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# Single-step synthesis of sulfonated polyoxadiazoles and their use as proton conducting membranes

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## Abstract

A single-step approach for the synthesis of sulfonated polyoxadiazoles from hydrazine sulfate was developed using non-sulfonated diacids in polyphosphoric acid. The post-sulfonation conditions were optimized by varying reaction time, medium and reagent concentrations in sulfuric acid, oleum and/or their mixtures. For the first time, a series of sulfonated polyoxadiazoles with ion exchange capacity (IEC) ranging from 1.26 to 2.7 meqiv. $g^{-1}$ and high molecular weight (about 40,0000 g $mol^{-1}$) were synthesized. The structures of the polymers were characterized by elemental analysis, $^1$H NMR, and FTIR. Sulfonated polyoxadiazole membranes with high thermal stability indicated by observed glass-transition temperatures ($T_g$) ranging from 364 to 442 °C in sodium salt form and from 304 to 333 °C in acid form and with high mechanical properties (storage modulus about 3 GPa at 300 °C) have been prepared. The membrane stability to oxidation was investigated by soaking the film in Fenton's reagent at 80 °C for 1 h. The sulfonated polyoxadiazole membranes exhibited high oxidative stability, retaining 98–100% of their weight after the test. Proton conductivity values with the order of magnitude of $10^{-1}$ to $10^{-2}$ S $cm^{-1}$ at 80 °C and with relative humidity ranging from 100% to 20% were obtained.

*Keywords:* Polyoxadiazole; PEMFC; Sulfonation; Proton conductivity; Fuel cell

## 1. Introduction

Oxadiazole-based polymers have recently attracted considerable attention as polymer light-emitting diodes [1–3], acid sensors [4], electron and proton conducting materials [5–7] due to their high chemical and thermal stability [8,9] as well as due to the aromatic and basic character of the oxadiazole ring [10]. The conjugated heterocyclic ring containing (C=N) pyridine-like nitrogen with the lone electron pair which does not participate of the aromatic sextet makes polyoxadiazoles and their derivatives potential candidates for application in fuel cells when doped and/or sulfonated because the nitrogen sites may favor additional points for proton jumps [5,6,11]. Recently, it was demonstrated that during the synthesis of polyoxadiazole by reaction between dicarboxylic acid and a salt of hydrazine a partial sulfonation occurs [5]. This fact had been overseen in the previous papers describing or applying this synthesis route [12–15]. Up to now an ion exchange capacity (IEC) of 1.26 mequiv. $g^{-1}$ could be confirmed [5,6]. This level of functionalization, however, is still too low to give a polyoxadiazole with high proton conductivity. The polyoxadiazole "dopping" by treatment with sulfuric acid in mild conditions [6] led to higher proton conductivity values (order of magnitude of $10^{-2}$ S $cm^{-1}$ at 50–80 °C), but covalently bonding sulfonic groups to the polyoxadiazole chain should potentially be a much more effective strategy to increase the polymer applicability in fuel cells. Besides increasing the ionic conductivity values, sulfonation of polymers might improve wet ability, antifouling capacity, solubility in solvents for processing and gas permeation properties, which are relevant for other applications in membrane technology.

Other routes for the synthesis of polymers and copolymers containing at least an ether and an oxadiazole group such as poly(ether oxadiazoles) and poly(ether ketones benzoxazole) is based on the nucleophilic substitution polymerization of bis-fluorphenyl and bis-hydroxy monomers [7,16–18]. By using sulfonated monomers, sulfonated oxadiazole telechelics were obtained [18] and used for functionalization of inor-

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ganic particles [11]. The synthesis of other sulfonated polymers starting from sulfonated monomers has also been reported in literature for fuel cell application [19–25]. Furthermore, sulfonated poly(ether oxadiazole)s were obtained in our group by the nucleophilic substitution polymerization of non-sulfonated monomers followed by post-sulfonation [16]. Post-sulfonation of polyoxadiazole or other polymers is possible by reaction under different conditions with a variety of sulfonated reagents such as sulfuric acid, sulfur trioxide, trimethylsilyl chlorosulfonate, chlorosulfonic acid and a mixture of them [16,26–29]. The choice of the sulfonation conditions depends on many factors such as the reactivity of the polymer and the sulfonated reagent, time for sulfonation, expected level of the functionalization degree, homogeneity, degradation, crosslinking and solubility of the sulfonated polymer. However, all these alternative routes led to sulfonated poly(ether oxadiazole)s with molecular weight not higher than 60,000 g $mol^{-1}$ [16,18]. A good polymer for fuel cell membrane formation, beside the high proton conductivity, should lead to flexible films, which could be easily manufactured in membrane-electrode-assemblies. When aiming large-scale production the polymer should be preferably prepared in a one-step procedure. These are exactly the main advantages of the polyoxadiazole synthesis by polymerization of dicarboxylic acid and hydrazine salt, which allows in one-step the production of polymers with molecular weight of about 40,0000 g $mol^{-1}$. However, in order to reach highly sulfonated polymers by this method a significant optimization of the conditions so far described in the literature has to be performed.

The aim of the present work is to find the optimal synthesis conditions which could lead to sulfonated polyoxadiazoles with high ion exchange capacity, high molecular weight and good mechanical properties to enable the casting of stable proton conducting membranes with high proton conductivity, especially at low humidity conditions. Proton conductive materials operating at these conditions are being worldwide searched to attend the requirements of the automotive industry for the implementation of fuel cells to power vehicles with low emission.

## 2. Experimental

### 2.1. Materials

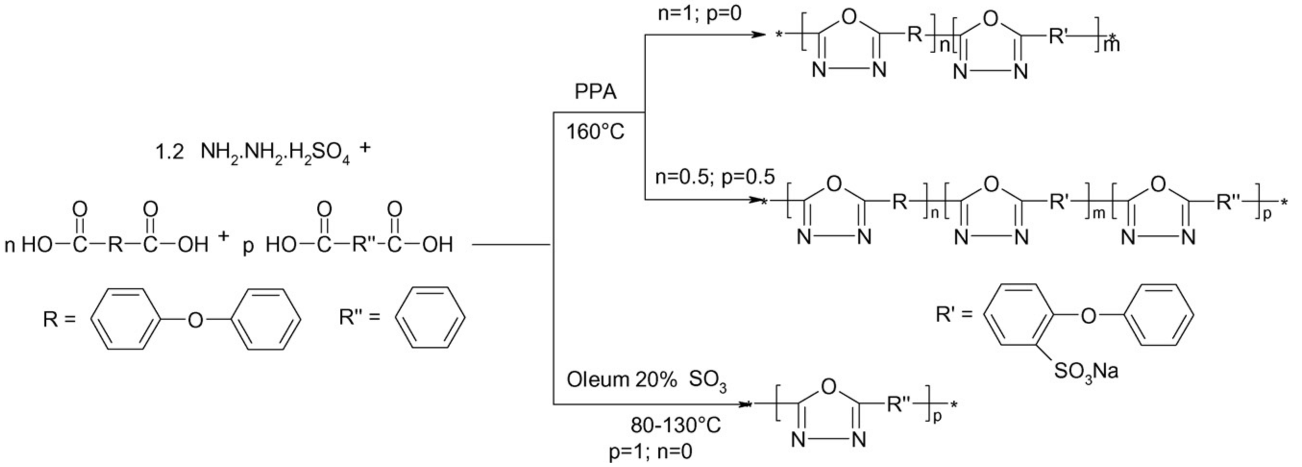
Dicarboxylic acid 4,4′-diphenylether (DPE) (99%, Aldrich), Dimethyl sulfoxide (DMSO) (>99%, Aldrich), fuming sulfuric acid (oleum) (puriss. pa. 20% $SO_3$, Riedel-de Häen, ACS reagent 30% $SO_3$, Aldrich and 65%, Merck), hydrazine sulfate (HS) (>99%, Aldrich), *N*-methyl-2-pyrrolidone (NMP) (99%, Aldrich), sodium hydroxide (NaOH) (99%, Vetec), sulfuric acid (95–97%, Vetec), poly(phosphoric acid) (PPA) (Aldrich), terephthalic acid (TA) (>99%, Fluka). All chemicals were used as received.

