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**One-Pot Synthesis of High Molecular Weight
Sulfonated Poly(Oxadiazole-Triazole) Copolymers for
Proton Conductive Membranes**

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Abstract

For the first time, a series of high molecular weight ($1-4 \times 10^5 \text{ g mol}^{-1}$) sulfonated poly(oxadiazole-triazole) copolymers have been synthesized at high temperatures and very short reaction time, by a single-step method based on solution polycondensation reaction of non-sulfonated dicarboxylic acid, hydrazine sulphate and aromatic primary amine (sulfonated and non sulfonated) in poly(phosphoric acid). By this fast synthetic procedure, copolymers with a high conversion to triazole groups (up to 93%) as well high sulfonation level ($\text{IEC} = 1.17-1.84 \text{ meq.g}^{-1}$) have been obtained. The structure of the polymers was characterized by elemental analysis and $^1\text{H NMR}$.

Since high sulfonation levels ($\text{IEC} = 1.17-1.84 \text{ meq g}^{-1}$) could be obtained, membranes were prepared from these polymers and have been characterized aiming the application in fuel cells. Proton conductivity up to $6 \times 10^{-2} \text{ S cm}^{-1}$ at 150°C was measured. The polymer films had good mechanical properties with storage modulus of about 3 Gpa at 300°C . These films exhibited high thermal stability with T_g up to around 440°C .

Keywords: polytriazole, polyoxadiazole, sulfonation, proton conductor, fuel cell

1. Introduction

The conventional proton conductive membranes like Nafion[®] are manufactured from sulfonated polymers. Proton conductivity in these cases requires high hydration levels and the proton transport is in great extent promoted by water movement inside the membrane. Sulfonated membranes tend to lose conductivity above 100°C due to dehydration, hence the maximum operation temperature of a polymer electrolyte fuel cell is usually kept below the boiling point of water, although at higher temperatures would bring considerable advantages from the point of view of reaction kinetics and catalyst susceptibility to contaminants. To overcome this drawback several groups are searching worldwide for alternative membranes able to transport protons by other mechanisms or at least able to properly operate at a broader temperature range and at lower humidification levels. The most investigated material for this condition is polybenzimidazole (PBI), which was introduced by Savinell [1] and is today after manufacture in membrane-electrode assembly commercialized by BASF Fuel Cell. Pristine PBI has a negligible proton conductivity, but when doped with phosphoric acid (ca. 5 H₃PO₄ molecules per PBI unit) the proton conductivity reaches values of 60 mS/cm at 180°C, as mentioned in an extensive review on PBI membranes recently published by Li and Jensen [2,3]. The idea behind it is that PBI contain rather basic groups, which act as proton acceptor in an acid-base “reaction” with the doping acid. In ideal case after protonation the imidazole group should be able also to donate the proton back to an acid molecule and further promote its effective migration. However this is not the only and not even the main event involved in the proton transport in PBI. Actually a large amount of free acid molecules is present and in great part they act as vehicle for the proton transport. The well known disadvantage is that under operation this acid can be leached out of the

membrane. Another disadvantage of PBI is the low proton conductivity at room temperature even when acid doped. When aiming application in the automotive industry this is also an important issue. In the last years a lot of efforts have been dedicated to improve PBI membranes by changing their chemical structure, like is reported in a review of Leikin et al. [4]. A strategy has been the introduction of sulfonic groups [5]. Promising results have been reported by incorporating pyridine into the backbone [6,7]. Our group has been investigating another class of polymers, also containing amphoteric heterocyclic groups, which could act as proton acceptor and donor. A series of papers based on polyoxadiazole has been published [8-11]. Here in this paper the focus is on polytriazoles. As mentioned before for working well not only basicity is required but the polymer must be able also to donate protons and therefore a very well balanced amphoteric character must be offered, otherwise the proton transfer might be blocked. Triazole and oxadiazole groups are less basic than pyridine and are expected to offer more convenient amphoteric sites for proton transfer. Furthermore acid sulfonic group could be additionally introduced. Both the amphoteric triazole/oxadiazole groups and the acid sulfonic groups are favorable sites for hydrogen bonding.

