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Characterization of Partially Sulfonated Polyoxadiazoles and Oxadiazole-triazole Copolymers

Characterization of Partially Sulfonated Polyoxadiazoles and Oxadiazole-triazole Copolymers

Dominique Gomes [*] *, Jerusa Roeder, Mariela L. Ponce and Suzana P. Nunes*

GKSS Research Centre Geesthacht GmbH, Institute of Polymer Research,
Max Planck Str. 1, D-21502, Geesthacht, Germany

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[*] Corresponding author. Tel.: +49 04152 87 2472; fax: +49 04152 87 2466
E–mail address: dominique.gomes@gkss.de (D. Gomes)

Abstract

Experimental evidences regarding the sulfonation of polyoxadiazole and oxadiazole-triazole copolymers during the preparation are given. The structures of the polymers were qualitatively and quantitatively characterized by elemental analysis, ^{1}H-NMR, and FTIR. Polymers with high molecular weights (up to 470,000 g/mol) exhibiting highly oxidative stability are obtained allowing the casting of mechanically stable membranes with high storage modulus (about 4 GPa at 100°C) and high proton conductivity values (order of magnitude of 10^{-2} S cm^{-1} at 80°C).

1. Introduction

Polymers containing heterocyclic rings with basic character such as polybenzimidazole have a particular interest for application for polymer electrolyte fuel cells (PEFCs), since when doped with phosphoric acid they are able to transport protons above 100°C [1-4]. Polyoxadiazole has been reported for proton conductive membranes [5]. However, due to its restricted solubility, membranes were prepared from polymer solutions in sulfuric acid by phase inversion giving porous membranes. The conductivity of the undoped porous membranes with 100% of relative humidity was around 10 $^{-7}$ S cm^{-1} [5]. High proton conductivities were obtained (10 $^{-1}$ S cm^{-1}) for doped uncompressed polyoxadiazole membranes with phosphoric acid and attributed to the fact that the acid fills the pores of these materials providing a conduction pathway through the liquid phase [5]. Recently new functionalized oxadiazole oligomers and polymers prepared by another route, as well as organic inorganic membranes, have been developed by our group [6-8]. Tailored structures containing oxadiazole groups and acid sites with improved solubility could be in this form synthesized and tested as fillers for dense fuel cell membranes based on sulfonated poly(ether ether ketone) [6]. Sulfonated poly(aryl ether ketones) containing benzoxazole were recently reported for proton conduction [9, 10].

Besides solubility a key issue in the synthesis of polyoxadiazole is the achievement of high molecular weight and good mechanical properties. An optimization of polyoxadiazole synthesis for preparation of membranes has been also previously reported [11]. The synthesis was performed with the diphenyl ether attached to the main chain. Poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD-DPE) soluble in N-methyl-2-pyrrolidone (NMP) could be obtained, allowing the preparation of dense films by solvent evaporation [11]. Nevertheless, depending on the synthesis route, differences in the solubility of the polymer samples was observed. The POD-DPE synthesis through thermal cyclodehydration of polyhydrazide in solutions of poly(phosphoric acid) (PPA) and in the film form only leads to

insoluble polymer in organic solvents like NMP [12], even when the synthesis in PPA was performed at temperatures above 160°C. On the other hand, POD-DPE synthesis through polymerization of a dicarboxylic acid and hydrazine sulfate (HS) in solutions of PPA at high temperatures (160°C) resulted only in soluble polymers [11]. Due to interest on posterior functionalization for electrochemical application, the ionic conductivity of dense polymer membranes prepared by both methods was measured. A difference of three orders of magnitude could be detected. These results lead to the suspect that the POD-DPE samples synthesized using hydrazine sulfate were already partially sulfonated during the preparation.

The sulfonation of POD-DPE with hydrazine sulfate has not been previously recognized [11], since the POD-DPE was insoluble in water and its TGA curve did not show any weight loss up to about 500°C. Acid sulfonic groups usually lead to a weight loss at about 300°C [13]. More recently, it has been reported that the salt form of the attached sulfuric acid might not necessary lead to weight loss in TGA curves around 300°C, being more stable than the acid form [14] and that the solubility of sulfonated polymers in water depends on the degree of the sulfonation [15].

The aim of this work is to show that sulfonation of the polyoxadiazoles and polytriazoles synthesized from hydrazine sulfate in PPA may occur during the polymer preparation. The structures of the polymers were characterized by elemental analysis, ^{1}H NMR, and FTIR. It must be pointed out that this sulfonation reaction has been completely overlooked in literature [16-18] and that for the first time, this sulfonation reaction is qualitatively and quantitatively characterized. Hensema et al. [17] have indeed detected sulfur in polymer samples by elemental analysis, but it was believed that the residual sulfur was not bound to the polymer and was present as free H_2SO_4. Differences between the experimental and theoretical values obtained from the elemental analysis were attributed to be residual impurities, most likely phosphoric acid [18].

In this work, we have collected a significant number of experimental evidences regarding the sulfonation of polyoxadiazole and oxadiazole-triazole copolymer in solutions of PPA using hydrazine sulfate, such as:

1. quantitative evaluation by elemental analysis, FTIR and ^{1}H-NMR;
2. high ionic conductivity values;
3. analysis by FTIR and ^{1}H-NMR of POD-DPE synthesized by different routes;
4. differences in the solubility of POD-DPE synthesized by different routes.

2. Experimental Section

2.1. Materials

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Aniline (99%, Aldrich), Dicarboxylic diacid 4,4'-diphenylether, DPE (99%, Aldrich), Hydrazine sulphate, 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). All chemicals were used as received. Poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD-DPE), poly(4,4'-diphenylether-hydrazide) (PH-DPE) and 2,5-bis(4-fluorphenyl)-1,3,4-oxadiazole (BFO) were synthesized and characterized as described elsewhere [7,11,12,19].