### 2.2. Polymer synthesis

The polymerizations were carried out according to Scheme 1, in a 500 mL three-necked flask equipped with a mechanical stirrer. Dry argon was continuously fed into the flask to keep the reaction atmosphere free of oxygen and water.

#### 2.2.1. Homopolymer sulfonated poly(diphenyether-1,3,4-oxadiazole) (SPODDPE)

The typical polymerization had the following steps: initially PPA was added to the flask and heated up to 100 °C under dry argon atmosphere. Then, HS was added to the PPA and homogenized through stirring and heating of the reaction medium. After reaching the reaction temperature (160 °C), DPE was added to the flask. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/DPE) were kept constants and equal to 10 and 1.2, respectively. The reaction conditions (temperature, molar dilution rate and molar monomer rate) were selected taking in account a previous study, where the optimization of the POD-DPE synthesis was performed with the help of a statistical experimental design [12]. Here, particularly the time of reaction was varied with the expectation to vary the sulfonation levels while keeping molecular weight high enough. After finishing the batch, the reaction medium was poured into tepid water (containing 5%, w $v^{-1}$



Scheme 1. Single-step synthesis for sulfonated polyoxadiazoles.

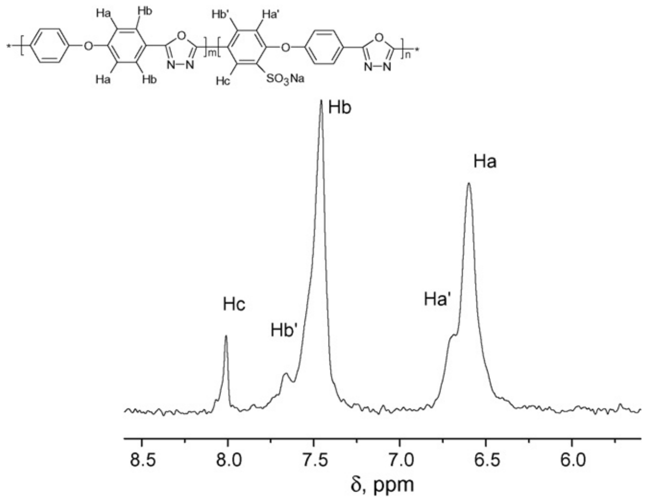


Fig. 1. $^1$H NMR spectrum of sulfonated poly(diphenylether-1,3,4-oxadiazole), SPODDPE (spectrum taken in $D_2SO_4$).

of sodium hydroxide), for precipitation of the polymer. The pH of this polymer suspension, initially acid, was neutralized and controlled through addition of 5% (w $v^{-1}$) NaOH aqueous solutions. The polymer was then filtrated and resuspended in water. Once more, the polymer suspension was neutralized with ‘a sodium hydroxide solution (ca. 5%, w $v^{-1}$). After neutralization, the polymer suspension was kept under stirring for 18 h at 25 °C, for removal of residual solvent. The polymer was filtered and resuspended in water at 80 °C under stirring for 3 h. Afterwards, the polymer was filtered once more and dried at 60 °C for 48 h. The final polymer yield was always close to 100% regarding the limiting reactant (HS or DPE, depending on the experimental condition). $^1$H NMR ($D_2SO_4$): $\delta = 8.0$ (s, Hc), 7.65 (d, Hb′), 7.45 (d, Hb), 6.70 (d, Ha′), 6.59 (d, Ha) (Fig. 1). FTIR (film, $cm^{-1}$): 3417, 3257 ($\nu$OH), 3096, 3070 ($\nu$C–H), 1597, 1487 ($\nu$C=C), 1467, 1417 ($\nu$C=N), 1396 ($\nu_{as}SO_2$ from covalent sulfonates, $R{-}SO_2{-}OR$), 1233 ($\nu$C–O–C), 1197 ($\nu_sSO_2$), 1065 ($\nu$C–O), 1085 ($\nu$C–O–C from oxadiazole ring), 1027 ($\nu_{as}$SO), 1010 ($\delta$C–H). [$(C_{14}H_8N_2O_2)$, IEC = 0] (236): Calcd. (%): C 71.19, N 11.86, S 0, N/C 0.167 S/C 0, [$(C_{14}H_8N_2O_2)_{0.5}\cdot(C_{14}H_8N_2O_5SNa)_{0.5}$, IEC = 1.74 meqiv. $g^{-1}$] (287): Calcd. (%): C 58.54, N 9.76, S 5.58, N/C 0.167 S/C 0.095; Found: [3 h, $(C_{14}H_8N_2O_2)_{0.65}\cdot(C_{14}H_8N_2O_5SNa)_{0.35}$, IEC = 1.26 meqiv. $g^{-1}$] (272): C 56.2, N 9.43, S 4.05, N/C 0.167 S/C 0.065, [4 h, $(C_{14}H_8N_2O_2)_{0.48}\cdot(C_{14}H_8N_2O_5SNa)_{0.52}$, IEC = 1.78 meqiv. $g^{-1}$] (289): C 48.6, N 8.14, S 4.74, N/C 0.167 S/C 0.098, [5 h, $(C_{14}H_8N_2O_2)_{0.46}\cdot(C_{14}H_8N_2O_5SNa)_{0..54}$, IEC = 1.86 meqiv. $g^{-1}$] (291): C 53.1, N 8.84, S 5.45, N/C 0.167 S/C 0.103, [6 h, $(C_{14}H_8N_2O_2)_{0.35}\cdot(C_{14}H_8N_2O_5SNa)_{0.65}$, IEC = 2.15 meqiv. $g^{-1}$] (303): C 45.7, N 7.74, S 5.65, N/C 0.167 S/C 0.124.

### *2.2.2. Copolymer sulfonated poly(diphenylether-phenylene-1,3,4-oxadiazole) (SpPODDPE)*

The copolymer SpPODDPE was prepared like procedure Section 2.2.1. with a reaction time of 3 h and by adding TA and DPE with the same total molar concentration. FTIR (powder, $cm^{-1}$): 3418, 3265 ($\nu$ OH), 3096, 3070 ($\nu$C–H), 2357 ($\nu N^+{-}H$), 1597, 1487 ($\nu$C=C), 1467, 1417 ($\nu$C=N), 1396 ($\nu_{as}SO_2$ from covalent sulfonates, $R{-}SO_2{-}OR$), 1233 ($\nu$C–O–C), 1197 ($\nu_sSO_2$), 1065 ($\nu$C–O), 1085 ($\nu$C–O–C from oxadiazole ring), 1028 ($\nu_{as}$SO), 1013 ($\delta$C–H). [$(C_{14}H_8N_2O_2)_{0.33}\cdot(C_{14}H_8N_2O_5SNa)_{0.33}\cdot(C_8H_4N_2O)_{0.33}$, IEC = 1.22 meqiv. $g^{-1}$] (237): Calcd. (%): C 60.17, N 11.82, S 4.45, N/C 0.196 S/C 0.074; Found: [$(C_{14}H_8N_2O_2)_{0.46}\cdot(C_{14}H_8N_2O_5SNa)_{0.25}\cdot(C_8H_4N_2O)_{0.29}$, IEC = 0.96 meqiv. $g^{-1}$] (235): C 43.78, N 8.31, S 2.37, N/C 0.190 S/C 0.054.