So far the reason for choosing polytriazole is explained above but this is only the first step. The most important issue in this paper is how to synthesize polytriazole with a rather simple and fast method and leading to a product not only with high proton conductivity but also with good enough mechanical properties to prepare membranes and in a future stage to manufacture them into stable membrane electrode assemblies.

The literature describes different routes for the synthesis of polymers containing the 4-phenyl- or 4-hydro-1,2,4-triazole unit in the structural backbone or

as pendant groups [12]. The reaction between ditetrazoles and diacid chlorides affords relatively low molecular weight polymers. On the other hand high molecular weight polymers can be obtained by the cyclocondensation reaction of aniline with aromatic polyhydrazides in polyphosphoric acid (PPA). However the conversion from polyhydrazides to polytriazoles is not always high. If polytriazoles are expected to be produced in a large scale, there is a need to synthesize high molecular weight polytriazoles in short reaction time at high temperatures without residual hydrazide groups and soluble in common polar aprotic organic solvents.

In this paper, we describe a short time one-pot synthesis of high molecular weight sulfonated poly(1,3,4-oxadiazole-1,2,4-triazole)s and the effect of the synthesis conditions (initial reaction time, t_1 , and total reaction time, t_T) on the polymer properties, specially taking into account the conversion degree and sulfonation level, for their application in fuel cells. The one-stage synthesis of polytriazoles is not only of technological but also of economical convenience compared to multiple-stage process. Therefore, sulfonated poly(oxadiazole-triazole)s copolymers were synthesized via one-step polycondensation reaction of hydrazine sulfate, a non sulfonated dicarboxylic acid and aromatic primary amine (sulfonated and non sulfonated) in polyphosphoric acid. The reaction time (t_1 and t_T) effect on the degree of conversion (N/C ratio) to polytriazoles was investigated. By using an aromatic primary amine containing in its structure at least one sulfonic acid group the sulfonation level (S/C ratio) was controlled. According to Figure 1, an optimum t_1 will allow the polymerization to take place following mechanism A, i.e., the synthesis of poly(4-phenyl-1,2,4-triazoles) with higher N/C and S/C values by cyclocondensation reaction between an intermediate polyhydrazide and an aromatic primary amine (e. g. aniline or sulfonated aniline)

(Figure 1)

2. Experimental

2.1. Materials

All chemicals were used as received. Aniline, ANI ($\geq 99\%$, Aldrich), 4-aminobenzenesulfonic acid, S-ANI (99%, Aldrich), 4,4'-diphenylether dicarboxylic diacid, DPE (99%, Aldrich), hydrazine sulphate, HS ($>99\%$, Aldrich), poly(phosphoric acid), PPA (Aldrich), sodium hydroxide, NaOH (99%, Vetec), sulfuric acid (95-97%, Vetec), n-methyl-2-pyrrolidone, NMP (Merck), dimethyl sulfoxide, DMSO (Merck), dimethylacetamide, DMAc (Merck), dimethylformamide, DMF (Merck).

2.2. Synthesis of sulfonated poly(oxadiazole- triazole) copolymers

The general synthesis procedure can be described as follow: PPA was initially heated up to 100°C 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 during the whole synthesis procedure. Once the temperature was reached, hydrazine sulfate (HS) was added to the PPA. Meanwhile the temperature was increased up to 160°C and the reaction media was stirred until homogenization. Once reached the reaction temperature, 4,4'-diphenylether dicarboxylic acid (DPE) was added to the reaction medium and left to react at this temperature for a period of time according to the experimental design (from 1 to 3 hours). The molar dilution rate (PPA/HS) and the molar monomer rate (HS/DPE) were kept constants and equal to 10 and 1.2, respectively [9,12,13,14]. Then, the temperature was increased up to 180°C and the reaction medium was kept

continuously stirring. Reaching this temperature, the aromatic primary amine (sulfonated or not) was added to the flask and left to react at this temperature in such a way that the total reaction time ranged from 3 to 16 hours. The aromatic amine was added with a molar ratio of 1:1 to the in situ formed polyhydrazide. After finishing the batch and to precipitate the polymer, the reaction medium was poured into a 5% w/v of cold (0°C) sodium hydroxide solution. The pH of this precipitation bath was controlled by addition of additional amounts of 5 % (w/v) NaOH aqueous solutions. The blue-dark fiber obtained in this way was gently washed with distilled water, then filtrated and re-immersed in water during 48 hours at 25 °C and then dried in vacuum oven at 100°C during 48 hours.