2.2. Synthesis of oxadiazole- triazole copolymers

The reaction condition for the synthesis of the oxadiazole-triazole copolymers (pPT-DPE) was selected based on the previous studies, where the optimization of the polyoxadiazole synthesis was performed [11,19]. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/DPE) were kept constants and equal to 10 and 1.2, respectively. After reacting DPE and HS at 160 °C, the reaction temperature was increase to 180 °C. Then, aniline was added to the flask and left to react for more 3h. A molar ratio of polyhydrazide formed in situ to aniline equal to 1 was used. After finishing the batch, the reaction medium was poured into tepid water (containing 5% w/v of sodium hydroxide), for precipitation of the polymer. The pH of this polymer suspension was controlled according to Gomes et al. [19].

2.3. Membrane preparation

Homogeneous membranes were cast from polymer solutions with a concentration of 4 wt. % in NMP. After casting, the NMP was evaporated in a vacuum oven at 60°C for 24h. For further residual solvent removal, the membranes were immersed in water bath at 60°C for 48h and dried in a vacuum oven at 60°C for 24h. The final thickness of the membranes was about 30 μm.

The sulfonated POD-DPE and pPT-DPE membranes were converted into its acid form by immersing the cast membranes in 1.6M H_3PO_4 at room temperature for 24 h, followed by immersion in water for 2 x 24 h to ensure total leaching of residual phosphoric acid.

2.4. 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 at the Fraunhofer Institute. ^{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 BFO

powder. The spectra were fitted, to evaluate the peak area at 1600 and 1394 cm^{-1}, using Origin 7.5 software.

2.5. Molecular weight measurements

A Viscotek SEC apparatus equipped with Eurogel columns SEC 10.000 and PSS Gram 100, 1000, with serial numbers HC286 and 1515161 and size 8 x 300 mm was employed to evaluate the weight average molecular weights of polymer samples. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 309 to 944,000 g/mol. A solution with 0.05 M lithium bromide in DMAc was used as the carrier.

2.6. 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 null phase shift (high frequency side) with 100% of relative humidity. The impedance measurements were carried out on stacks containing up to five membranes (similar cumulative thickness, around 500 μm). The measurements were performed using water vapor as described by Alberti et al. [20]. The spectrometer used was a Zahner IM6 electrochemical workstation.

2.7. 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 δ). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1Hz and 0.1 N initial static force. The temperature was varied from 25 to 400 °C at a heating rate of 2°C/min and at a constant strain of 0.05%.

2.8. Water uptake and oxidative stability

The membranes were dried in a vacuum at 80°C for 24h before the measurement. After measuring the weights of dry membranes, the samples were immersed in deionized water at 25°C and 60°C for 24h. Before measuring the weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel. Water uptake was calculated using Equation (1):

$$\text{Water uptake (wt. \%)} = \frac{(m_{wet} - m_{dry})}{m_{dry}} \times 100 \tag{1}$$

where: m_{wet} and m_{dry} are the weights of dried and wet samples, respectively.

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 1h.

3. Results and Discussion

3.1. Structural Characterization

The structural characterization obtained from elemental analysis, the weight average molecular weight, ionic conductivity and the theoretical structures of the polymer samples are presented in Table 1. The sulfonation degree (SD) is defined here as 100 when each phenylene ring contains a sulfonic group. The analysis of Table 1 indicates that polymers synthesized in poly(phosphoric acid) (PPA) using hydrazine sulfate (HS) as monomer are partially sulfonated, with SD up to 21. On the other hand, the polyhydrazide as well as the polyoxadiazole synthesized through the thermal treatment of the polyhydrazide films at 260°C were not partially sulfonated. This result may be explained by the reagents used during synthesis. The polyhydrazide was synthesized through polycondensation reaction in NMP solution at low temperature, using equimolar amounts of dihydrazide and dichloride [12]. Since no source of sulfuric acid is present in the reaction medium, the polymer should not be sulfonated. The same is valid for the polyoxadiazole synthesized through the thermal treatment of the polyhydrazide. On the other hand, for the polyoxadiazole and oxadiazole-triazole copolymer synthesized in PPA with HS, the sulfonation of the polymers may occur by the presence of sulfuric acid in the solution of HS at the temperature of 160-180°C. In the case of the oxadiazole- triazole copolymer the high SD can be attributed to the high reaction time and temperature in contrast to the polyoxadiazole.

(Table 1)

From the S/C ratio obtained from elemental analysis for the POD-DPE, the SD obtained was equal to 17. The sulfonation was also confirmed by NMR and FTIR. The characterization of the polyhydrazide and the polyoxadiazole synthesized in PPA with HS by ^{1}H-NMR spectra in DMSO-d_6 has been already performed [11,12]. However, because the polyoxadiazole samples synthesized through the thermal treatment of the polyhydrazide were insoluble in organic solvents, these samples were not characterized by ^{1}H-NMR. In this work, these polymer samples are characterized by ^{1}H-NMR spectra in D_2SO_4. Figure 1 shows the ^{1}H-NMR spectra of these polymer samples. Doublets at 7.53-7.50 ppm for 4 H_2 protons and at 6.53-6.50 ppm for 4 H_3 protons are observed for the polyhydrazide, as expected by analyzing the structure of this polymer. The singlet for 2 H_1 protons of polyhydrazide could not be observed because of the D_2SO_4 signal at the same spectral region (about 10 ppm). Signals at 7.45 ppm for 4 H_5 protons and at 6.58 ppm for 4 H_4 protons are observed for the polyoxadiazole synthesized through the thermal treatment of the