### *2.2.3. Homopolymer poly(phenylene-1,3,4-oxadiazole (pPOD))*

The polymerization was conducted following a modified procedure reported by Iwakura et al. [30] with the molar dilution rate (oleum/HS) and the molar monomer rate (HS/TA) equal to 10 and 1.2, respectively. Reaction time and temperature were also changed as follows: in a 500 mL three-necked flask equipped with stirrer, an air-condenser protected by a calcium chloride tube and stopper was placed oleum 20% $SO_3$. Under mechanical stirring, HS was added gradually and into the resulting homogeneous solution was dissolved TA. The mixture was heated at 90 °C for 2 h and then at 130 °C for 5 h. After finishing the batch, the reaction medium was poured into tepid water (containing 5%, w $v^{-1}$ of sodium hydroxide), for precipitation of the polymer. The pH of this polymer suspension was controlled according to Gomes et al. [13]. The polymer precipitate was filtered, washed several times with distilled water and dried for 48 h at 60 °C. $^1$H NMR ($D_2SO_4$): $\delta = 8.0$ (s, Hd) (Fig. 2). [$(C_8H_4N_2O)$, IEC = 0] (144): Calcd. (%): C 66.70, N 19.44, S 0, N/C 0.292 S/C 0; Found: [7 h, $(C_8H_4N_2O)$, IEC = 0] (235): C 57.38, N 16.9, S 0.36, N/C 0.294 S/C 0.0063. FTIR (powder, $cm^{-1}$): 3415 ($\nu$OH), 3091 ($\nu$C–H), 2358 ($\nu N^+{-}H$), 1568, 1479 ($\nu$C=C), 1429, 1415 ($\nu$C=N), 1352 ($\nu_{as}SO_2$ from alkyl sulfonic acid, $R{-}SO_2{-}OH$), 1188 ($\nu_sSO_2$), 1075 ($\nu$C–O–C from oxadiazole ring), 1014 ($\delta$C–H).

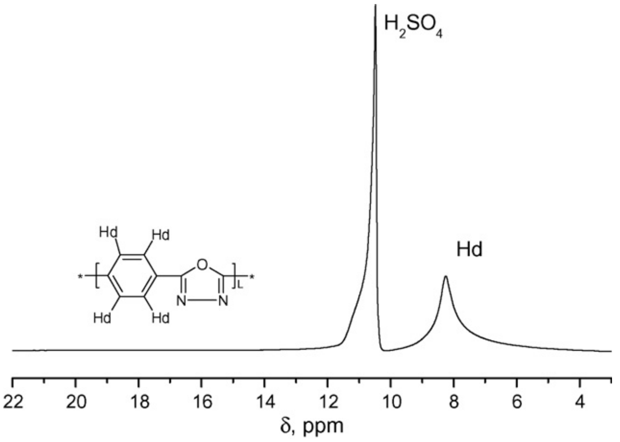


Fig. 2. $^1$H NMR spectrum of the homopolymer poly(phenylene-1,3,4-oxadiazole), pPOD (spectrum taken in $D_2SO_4$).

### 2.3. Post-sulfonation

Polymers were post-sulfonated by reacting with sulfuric acid (95–97%) and/or fuming sulfuric acid 20–65% $SO_3$ at 45–60 °C during 1 h to 40 days (960 h). As a typical example, 1 g of sufonated polyoxadiazole polymer was dissolved in 15 mL of concentrated sulfuric acid (95–98%) and vigorously stirred at 60 °C. Then, the polymer solution was gradually precipitated into ice-cold water containing $K_2CO_3$ under mechanical stirring until achieving a neutral pH. The polymer precipitate was filtered, washed several times with distilled water and dried for 12 h at 80 °C.

### 2.4. Membrane preparation

Homogeneous membranes were cast from polymer solutions with a concentration of 4 wt.% in NMP and DMSO. After casting, the NMP or DMSO was evaporated in a vacuum oven at 60 °C for 24 h. For further residual solvent removal, the membranes were immersed in water bath at 60 °C for 48 h and dried in a vacuum oven at 60 °C for 24 h. The final thickness of the membranes was about 30 μm. The sulfonated membranes were converted into its acid form by immersing the cast membranes in 1.6 M $H_3PO_4$ at room temperature for 24 h, followed by immersion in water for 2× 24 h to ensure total leaching of residual phosphoric acid.

### 2.5. Structural characterization

The polymer structures were characterized by elemental analysis, $^1$H NMR and infrared spectroscopy. Elemental analyses were conducted on a Carlo Erba Elemental Analyzer-Mod 1108. $^1$H NMR spectra were obtained in $D_2SO_4$ at 25 °C using a Bruker DMX-300 spectrometer. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000–400 $cm^{-1}$, using polymer films and polymers in the bulk form.

### 2.6. Molecular weight measurements

A Viscotek SEC apparatus equipped with SEC 10.000 Eurogel and PSS Gram 100, 1000 columns, with serial numbers HC286 and 1,51,5161 and size 8 mm × 300 mm was employed to evaluate the weight average molecular weights of the polymer samples. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 309 to 94,4000 g $mol^{-1}$. A solution with 0.05 M lithium bromide in DMAc was used as carrier.

### 2.7. Ionic conductivity

Ionic conductivity was measured by the AC impedance spectroscopy in the frequency range 10–$10^6$ Hz at signal amplitude $\leq$100 mV and obtained from the impedance modulus at zero phase shift (high frequency side) with 20–100% of relative humidity (RH). Measurements were performed with a flow cell purged with wet nitrogen; relative humidity was controlled by bubbling nitrogen gas in water heated at a suitable temperature between 30 and 80 °C. The impedance measurements were carried out on stacks containing up to five membranes (cumulative thickness around 500 μm). The spectrometer used was a Zahner IM6 electrochemical workstation.

### 2.8. Water uptake

Water uptake was measured by immersing two samples (around 100 mg each) of membrane in deionized water bath conditioned at 25–60 °C for 24 h. Before measuring the weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel. The water uptake was calculated as the ratio (in weight) of adsorbed water on the dry sample weight. The water uptake values reported correspond to the average value of the two samples.

### 2.9. Oxidative stability

Oxidative stability of membranes was evaluated by immersing the films into Fenton's reagent (3% $H_2O_2$ containing 2 ppm $FeSO_4$) at 80 °C for 1 h.

### 2.10. Thermal and mechanical analysis

Dynamic mechanical thermal analysis (DMTA) was used for determination of glass transition temperature ($T_g$), storage modulus ($E'$), loss modulus ($E''$) and loss tangent ($\tan\delta$). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1 Hz and at an initial static force of 0.1 N. The temperature was varied from 25 to 500 °C at a heating rate of 2 °C $min^{-1}$ and at a constant strain of 0.05%.