2.2.1. *Poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneoxy-1,4-phenylene)-co-poly[4-(4'-sulfophenyl)-1,2,4-triazole-3,5-diyl-1,4-phenyleneoxy-1,4-phenylene] (s-POD-SPT)*

The structural characterization of polymers prepared with sulfonated aniline was obtained by elemental analysis. The proposed theoretical structures of the polymer samples are presented in Table 1 (samples 1 to 7) and Figure 2 (a). The final polymer yield was in the range 82-95% regarding the limiting reactant (DPE).

(Figure 2)

(Table 1)

2.2.2. *Poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneoxy-1,4-phenylene)-co-poly(4-phenyl-1,2,4-triazole-3,5-diyl-1,4-phenyleneoxy-1,4-phenylene) (s-POD-PT)*

For polymers prepared exclusively with non-sulfonated aniline, the final polymer yield was always around 95% regarding the limiting reactant (DPE). The structural characterization obtained by elemental analysis and the proposed theoretical structures of the polymer samples are presented in Table 1 (samples 8 to 11) and Figure 2 (b).

2.3. Membrane preparation

A homogeneous solution containing 5 wt. % of polymer dissolved in NMP or DMSO was stirred for 4 hours at 65°C and cast on a glass plate (previously hydrophobized with octadecyl trichlorosilane) at the same temperature during 24 hours for solvent evaporation. The final film thickness was controlled by pouring the polymer solution into a stainless steel ring of 10 cm diameter. After casting, the membrane was dried in a vacuum oven for 24 hours at 80°C. To remove the residual solvent, 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 blue-dark membrane was around 100 µm.

In order to analyze the cation size effect upon the proton conductivity, some sulfonated s-POD-SPT and s-POD-PT membranes prepared using DMSO as solvent were converted into their acid form by immersion in 0.1M HCl at room temperature for 24 h, followed by immersion in water for 2 x 24 h to ensure total leaching of residual chlorhydric acid.

2.4. Characterization

The polymer structures were characterized by elemental analysis and ¹H-NMR spectroscopy. Elemental analyses were conducted on a Thermo Finnigan - CE Instruments Model Elemental Analyser 1112 series at the Laboratório de Análises, C.Q.F.B., Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa. ¹H-NMR spectra were obtained in deuterated DMSO-d₆ at 25°C using a Bruker DMX-300 spectrometer.

Molecular weight measurements were performed with a Viscotek SEC apparatus equipped with Eurogel columns SEC 10.000 and PSS Gram 100, 1000, with size 8 x 300 mm, was employed to evaluate the average mass molecular weights of polymer samples. The equipment was calibrated using polystyrene standards (Merck) with average mass 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.

Ionic conductivity was measured by the AC impedance spectroscopy in the frequency range 10-10⁶ Hz at signal amplitude \leq 10 mV and derived from the high frequency intercept of the complex impedance with the real axis, using a two electrode arrangement and at 100% of relative humidity. The impedance measurements were carried out on stacks containing up to five membranes (similar cumulative thickness, around 500 μ m). The measurements were performed at 100 % relative humidity, using a cell similar to that described by Alberti et al. [15]. The spectrometer used was a Zahner IM6 electrochemical workstation.

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 1Hz and initial static force of 0.1 N. The temperature was varied from 25 to 500 °C at a heating rate of 2°C/min and at a constant strain of 0.05%.

The viscosity of PPA solutions was measured at 30 °C in a LVTD Brookfield digital viscometer.