polyhydrazide. Additionally to the signal assigned to the H_5 protons and to the H_4 protons, for the polyoxadiazole synthesized in PPA with HS, a singlet at 8.00 ppm is observed (correspondent to the singlet observed at 8.50 ppm in DMSO-d_6 [21]). Contrary to the previous attribution of the singlet at 8.5 ppm to aromatic protons of degradation products [21], this singlet is indeed assigned to the H_6 aromatic protons in the POD-DPE structure. Based on the proposed assignments, the SD can be calculated as:

$$SD = (A_6/A_{4,4'}) \times (25/0.143) \qquad (1)$$

where A_6 is the integral of the signal of H_6 proton at 8.00 ppm and $A_{4,4'}$ is the integral of the signal of H_4 and $H_{4'}$ protons at 6.60 ppm (Fig. 1). In Equation (1), the value 0.143 corresponds to the theoretical $(1H_6/7(H_4+H_{4'}) = 0.143)$ integral ratio for a POD-DPE structure with theoretical SD equal to 25%. From Equation 1, the SD of POD-DPE is equal to 18, as already obtained from elemental analysis. Thus, the structure that corresponds to the obtained POD-DPE is depicted in Scheme 1. For the SD equal to 18 the number of repeating units of m and L are respectively equal to 0.65 n_o and 0.35 n_o, where n_o is equal to the rate of the average molecular weight to the number of the repeating units of POD-DPE (theoretical N/C 0.167; S/C 0.067).

(Figure 1)

The infrared spectra of the polyhydrazide (PH), polyoxadiazole synthesized from polyhydrazide and polyoxadiazole synthesized in PPA with HS (POD-DPE) are shown in Figure 2. In this Figure, the spectrum of the bis(4-fluorphenyl)-1,3,4-oxadiazole (BFO), a substance containing aromatic non sulfonated phenyl and oxadiazole rings, is also included. The two peaks at ca. 1600 and 1485 cm^{-1} arise from C=C stretching of the aromatic groups and are observed in all spectra. The asymmetric SO$_2$ stretch is observed at 1394 cm^{-1}. In covalent sulphonates, 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 [22,23] while the asymmetric and symmetric SO stretching vibration bands occur at 1020-850 cm^{-1} and 830-690 cm^{-1}, respectively [22]. Symmetric SO$_3$ stretching vibration band of sulfonic acid salts (SO$_3^-$M$^+$) occurs at 1070-1030 [22] and for the polyoxadiazole synthesized in PPA from HS this band is observed at 1030 cm^{-1}. The oxadiazole ring in the samples can be characterized through the assignments placed at 1467 cm^{-1} and 1413 cm^{-1} related to the C=N stretching and by the assignment placed at 1065 cm^{-1} related to the -C-O-C- stretching. The peak at 1630 cm^{-1} arises from C=O stretching of the polyhydrazide. The asymmetric SO$_2$ stretching, characteristic of a sulfonated material, can be only observed for the polyoxadiazole synthesized in PPA from HS. The same asymmetric SO$_2$ stretching is observed for the oxadiazole-triazole copolymer (Figure 3). The deconvolution of the peaks of POD-DPE at 1394 cm^{-1} related to the asymmetric SO$_2$ stretching and of the peak at 1600 cm^{-1} related to the C=C stretching allows the quantitative determination of SD, which can be calculated as:

$$SD = (A_{SO2}/A_{C=C}) \times (17/\ 0.132) \qquad\qquad (2)$$

where A_{SO2} is the integral of the peak at 1394 cm^{-1} related to the asymmetric SO$_2$ stretching and $A_{C=C}$ is the integral of the peak at 1600 cm^{-1} from C=C stretching of the aromatic groups (Fig. 3). In Equation (2), the value 0.132 corresponds to the experimental value of the ($A_{SO2}/A_{C=C}$) ratio obtained by FTIR for the POD-DPE film with experimental SD equal to 17% (determined by elemental analysis).

(Figures 2 and 3)

From Equation (2), the SD of the pPT-DPE is equal to 20, as already obtained from elemental analysis. The conversion of triazole groups from elemental analysis can be calculated as:

$$\% \text{ conversion} = [(N/C) - 0.167]/0.008) \times\ 100 \qquad\qquad (3)$$

For the pPT-DPE, 30% of conversion of triazole groups were obtained. Based on these results, the structure that corresponds to the obtained pPT-DPE is depicted in Scheme 1. For the SD equal to 21 and content of triazole groups equal to 0.30, the approximated number of repeating units of m, L, y and x can be respectively given as 0.35 n_t, 0.35 n_t, 0.15 n_t and 0.15 n_t, where n_t is equal to the rate of the average molecular weight to the number of the repeating units of the pPT-DPE (theoretical N/C 0.170; S/C 0.084).

Figure 4 shows the FTIR spectra of the pPT-DPE with a SD equal to 21 (a), POD with SD equal to 17, synthesized with HS (b) and POD synthesized from PH with SD equal to 0 (c). At 3098 and 3070 cm^{-1}, aromatic CH stretching vibrations are observed. The peaks at 3414 cm^{-1} and at 3220 cm^{-1} are related to the absorbed water and are assigned to the O-H stretch of the hydrogen-bonded O-H groups intramolecular and intermolecular, respectively. As expected, the higher the sulfonation degree, the higher the water absorption.

(Figure 4)

3.2. Ionic Conductivity

Table 1 shows the ionic conductivities at 50°C of the polymer samples. For comparison, the proton conductivity value of a porous polyoxadiazole membrane reported by Zaidi et al. is also listed. The SD as expected has a direct impact in the conductivity. Non sulfonated polymers had low conductivity values around 10^{-3} mS cm^{-1}, while samples with confirmed sulfonation had high ionic conductivity (about 3 mS cm^{-1}). In the literature, it has been shown that non sulfonated polymeric membranes have conductivity lower than 10^{-3} mS cm^{-1}. For instance, non sulfonated poly(benzimidazole) has very low conductivity, which does not exceed 10^{-8} mS cm^{-1} [24]. The conductivity of undoped porous polyoxadizole membranes prepared by Zaidi et al. [5], as shown in Table 1, was around 10^{-4} mS cm^{-1}. The low values of conductivity for the reported [5] porous polyoxadiazole membranes can be attributed to the fact that the conduction process was mainly governed by the absorbed water in the pore of the membranes and not by the polymeric matrix. An additional factor is that

due to the characteristic of the rigid aromatic attached group to the main polyoxadiazole chain, polymers could not be sulfonated (or had a very low sulfonation) during the synthesis.