## 3. Results and discussion

A series of novel sulfonated polyoxadiazoles were synthesized by three different methods: (1) post-sulfonation in mixture of fuming sulfuric acid 20–65% $SO_3$ and sulfuric acid (95–97%) at 45 °C during 1–120 h, (2) post-sulfonation in sulfuric acid (95–97%) at 60 °C during 1–40 days and (3) single-step optimized method of synthesis at high temperature (160 °C) using hydrazine sulfate in poly(phosphoric acid) during 3–6 h. The homopolymer poly(phenylene-1,3,4-oxadiazole) (pPOD), was synthesized in fuming sulfuric acid 20% $SO_3$ because the oleum has been shown to be a better solvent than poly(phosphoric acid) for this polymer [31,32]. Reaction time and temperature were slightly higher than all conditions reported by Iwakura et al. [30] in order to investigate whether the sulfonation of polyoxadizoles containing only a phenylene ring attached to the main chain could occur or not. On the other hand, as shown in Scheme 1, for the other polyoxadiazoles containing a diphenylether group attached to the main chain, poly(phosphoric acid) was selected as solvent to avoid sulfonation of polymers and production of water soluble polymers due to the high sulfonation degree as a consequence of the high reaction time and temperature for polyoxadiazole synthesis.

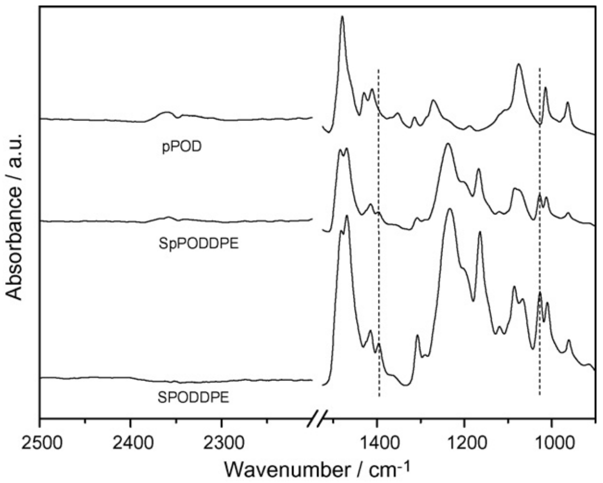


Fig. 3. FTIR spectra of SPODDPE (IEC = 1.26 meqiv. $g^{-1}$), SpPODDPE (IEC = 0.96 meqiv. $g^{-1}$) and pPOD (IEC = 0) in the region 1500–900 $cm^{-1}$.

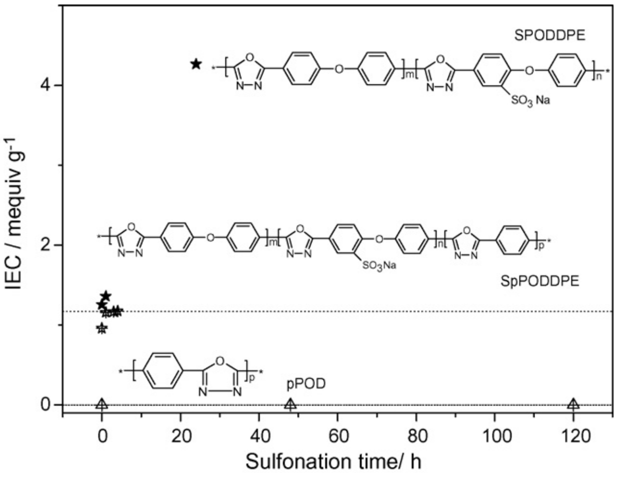


Fig. 4. Ion exchange capacity (IEC) as a function of post-sulfonation time in a mixture of fuming sulfuric acid (20–65% $SO_3$) and sulfuric acid (95–97%) at 45 °C for the SPODDPE, SpPODDPE and pPOD polymers.

### 3.1. Polymer synthesis

The sulfonation of all polyoxadiazoles involves an eletrophilic substitution reaction which is activated by electron donating groups attached to the aromatic ring. For the synthesis performed in poly(phosphoric acid), the eletrophilic agent ($SO_3$) comes from the sulfuric acid inherent to the hydrazine sulfate salt ($N_2H_4{\cdot}H_2SO_4$). Despite of the fact that the homopolymer pPOD was synthesized in oleum and at high temperature (up to 130 °C), it should not be expected that sulfonation occurs under this synthesis condition. The oxadiazole ring is an electron-withdrawing group and the phenylene ring is an extremely electron-deficient group which reduces considerably the reactivity of the eletrophilic substitution reaction in the aromatic ring. This expectation is confirmed by analyzing the elemental analysis, FTIR and $^1$H NMR results. Though traces of sulfur (0.36%) are detected by elemental analysis for the homopolymer pPOD, the analysis of the infrared spectrum indicates that this residual sulfur is not bound to the polymer. Infrared spectra for the polymer samples are shown in Fig. 3. The analysis of this figure indicates that the sulfonic acid groups are chemically attached to the polymer chain only for the polyoxadiazoles containing the ether linkage. In addition to the two peaks at ca. 1600–1480 $cm^{-1}$ arising from C=C stretching of the aromatic groups observed in all spectra, peaks placed at 1396, 1197 and 1027 related to the asymmetric $SO_2$, symmetric $SO_2$ and asymmetric SO stretches, respectively, are observed for the polyoxadiazoles containing the ether linkage only. In covalent sulfonates, $R{-}SO_2{-}OR$, the asymmetric and symmetric $SO_2$ stretching vibration bands occur at 1420–1310 $cm^{-1}$ and 1235–1145 $cm^{-1}$, respectively [33,34]. Weak signals placed at 1352–1188 $cm^{-1}$ are indeed observed for the homopolymer pPOD, but these signals are believed to be related to asymmetric and symmetric $SO_2$ stretch of sulfonic acids, respectively [33]. A signal placed at 2358 $cm^{-1}$ with higher intensity is observed for pPOD polymer, indicating the protonation of the nitrogen of the oxadiazole rings by residual sulfonic acids. The $^1$H NMR spectrum with only a singlet (Fig. 2) confirms that the homopolymer pPOD is not sulfonated during the synthesis.

Optimized synthesis methods for polyoxadiazoles containing a diphenylether group attached to the main chain with high molecular weight and solubility in organic solvent have been reported in literature [12,13]. In the present work, these methods were taken as starting point, keeping constant all synthesis variables and producing SPOD-DPE with ion exchange capacity (IEC) equal to 1.26 meqiv. $g^{-1}$. The IEC values for the polymers were determined by elemental analysis, which usually has an excellent agreement to other quantitative analysis like $^1$H NMR and infrared spectroscopy as shown by Gomes et al. [5]. Herewith, IEC is used instead of sulfonation degree (SD) to quantify the sulfonation level [5] because IEC takes into account the effective number of sulfonic acid groups per polymer unity, making the comparison easier.

