed in 2 M KOH, like in Refs. [53—55]. The higher ionic conductivities observed in 2 M KOH are due to some KOH sorbed by the membrane [56—58]; however, the amount of conductivity enhancement is generally related to the degree of amination, probably due to some specific adsorption on cationic groups. The lower conductivity of DBN-PSU is related to the lower IEC. The ionic conductivity maximum is observed around IEC = 1.7 meq/g, where values above 10 mS/cm are attained at 25 °C in pure water. Higher IEC values make the AEM labile to swelling and gelification, such as sample 4 in Table 1; evidently, the large swelling leads to difficult contact with the electrodes for the conductivity measurement. From the point of view of conductivity, ionic exchange capacities around 1.7 meq/g seem optimal.

The ionic conductivity σ_i can be written:

$$\sigma_i = Fu_ic_i \tag{1}$$

Where F is Faraday's constant (96,500 C/mol). The hydroxide ion mobility u_i can be calculated from the ionic conductivity while the hydroxide ion concentration c_i is determined from the IEC of the AEM and its water uptake WU (in %). The calculated hydroxide ion mobility is plotted in Fig. 6 against the hydration number λ (or water uptake coefficient), which is inversely proportional to the hydroxide ion concentration and is defined according to the equation:

$$\lambda = \frac{WU \cdot 10}{IEC \cdot M(H_2O)}. \tag{2}$$

Where $M(H_2O)$ is the molar mass of water (in g/mol). Fig. 6 shows a linear correlation between the hydroxide ion mobility and the hydration number for all PSU derivatives, using the data reported in Table 1, which is consistent with the behaviour of strong electrolytes [59]. The interesting conclusion is that the molecular volume of the functionalizing amine does not modify the hydroxide ion mobility.

Previously investigated sulfonated aromatic polymers, such as SPEEK, show a much stronger power law dependence of the proton mobility on concentration, because the degree of
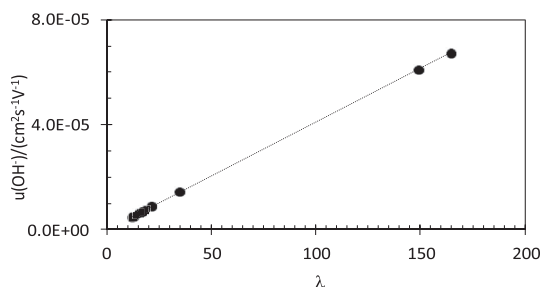

Fig. 6 — Hydroxide ion mobility as function of the hydration number for all AEM based on PSU. The data used for calculation are reported in Table 1.

dissociation of the sulfonic acid groups depends also on the hydration [23,31,60—64]. In AEM, the hydroxide groups are always dissociated and the mobility dependence is only due to the diffusion conditions in the more or less hydrated channels. Even at high dilution, the calculated hydroxide ion mobility is much below the reported value of 6×10^{-4} cm^2/V at infinite dilution in water [65], which can be related to the low connectivity and/or high tortuosity of ion-conducting hydrated channels, due to low hydrophilic-hydrophobic phase separation in AEM. This finding confirms recent reports for hydroxide-conducting ionomers [37,38,56,57,66,67].

Stability tests made by treatment of membranes during 168 h in 2 M KOH at 60 °C revealed an increased brittleness, indicating that the PSU backbone is indeed attacked by the OH$^-$ ions, as very recently reported [18]. For this reason, most ionic conductivity measurements could not be performed, because the samples broke inside the Swagelok cell. The ionic conductivity in 2 M KOH of the TMA derivative with the lowest DAM could instead be measured but not in water. The anionic conductivity in water of the DBN derivative after treatment is actually equal to the initial one (0.2 mS/cm) showing a low degradation in KOH, probably due to the bulky compound and the better delocalization of the positive charge on the two nitrogens of the cyclic amine. The cross-linked derivative shows also a stable ionic conductivity (0.2 mS/cm) indicating a low degradation, due to the stabilizing polymer reticulation. The two stabilization strategies investigated show thus a significant enhancement of the stability.

Conclusions

We studied the synthesis, properties and stability of AEM membranes containing quaternary ammonium ions, functionalized with various degrees of amination and using amines with different molecular volumes and different capacity to delocalize the positive charge, rendering a nucleophilic attack on the ammonium group and on the backbone more difficult.

The mechanical properties are typical of a rigid polymer with large elastic modulus and low elongation at break. The ionic conductivity can be above 10 mS/cm in water at 25 °C. The volume of the functionalizing amine does not modify the mobility of hydroxide ions. The stability test in 2 M KOH at 60 °C shows an increased brittleness of many ionomers, indicating an attack of the polymer backbone, except for the DBN derivative, where the positive charge of the nitrogen is probably better stabilized, and the cross-linked ionomer, demonstrating the stabilizing effect of a polymer reticulation.

The two stabilization strategies investigated should be considered for further optimization of AEM for operation under alkaline conditions.

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