The dependence of ionic conductivity on temperature for the sulfonated POD-DPE and pPT-DPE membranes in salt and in acid form is shown in Figure 5. As expected the pPT-DPE membrane with higher sulfonation degree has higher ionic conductivity than the POD-DPE membrane in all range of temperatures. The conductivity values showed in Figure 5 for the salt samples might not be influenced by residual phosphoric acid, once samples were well neutralized after polymerization, according to the protocol described in the previous publication [19]. The lower conductivity values observed for the polymers in the salt form are due 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 [25-27].

(Figure 5)

Taking into account the low SD (up to 21), it can be affirmed that the proton conductivity values (10^{-2} S cm^{-1} at 80°C and 100% relative humidity) are high and close to the value of Nafion115 [15, 28, 29]. Undoped sulfonated polymer containing basic nitrogen (polybenzimidazole) with sulfonation degree up to 66% with proton conductivity in the order of 10^{-5} S cm^{-1} at 80°C and 100% relative humidity has been characterized in literature [30]. According to Staiti et al. [30], the lower proton conductivity compared to other sulfonated polymers with similar or even lower sulfonation degree is attributed to the effect of nitrogen protonation by the sulfonic acid groups. Self doping with subsequent reduction of proton conductivity was also observed by blending polyaniline and sulfonated poly(ether ether ketone), where sulfonic groups from sulfonated poly(ether ether ketone) protonated the nitrogen atoms from polyaniline [31]. In the present work, the higher proton conductivity values obtained compared to the sulfonated polybenzimidazole [30] is attributed to the higher hydrophilicity and flexibility of the polymer chains due to the diphenyl ether group attached in the main chain as well as the higher effective number of sulfonic acid groups per polymer unity, which probably favor the proton jumps through the pyridine-like N sites and the sulfonic acid groups.

3.3. Water uptake and oxidative stability

The degree of water uptake for the sulfonated membranes at 25 and 60°C is summarized in Table 2. As expected, water uptake increases with increasing sulfonation degree and temperature. As the sulfonation degree increases, the increase in the number of sulfonic acid groups leads to a higher absorption of water. The water within the membrane provides a carrier for the proton and justifies the higher proton conductivity values obtained for the pPT-POD membrane compared to the POD-DPE.

Membrane stability to oxidation was investigated by soaking the film in Fenton's reagent at 80°C for 1h. This method has been used to simulate oxidative reaction by the attack of radical species (HO⋅ and HOO⋅) during fuel cell operation [32]. The POD-DPE and pPT-DPE membranes exhibited highly oxidative stability, retaining 98 and 95% of their weight after the test, respectively. While under the same conditions, Nafion 112 retains 98 % and aliphatic/aromatic polyimides retain from 62 to 98% of their weight after the test [32]. The high chemical stability of the POD-DPE and pPT-DPE membranes may be attributed to the chemical stability conferred to the polymer chains by the heterocyclic ring, which is spectrally and electronically equivalent to the p-phenylene ring strucuture [33]. Chen et al. [34] have shown that poly(phthalazinone ether ketone) containing N-C heterocyclic bond also shows very stable oxidation property because the nitrogen atom are located on an aromatic ring, which stabilizes the N-C bonds.

(Table 2)

3.4. Thermal and mechanical analysis

The thermal and mechanical properties of POD-DPE and pPT-DPE membranes in salt and in acid form were evaluated by means of dynamic mechanical thermal analysis (DMTA). In Figures 6 and 7 the DMTA plots of POD-DPE and pPT-DPE membranes in Na-form, are respectively shown. The DMTA plots clearly confirm the good dimensional stability and the high storage modulus (E'), about 4 GPa at 100°C. No significant changes in the modulus values were observed for the membranes in the acid form, except for the glass transition temperatures (T_g) values. Table 3 shows the T_g taken as the maximum in the tan δ and loss modulus (E'') curves. The T_g determined by the maximum of E'' curve are usually lower than those calculated by the maximum damping ratio, since the later represent the end of the transition period [35]. The T_g obtained from the maximum in the tan δ curves have been related with the T_g measured by DSC in various works [36-38]. The dynamic mechanical T_g's are normally higher than those measured by DSC as a consequence of the higher effective measuring frequency of DMTA [36]. As shown in Table 3, 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, since the dipole-dipole interaction between sodium sulfonate groups is much stronger than hydrogen-bond interaction between the SO_3H groups [39].