### 3.2. Post-sulfonation

The post-sulfonation was first performed in a mixture of fuming sulfuric acid (20–65% $SO_3$) and sulfuric acid (95–97%) (oleum:$H_2SO_4$ 1:2) at 45 °C. Fig. 4 shows the IEC values as a function of post-sulfonation time for the SPODDPE, SpPODDPE and pPOD polymers. For the SPOD-DPE, after 1 h post-sulfonation in oleum (20% $SO_3$):$H_2SO_4$ (1:2) at 45 °C only water soluble polymers were obtained. Increasing the proportion of sulfuric acid, oleum (20% $SO_3$):$H_2SO_4$ (1:3), after 1 h it was possible to obtain a SPODPDE with higher IEC (1.36 meqiv. $g^{-1}$) than the starting polymer (1.26 meqiv. $g^{-1}$) and with quantitative yield. However, the molecular weight decreased significantly (from 3,58,000 to 17,000 g $mol^{-1}$). Under these conditions and with further increase of time from 2 to 96 h, only water soluble polymers were obtained. By using only fuming sulfuric acid (65% $SO_3$), a water insoluble polymer with IEC equal to 4.27 meqiv. $g^{-1}$ was indeed synthesized but it was also insoluble in organic solvents and therefore not useful for membrane preparation. For the SpPOD-DPE, the post-sulfonation reaction in oleum (20% $SO_3$):$H_2SO_4$ (1:2) during 1–4 h at 45 °C resulted in water insoluble polymers with slightly higher IEC values (about 1.17 meqiv. $g^{-1}$) than the starting IEC polymer (0.96 meqiv. $g^{-1}$) but with very low yield (lower than 25%). As the starting polymers, all post-sulfonated SpPOD-DPE polymers were insoluble in organic solvents like NMP and DMSO and therefore not useful for dense membrane preparation. For the pPOD, the post-sulfonation reaction in oleum (30% $SO_3$):$H_2SO_4$ (1:2) during 1–120 h at 45 °C did not result in sulfonated polymers. These results show very clearly the difference in the reactivity of the polymers, which is explained by the electron-donating effect of the ether linkage which activates the ring for the eletrophilic sulfonation reaction. Despite decreasing the reactivity for the sulfonation reaction, it was expected that the introduction of phenylene groups in the polyoxadiazole chain (copolymer SpPODDPE) should enable a tight control of the sulfonation level, preventing solubility of the polymer in water. An additional reason was the increase of stability and acidity due to the electron-deficient phenylene group attached to a deactivating oxadiazole ring. The preliminary results indicate that by this method, it is very difficult to have a strict control of the IEC with quantitative yield and that the increase of the sulfonation level does not result in polymers soluble in organic solvents. The insolubility of pPOD and SpPODDPE makes their characterization very difficult, thus further post-sulfonation syntheses were performed with the SPODDPE polymer only. Due to the strong polymer degradation observed in mixture of fuming sulfuric acid (20% $SO_3$) and sulfuric acid (95–97%), further tests were performed in sulfuric acid (95–97%) only.

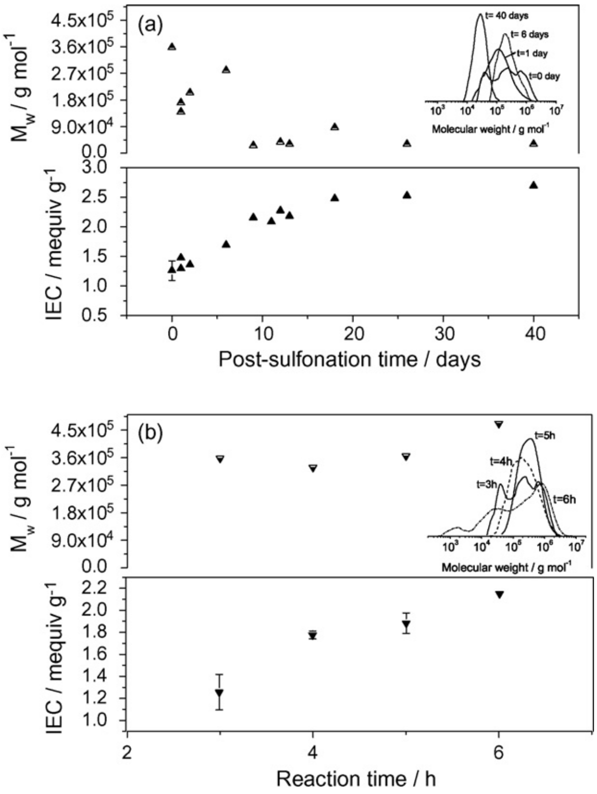


Fig. 5. Ion exchange capacity (IEC) and average mass molecular weights as a function of (a) post-sulfonation time for the SPODDPE polymers in sulfuric acid (95–97%) at 60 °C; (b) single-step reaction time at 160 °C using hydrazine sulfate in poly(phosphoric acid). The insert shows the SEC profiles relative to polystyrene standard.

### 3.3. Ion exchange capacity and average mass molecular weight

Fig. 5(a) shows the IEC values and average mass molecular weights ($M_w$) as a function of post-sulfonation time in sulfuric acid (95–97%) at 60 °C for the SPODDPE polymers. The analysis of Fig. 5 indicates that the sulfonation level could be well controlled for each time, reaching an IEC value of 2.70 meqiv. $g^{-1}$ after 40 days. High molecular weights were confirmed by size exclusion chromatography (SEC), as shown by the insert SEC profiles relative to polystyrene standard. Though the molecular weights of the sulfonated samples decrease with increasing sulfonation time, high molecular weights in the order of magnitude of $10^4$ g mol$^{-1}$ were achieved enabling the casting of stable membranes. Additionally to the IEC, molecular weight is an important variable to control the film forming capacity and water swelling [20]. High molecular weights lead to the formation of stable membranes and reduce swelling. The high molecular weight obtained for the SPOD-DPE (3,58,000 g mol$^{-1}$) can be attributed to the formation of three-dimensional crosslinked structures [12]. The low polycondensation reaction time (3 h) leads to sample heterogeneity which is reflected in the trimodal SEC curve characterized by high polydispersity. With the post sulfonation the $M_w$ decreases as well as the polydispersity. In order to obtain higher molecular weights and lower polydispersity by a one-step reaction, further synthesis conditions were tested, keeping constant all synthesis parameters optimized in previous works, except the time [12,13], which was increased from 3 to 6 h. The results are shown in Fig. 5(b). As one may see in this figure, polymers with higher average mass molecular weights and simultaneously with higher IEC were obtained, by increasing the synthesis time. The increase of time also resulted in more homogeneous samples with monomodal distribution as seen in the insert SEC profiles. The optimum time seems to be 5 h. Increasing further the time to 6 h, species with lower molecular weights in the order of magnitude of $10^3$ g mol$^{-1}$ started to be formed due to the simultaneous degradation reaction [12].

Comparison between both methods shown in Fig. 5, clearly indicates that the post-sulfonation method (Fig. 5a) requires larger time to obtain the same sulfonation level compared to the single-step optimized method of synthesis at high temperature (Fig. 5b). For instance, the polymer IEC equal to 2.15 meqiv. $g^{-1}$ is only obtained after 11 days using the post-sulfonation method in contrast to 6 h for single-step method. An additional disadvantage is the lower molecular weight obtained by post-sulfonation, in the order of $10^4$ g mol$^{-1}$. Thus, the optimized single-step method for synthesis of sulfonated polymers at high temperature provides an efficient method to obtain SPODDPE polymers with lower reaction times and higher molecular weights than by the post-sulfonation reaction.

The infrared spectra of the SPODDPE films with IEC ranging from 1.36 to 2.48 meqiv. $g^{-1}$ are shown in Fig. 6. The polyoxa-

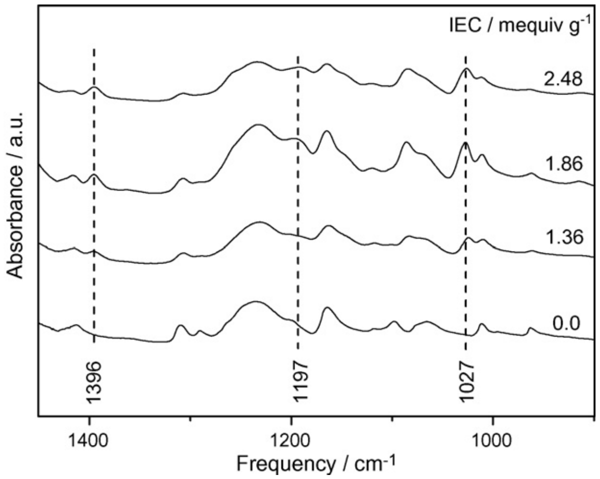


Fig. 6. FTIR spectra of SPODDPE with different IEC in the region 1,450–900 cm$^{-1}$.

diazole containing a diphenylether group attached to the main chain with IEC equal to zero was synthesized and characterized in a previous work [35]. As seen in this figure, the assignments placed at 1396, 1197 and 1027 cm$^{-1}$ characteristics of asymmetric $SO_2$, symmetric $SO_2$ and asymmetric SO stretches of covalent sulfonates, respectively, increase with IEC.