(Figures 6 and 7)

(Table 3)

4. Conclusions

The sulfonation of polyoxadiazole and oxadiazole-triazole copolymer in solutions of poly(phosphoric acid) using hydrazine sulfate was confirmed with the structural characterization of these polymers by elemental analysis, ^{1}H-NMR, and FTIR. Polymers with high molecular weights (up to 470,000 g/mol) exhibiting highly oxidative stability are obtained allowing the casting of mechanically stable membranes with high storage modulus (E'), about 4 GPa at 100°C and high proton conductivity values (order of magnitude of 10^{-2} S cm^{-1} at 80°C).
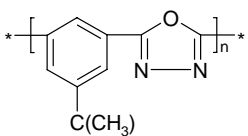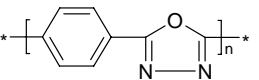
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Table 1: Characterization of the polymer samples

Structure	Polymer	Elemental Analysis				Sulfonation degree (SD)[d]	$\overline{M_w}$ (g/mol)	Conductivity at 50°C (mS cm^{-1})
		N/C		S/C				
		theoretical	found	theoretical	found			
PH-DPE	PH-DPE	0.167	0.166	0	0	0	74,000	10^{-3}
POD-DPE	POD-DPE	0.167	0.157	0	0	0	insoluble in DMAc	10^{-3} [a]
		0.167	0.167	0	0.065	17	358,000	2.7 [b]
pPT-DPE	pPT-DPE	0.172	0.1694	0	0.083	21	470,000	3.9
POD-TBI pPOD	POD-TBI pPOD	not provided				not provided	not provided	10^{-4} [c]

[a] synthesized by heating PH-DPE; [b] synthesized in PPA with HS; [c] datum of porous membranes prepared with both polymers [5]; [d] determined by elemental analysis.

Table 2: Water uptake and oxidative stability of POD-DPE and pPT-DPE membranes

Membrane	Water uptake (wt. %)		Residue after oxidative testing (wt. %) [a]
	25°C	60°C	
POD-DPE	19	21	98
pPT-DPE	24	36	95

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

Table 3: T_g values of POD-DPE and pPT-DPE membranes

Membrane	T_g (°C)	
	E''	Tan δ
POD-DPE (Na)	364	396
POD-DPE (H)	304	307
pPT-DPE (Na)	360	382
pPT-DPE (H)	317	329

BFO

POD-DPE

pPT-DPE

Scheme 1

18
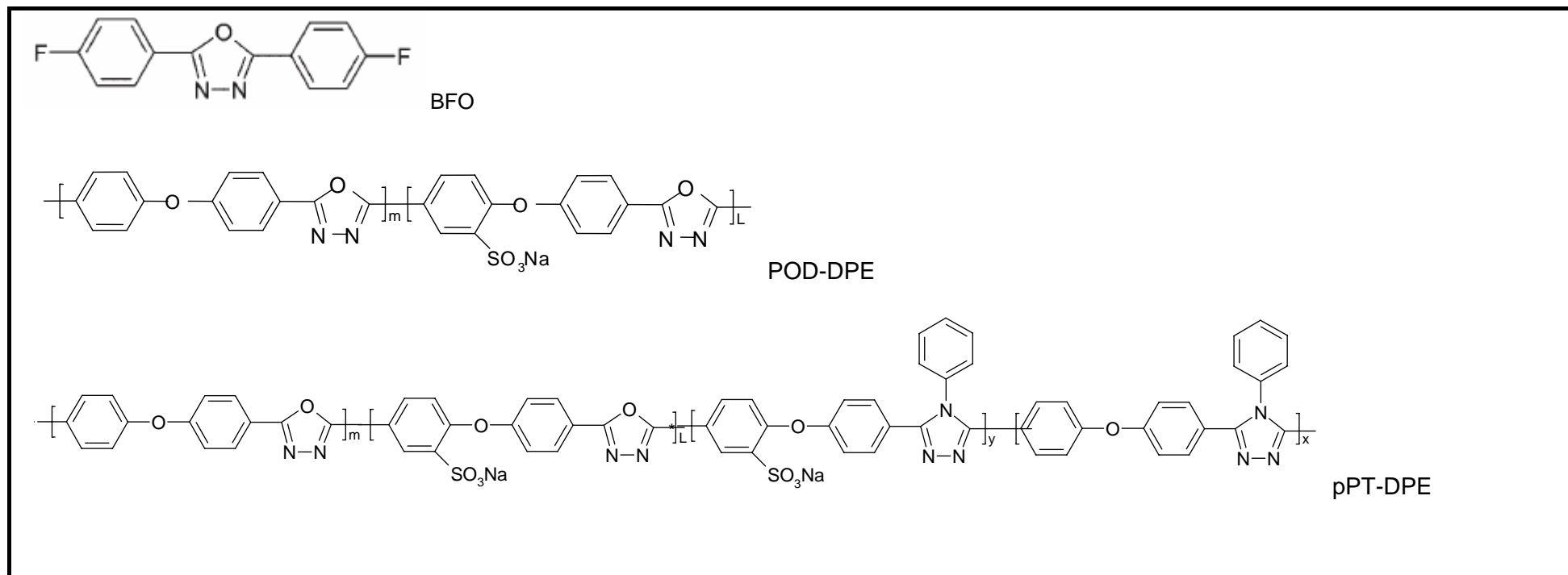
Figure captions

Scheme 1. Structures of the monomer BFO and the investigated polymers POD-DPE and pPT-DPE.

Figure 1: ^{1}H-NMR spectra of (a) PH, (b) POD synthesized from PH and (c) POD synthesized with HS (spectra taken in D_2SO_4).

Figure 2: FTIR spectra of the BFO, PH, POD synthesized from PH and POD synthesized with HS in the region 1800 – 950 cm^{-1}.

Figure 3: Deconvolution curves of the FTIR spectra of the POD-DPE and pPT-DPE in the region 1700 – 1350 cm^{-1}.

Figure 4: FTIR spectra of the pPT-DPE (a), POD synthesized with HS (b) and POD synthesized from PH (c) in the region 4000 – 2600 cm^{-1}.

Figure 5: Dependence of ionic conductivity on the temperature for the sulfonated POD-DPE and pPT-DPE membranes in salt and in acid form.