### 3.4. Ionic conductivity and water uptake

Membranes with the SPODDPE polymers were prepared and their ionic conductivity values tested. In Fig. 7a the ionic conductivity values of SPODDPE membranes are shown as a function of IEC measured at 25 °C with RH = 100%. As expected, the higher the IEC, the higher the ionic conductivity. The analysis of Fig. 7a also indicates that for the IEC about 1.7 meqiv. g$^{-1}$, a sharp increase in the conductivity values is observed. This result may be attributed to the beginning of the ionic cluster percolation and the hydratation state of the membranes with different IEC values. Similar explanation has been given in the literature for sulfonated copoly (aryl ether nitrile)s [23]. The effect of the sulfonation level on the polymer hydrophilicity is qualitatively illustrated in Fig. 7b by FTIR in the region 3750–2850 cm$^{-1}$. The peaks at 3414–3220 cm$^{-1}$ are related to the absorbed water and are assigned to the O–H stretch of the hydrogen-bonded groups intramolecular and intermolecular, respectively. The absorbed water shown in this figure is originated after drying the films and exposing them to the atmospheric moisture for 5 min at room temperature. As expected, the higher the IEC, the higher is the polymer hydrophlicity. The higher water absorption with increasing polymer IEC observed by FTIR supports the quantitative water uptake experiments measured by weight difference between dry and wet polymer samples after immersion in water bath, as shown in Fig. 8.

Taking into account the high ionic conductivity values shown in Fig. 7a, the membranes with IEC higher than 1.7 meqiv. g$^{-1}$ were chosen to be converted into their acid form and their proton conductivity values as a function of temperature with RH = 100% were measured. SPODDPE membranes with IEC

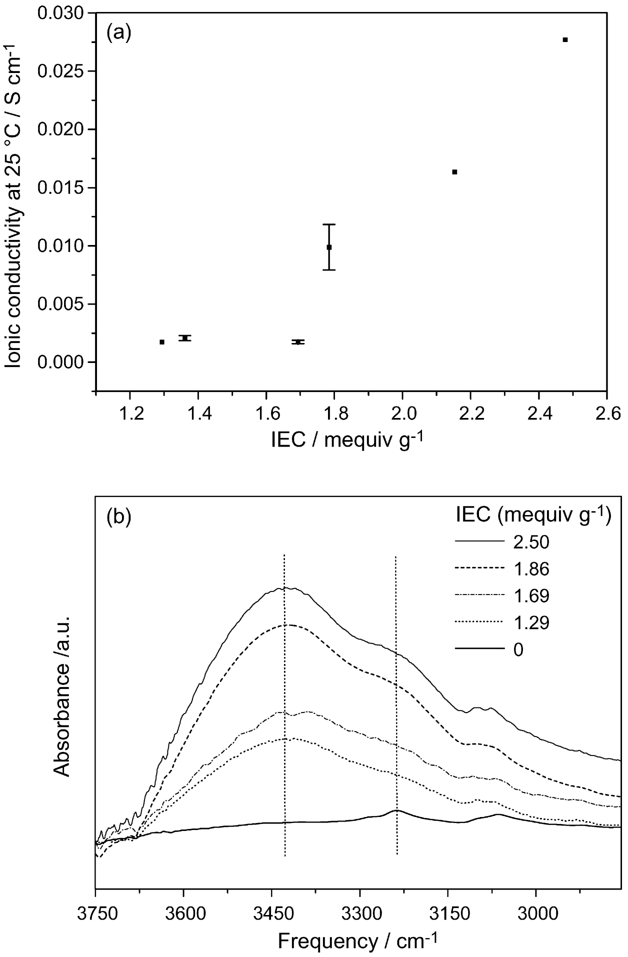


Fig. 7. (a) Ionic conductivity of SPODDPE membranes as a function of IEC measured at 25 °C with RH = 100%; (b) FTIR spectra of SPODDPE with different IEC in the region 3750–2850 cm$^{-1}$.

higher than 2.15 meqiv. g$^{-1}$ were water soluble at temperatures of 60 °C and not further tested. The results are shown in Fig. 8. The significant difference between the ionic conductivity of polymers in salt (Fig. 7a) and in acid form (Fig. 8) was also previ-

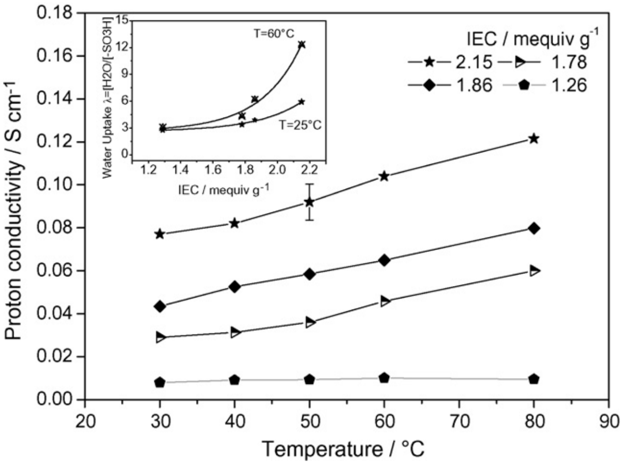


Fig. 8. Proton conductivity of SPOD-DPE membranes with different IEC as a function of temperature with RH = 100%. The insert shows the water uptake (expressed in number of water molecules per sulfonic acid group) in liquid water as a function of the polymer IEC and temperature.

ously reported by us for the sulfonated polyoxadiazoles with IEC equal to 1.26 meqiv. $g^{-1}$ (SD = 17) in salt and in acid form [5] and attributed to the fact that larger ions tend to have lower conductivity and their relative values to the polymers in acid form agree well with some reports in literature for Nafion with $H^+$ and alkali metal cations [36]. Proton conductivity of membranes in the acid form reached the order of magnitude of $10^{-1}$ S $cm^{-1}$ at 80 °C. The high proton conductivity values obtained may be attributed to the structure of the SPODDPE, which possess in its structure both proton donor ($SO_3H$) and acceptor sites (nitrogen of oxadiazole rings) being able to transport protons by the dissociation of their anionic counterion. Furthermore, the flexibility of the polymer chains due to the diphenyl ether group attached in the main chain, as well as the oxygen lone pair in the same ether group probably favor the proton jumps through the pyridine-like nitrogen sites and the sulfonic acid groups.

Compared to other polymers with IEC values in the range of 1.78–2.15 meqiv. $g^{-1}$, it can be affirmed that the proton conductivity values measured for the polyoxadiazoles described in this paper ($10^{-2}$ S $cm^{-1}$ at 25 °C and 100% RH) are high. For instance proton conductivity in the order of $10^{-6}$ to $10^{-4}$ S $cm^{-1}$ at room temperature and 100% RH has been measured [37] for polybenzimidazoles with IEC in the range 0–2.57 meqiv. $g^{-1}$. The lower proton conductivity of other sulfonated polymers containing basic nitrogen with similar or even higher IEC reported in literature can be attributed to the effect of nitrogen protonation by the sulfonic acid groups, which depends on chemical structure and the basicity of groups bearing nitrogen sites, polymer architecture which influences proton conduction and/or phase separation, effective number of sulfonic acid groups per polymer unity and polymer hydrophilicity.