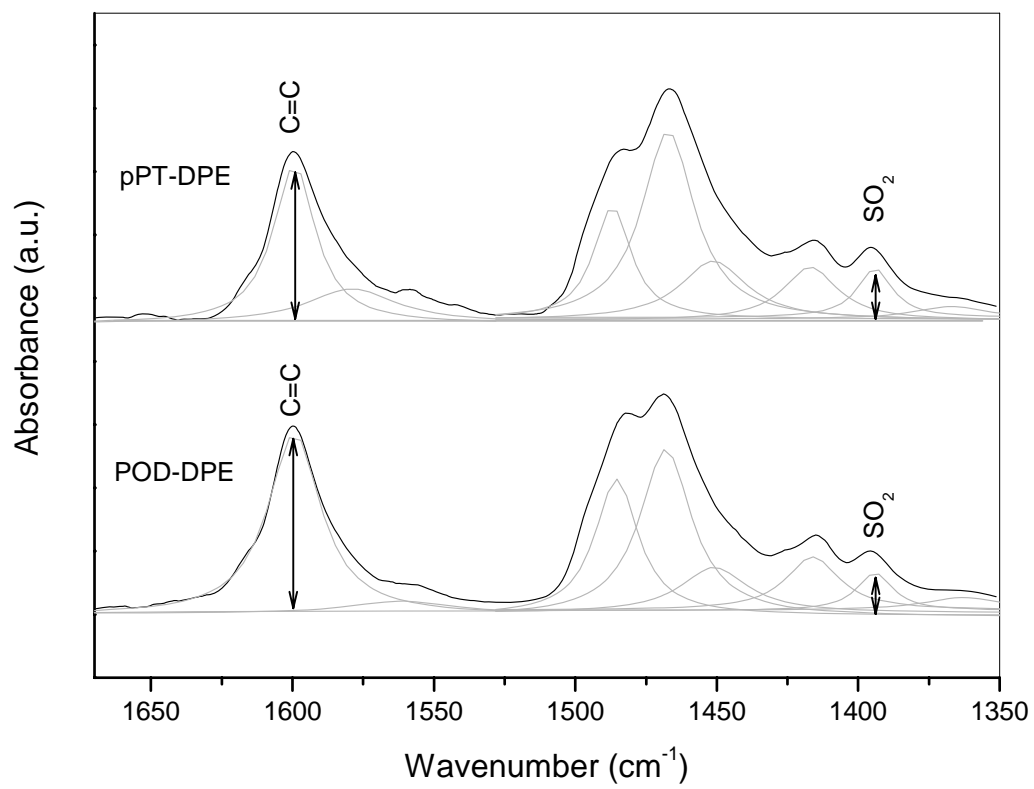Figure 6: DMTA plot of POD-DPE membrane in Na-form.
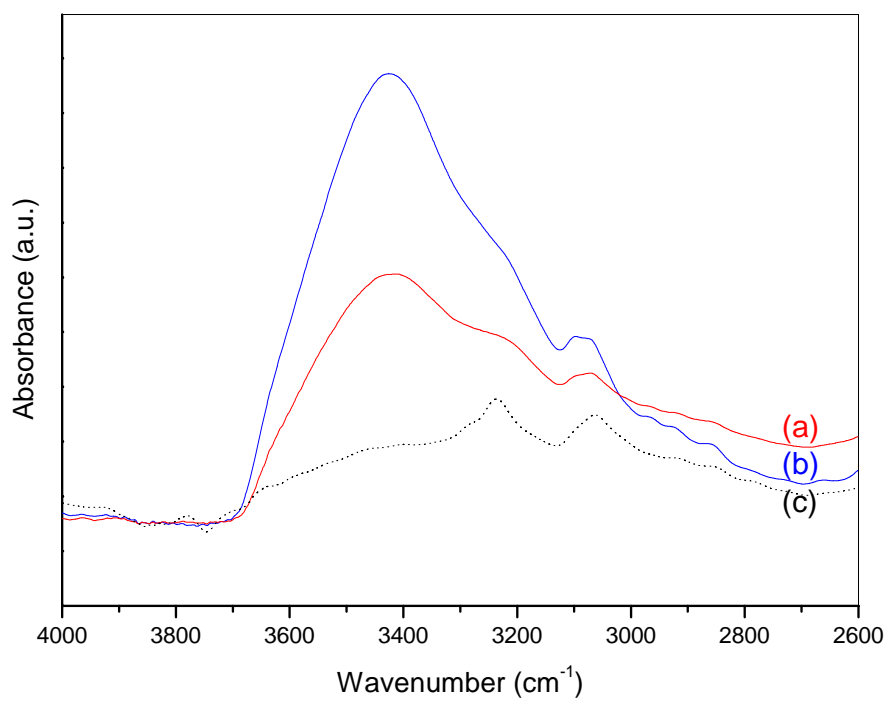