The proton transport through the sulfonated polymer is strongly dependent on the number of water molecules per sulfonic group (λ). As shown in Fig. 8, water uptake increases with increasing IEC and temperature. As the IEC increases, the increase in the number of sulfonic acid groups leads to a higher absorption of water. The water within the membrane works as carrier for the proton and justifies the higher proton conductivity values obtained for membrane with higher IEC.

The λ value gives information about the mechanism of proton transport, whether protons coordinated to $H_2O$ molecules and/or to the sulfonic acid groups are a result of the rather free mobility of $H_3O^+$ cations in a liquid like phase or whether the transport occurs within a hydrogen bonded structure where the proton jumps between more stationary donor and acceptor sites [38]. According to Kreuer et al. [39], electronic structure calculations indicate that 2–3 molecules of water per sulfonic acid group are necessary for dissociation of perfluorinated polymers like Nafion and when six molecules of water are added, separation of the dissociated anion is observed. The conductivity is essentially carried by the diffusion of hydrated protons such as $H_3O^+$ and $H_5O_2^+$ which originate from the complete dissociation of the sulfonic acid functions [40]. By increasing the number of molecules of water per sulfonic acid group (higher than 10 in sulfonated polyaromatic membrane and higher than 13 in Nafion membranes) water as a second phase is usually formed and the proton diffusion occurs like in a liquid system [40]. Based on the water uptake (λ) values of about 3 at 25–60 °C for the SPODDPE membrane with IEC equal to 1.26 meqiv. $g^{-1}$ (Fig. 8), it should be expected for this temperature range that the polymer proton conductivity is essentially carried by the diffusion of protons within a hydrogen bonded structure. In Fig. 9(a)

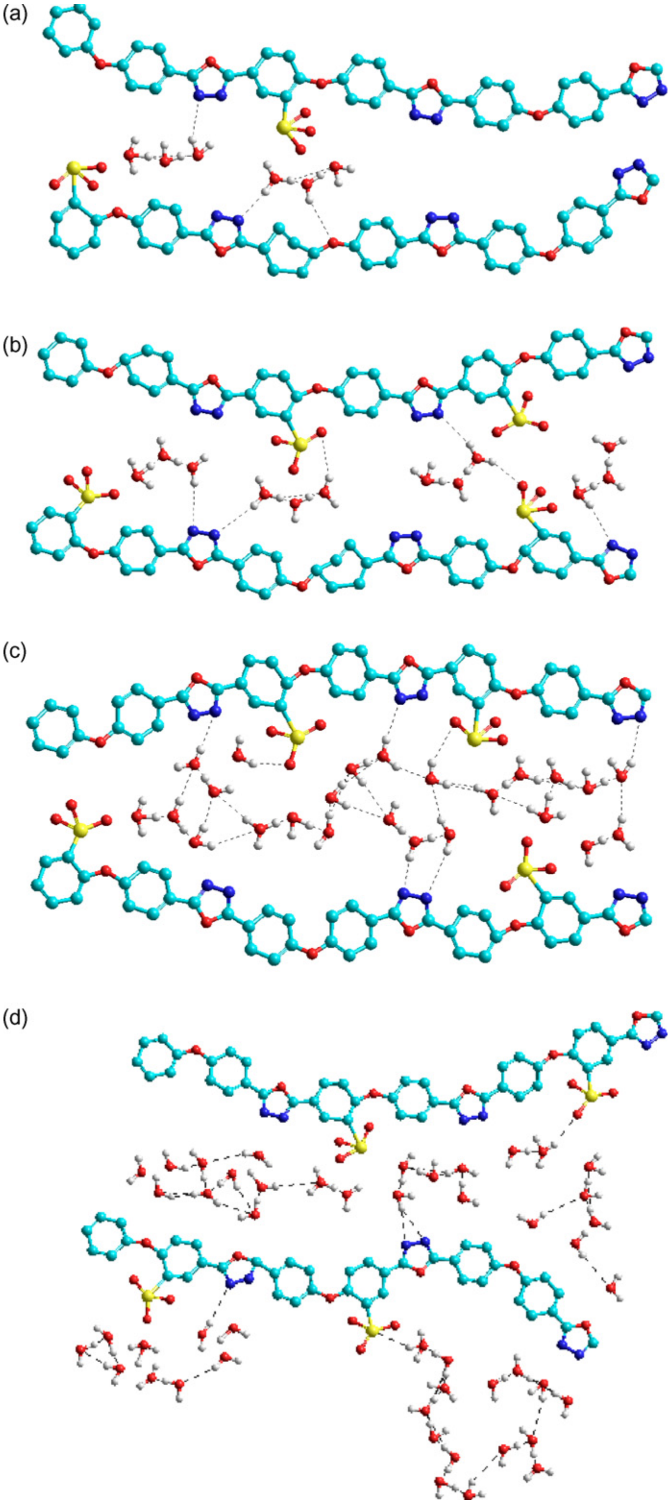


Fig. 9. Expected hydration mechanisms for protonated SPODDPE membranes with IEC equal to 1.26 meqiv. $g^{-1}$ at high RH (a), IEC equal to 2.15 meqiv. $g^{-1}$ at low RH (b) and IEC equal to 2.15 meqiv. $g^{-1}$ at high RH (c–d).

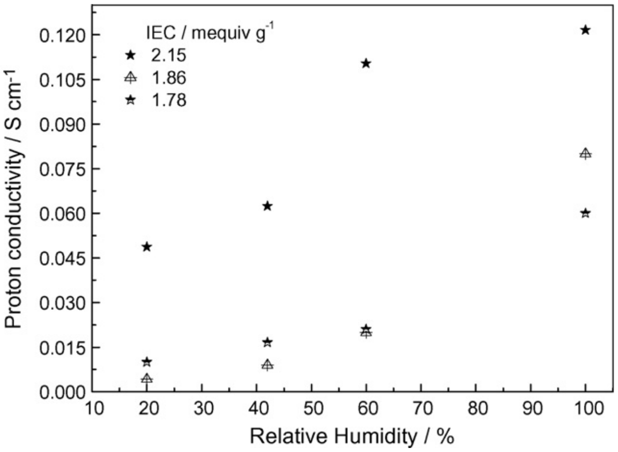


Fig. 10. Proton conductivity of SPOD-DPE membranes with different IEC as a function of relative humidity (RH) measured at 80 °C.

an expected hydration mechanism of the protonated SPODDPE membrane with IEC equal to 1.26 meqiv. $g^{-1}$ is shown. On the other hand, for the "protonated" SPODDPE membrane with IEC equal to 2.15 meqiv. $g^{-1}$, a higher hydration level is experimentally achieved ($\lambda = 6$ at 25 °C and $\lambda = 12$ at 60 °C). In this case, the proton should associates with more water molecules which could assume the structure depicted in Fig. 9c and d.