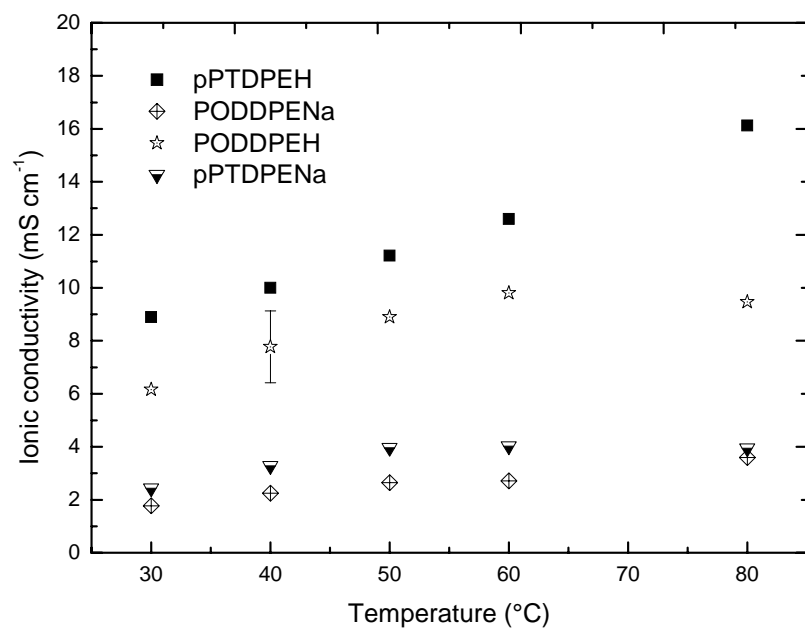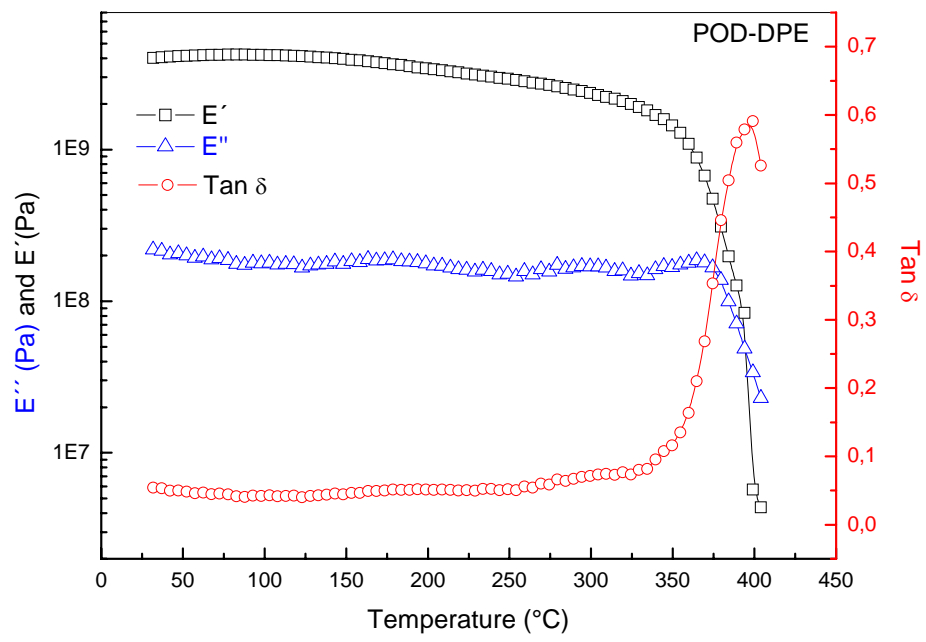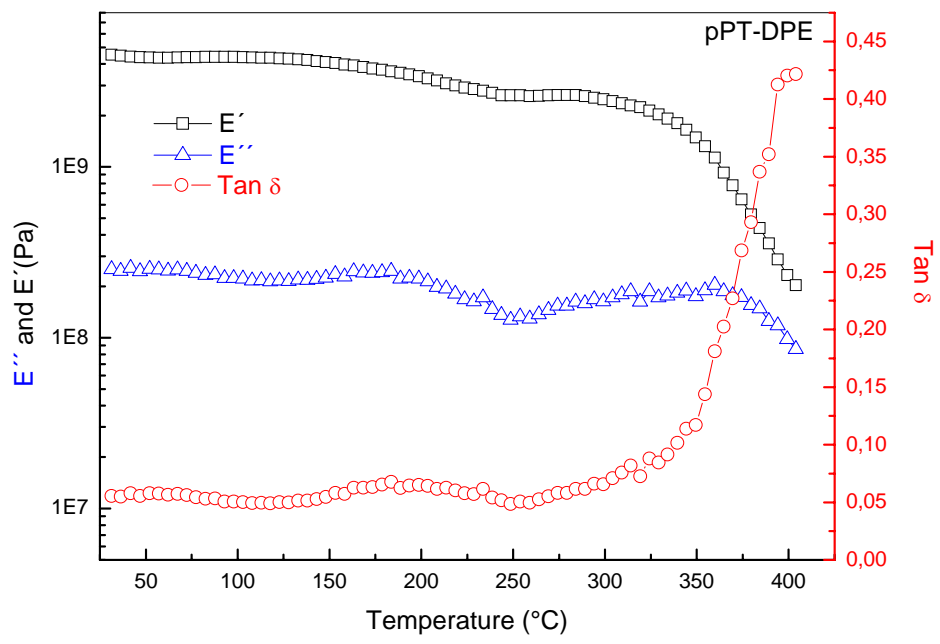Figure 7: DMTA plot of pPT-DPE membrane in Na-form.