Fig. 10 shows the proton conductivity of SPOD-DPE membranes with different IEC as a function of relative humidity (RH) measured at 80 °C. As expected, the conductivity of SPOD-DPE membranes has a strong dependence on the level of hydration. The high proton conductivity values at RH = 100% sharply decrease upon dehydration. The high proton conductivity for the SPOD-DPE membrane with IEC equal to 2.15 meqiv. $g^{-1}$ may be attributed to the high water retention capacity of this membrane, keeping a minimum hydration level in the membrane. As one may see, for all membranes high proton conductivity in the order of magnitude of $10^{-2}$ S $cm^{-1}$ at 20% RH were obtained. Taking into account the low level of external humidification under this condition, this result can be attributed first to the fact of the $-SO_3H$ groups are not much separated from each other [38] and also to the presence of additional sites for protonation which strengthen the mechanism of proton transport by the diffusion of protons within a hydrogen bonded structure. This structure might resemble that depicted in Fig. 9b. Due to the high number of interaction sites not only the transport is favored but the water is also better retained. In polymers with lower functionalization the hydrogen bond structure for the proton transport cannot be well formed and the proton conductivity is much reduced at low humidity level.

### 3.5. *Oxidative stability*

The membranes were characterized by oxidative stability by soaking the film in Fenton's reagent at 80 °C for 1 h (Table 1). This method has been used to simulate oxidative reaction by the attack of radical species ($HO^\bullet$ and $HOO^\bullet$) during fuel cell operation [19]. The sulfonated membranes exhibited highly oxidative stability, retaining 98–100% of their weight after the test. While under the same conditions, Nafion 112 retains 98% and aliphatic/aromatic polyamides retain from 62% to 98% of their weight after the test [19]. The high chemical stability of the membranes may be conferred to the polymer chains by the heterocyclic ring, which is spectrally and electronically equivalent to the *p*-phenylene ring strucuture [10].

### 3.6. *Thermal and mechanical analysis*

The thermal and mechanical properties of the sulfonated polyoxadizole membranes in salt and in acid form were evaluated by means of dynamic mechanical thermal analysis. Good dimensional stability and high storage modulus ($E'$) of about 3 GPa at 300 °C (Fig. 11a) were observed. No significant changes in the loss modulus and tan $\delta$ values were observed for the membranes with increasing of sulfonation level and in the acid form, except for the glass transition temperatures ($T_g$). Table 1 shows the $T_g$ taken as the maximum in the tan $\delta$ and loss modulus ($E''$) curves. The increase of the sulfonation level of polymers resulted in an increase of the $T_g$. This result may be attributed to the introduction of bulky substituent on the aromatic rings, an increase of chain–chain interactions though hydrogen bonds and the inonic character of the substituent [26,27]. As shown in Table 1 and Fig. 11(b), the type of counterion has a very strong effect on the dynamic mechanical properties of the membranes. When converted to the H-form, the $T_g$ shifted to slightly lower temperatures. A higher $T_g$ for the sodium salt form is expected [26,27], since the dipole–dipole interaction between sodium sulfonate groups is much stronger than hydrogen-bond interaction between the $SO_3H$ groups. As one may see, SPOD-

Table 1
$T_g$ values and oxidative stability of sulfonated poly(diphenylether-1,3,4-oxadiazole) membranes

| S/C (molar ratio)[a] | IEC (meqiv. $g^{-1}$) | Residue after oxidative testing (wt.%)[c] | $T_g$ (°C) | | | |
|---|---|---|---|---|---|---|
| | | | $E''$ | | tan $\delta$ | |
| | | | —Na | —H | —Na | —H |
| 0.065[b] | 1.26 | 98 | 364 | 304 | 396 | 307 |
| 0.098 | 1.78 | 100 | 415 | 322 | 429 | 328 |
| 0.103 | 1.86 | 100 | 416 | 321 | 430 | 333 |
| 0.124 | 2.15 | 98 | 430 | 330 | 442 | 340 |

[a] Determined by elemental analysis.

[b] Data from [5].

[c] Immersed in a Fenton's solution at 80 °C for 1 h.

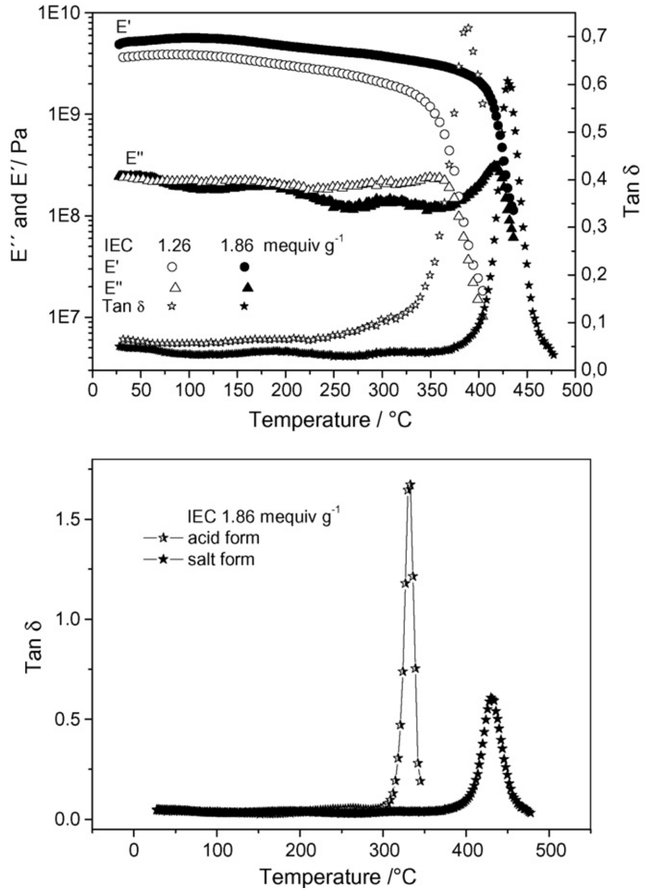


Fig. 11. (a) DMTA plots of POD-DPE membranes in salt form; (b) tan $\delta$ as a function of temperature for SPODDPE membrane with IEC equal to 1.86 in the salt and acid form.

DPE with glass-transition temperatures ($T_g$) ranging from 364 to 442 °C in sodium salt form and from 304 to 333 °C in acid form and good mechanical properties were obtained.

## 4. Conclusions

A series of novel sulfonated polyoxadiazoles with IEC ranging from 1.26 to 2.7 meqiv. g$^{-1}$ can be synthesized by three different methods: (1) post-sulfonation in mixture of fuming sulfuric acid with 20–65% $SO_3$ and sulfuric acid (95–97%) at 45 °C, (2) post-sulfonation in sulfuric acid (95–97%) at 45 °C and (3) single-step optimized method of synthesis at high temperature (160 °C) using hydrazine sulfate in poly(phosphoric acid). For the method (1) strong polymer degradation was observed. Comparison between methods (2) and (3) clearly indicates that the post-sulfonation method takes longer to obtain the same sulfonation level compared to the single-step optimized method of synthesis at high temperature. Additional disadvantage is the lower molecular weight obtained for the post-sulfonation method compared to the single-step method, indicating that the later is a better method to obtain sulfonated polyoxadiazoles with lower reaction times and higher molecular weights than by the post-sulfonation reaction. The ether linkages are electron-donating groups and activate the ring for the eletrophilic sulfonation reaction, being necessary to accomplish the sulfonation by the single-step method.

Sulfonated polyoxadiazole membranes with high thermal stability with glass-transition temperatures ($T_g$) ranging from 364 to 442 °C in sodium salt form and from 304 to 333 °C in acid form, high stability in Fenton's test and with good mechanical properties (storage modulus about 3 GPa at 300 °C) have been prepared.

High proton conductivity values with the order of magnitude of $10^{-2}$ S cm$^{-1}$ at 80 °C and RH = 20% suggest that the $-SO_3H$ groups are less separated from each other increasing the contribution of the mechanism of proton transport by the diffusion of protons within a hydrogen bonded structure.

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