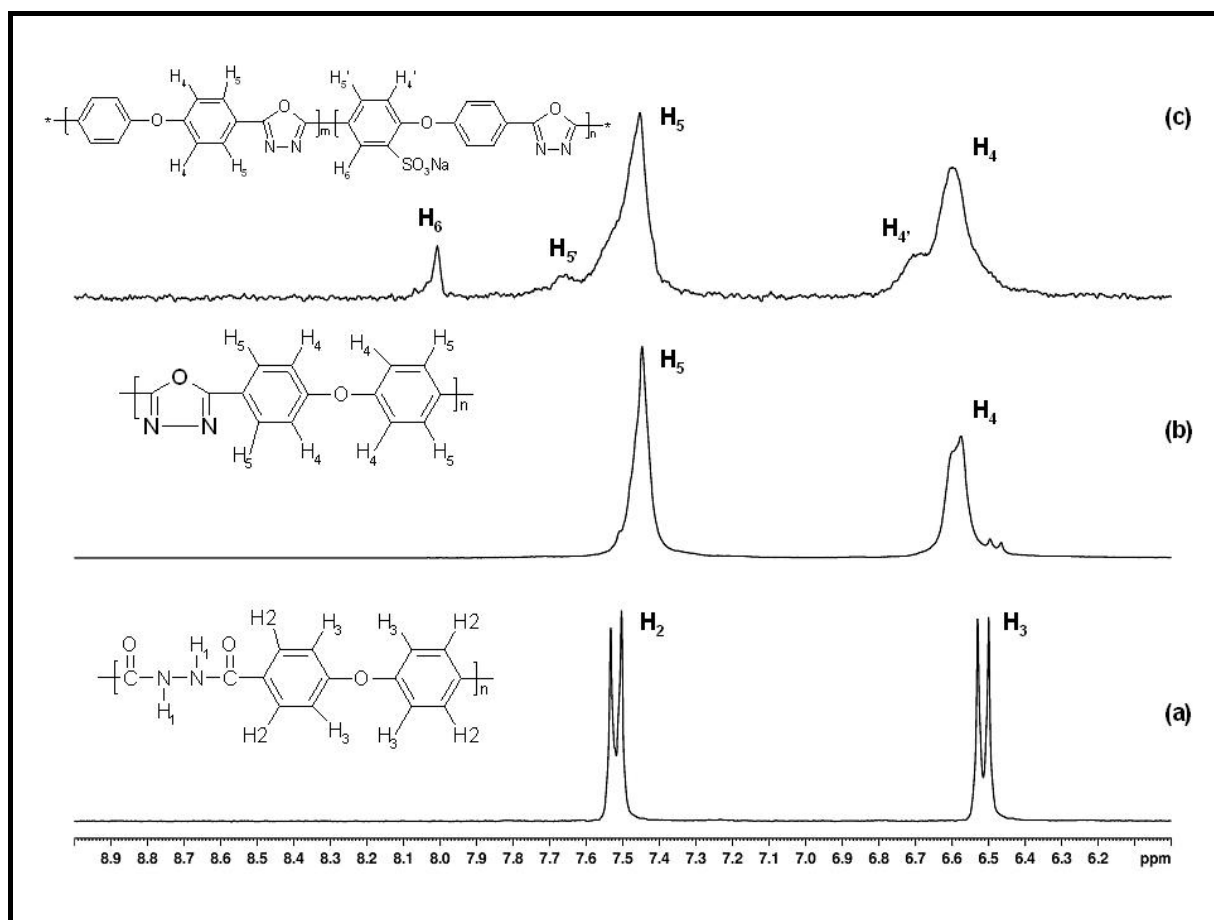
(Figure 1)
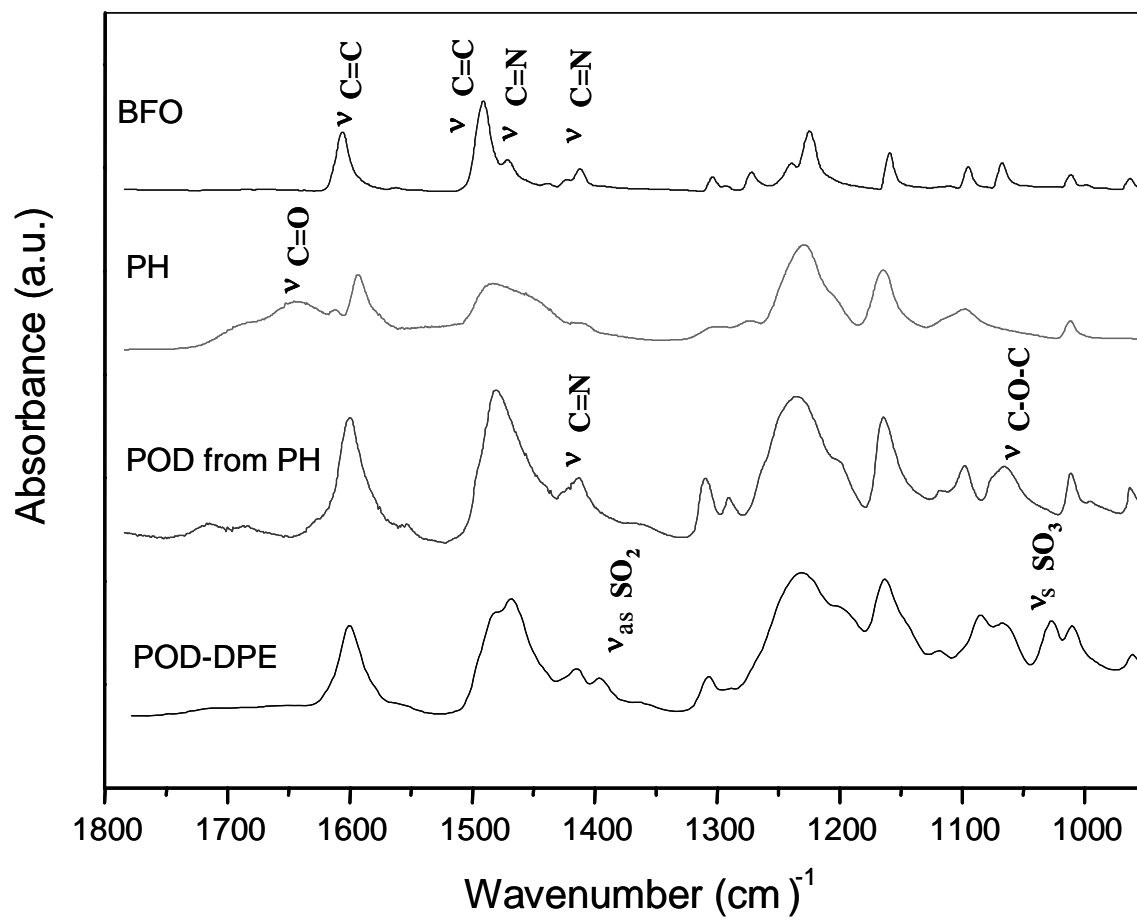
(Figure 2)

(Figure 3)

(Figure 4)

(Figure 5)

(Figure 6)

(Figure 7)