3. Results and Discussion

3.1. Polymer Synthesis

The synthesis conditions for the poly(oxadiazole-triazole) copolymers have been selected considering previously reported optimized synthesis method for polyoxadiazoles (POD) with high molecular weight, high sulfonation level (IEC around 1.26 mequiv g⁻¹), soluble in organic solvents [9,13,14] and good proton conducting properties. In the present work and in order to improve the synthesis conditions of the polytriazole polymers depicted in Figures 2, the effect of the reaction time (t_1 and t_T) on the degree of conversion (N/C ratio) to polytriazoles, as well as on the sulfonation level (S/C ratio) was investigated using aniline and an aniline derivative containing a sulfonic acid group in para-position, 4-aminobenzenesulfonic acid, S-ANI. For these sPOD-PT copolymers, the conversion of oxadiazole rings to triazole (N/C ratio) was determined by elemental analysis and calculated according to equation (1) [9]:

$$\% \text{ Conversion} = [(N/C - 0.167)/0.008] \times 100 \quad (1)$$

Effect of t_1 and t_T on the N/C ratio: Taking into account the proposed reaction mechanisms described in Figure 1, an optimum t_1 should lead to a high or total consumption of the initial monomers (HS and DPE) to render polymers with a high content of triazoles rings (N/C close to 0.175); the optimum t_1 favor the prior in-situ formation of polyhydrazide, which will be cyclocondensated with S-ANI to render a polytriazole (mechanism A, Figure 1). However if t_1 is too long, the polyhydrazide will start to cyclodehydrate to POD (mechanism D, Figure 1) and as a consequence the conversion to polytriazoles will be low. In the opposite case, if t_1 is too short part of the starting monomers will remain unreacted in the solution and as soon as S-ANI is added they will react according to mechanism B and C. Also in this case the conversion to polytriazole would be low. Analyzing the results of Table 1, a high conversion to triazole rings (N/C = 0.1739) has been reached when the starting

monomers (HS and DPE) were left to react for a $t_1 = 1-2$ hours and implies 86-93% of triazole content (Figure 2 (a)). That means that during the first 1-2 hours just a minimal amount of polyhydrazides has been cyclodehydrated to POD (mechanism D, Figure 1) and that for these synthesis conditions the cyclocondensation of polyhydrazide and S-ANI is much more feasible to take place than the opening ring reaction of POD by S-ANI [16], at least in the synthesis conditions of samples 1 and 7.

Concerning the effect of the total reaction time (t_T) on the degree of conversion, it was observed that with an increase of t_T from 3 to 16 hours the degree of conversion (N/C) decreases with an increase of the total reaction time (Figure 3), even for polymers synthesized under the same initial reaction time. This detrimental effect of t_T can be explained as a degradation of the polymer with the time due to the harsh synthesis conditions, that is, a high reaction temperature and the acidity of the reaction medium.

(Figure 3)

For similar synthesis conditions, it is noted that higher conversions to polytriazole have been reached when copolymers were synthesized using S-ANI instead of aniline, indicating that the incorporation of sulfonated aniline (S-ANI) is favored over aniline itself. Similar observations have been reported by Hensema et al. [17] when synthesizing polytriazoles using aniline in combination with chloro aniline; it was determined that incorporation of the aniline derivative is easier than the incorporation of aniline itself. It is known that aniline and its derivatives forms a complex with PPA (anilinium or phenylammonium ion, $C_6H_5-NH_3^+$), which is in equilibrium with the free amines [16]. Taking into account the basicity of aniline (pKa: 4.58), chloro aniline (pKa: 3.98) and sulfonated aniline (pKa: 3.12), it is clear

that relatively more free sulfonated aniline and chloro aniline would be available in the reaction medium [16,18]. This means that the presence of the electron withdrawing group (-SO₃H) in S-ANI shifts the equilibrium between complex and free amine in the direction of the sulfonated aniline (S-ANI). As only free amines can react with polyhydrazide and due to the strong complex formation between polyphosphoric acid and aniline [16], the concentration of the free amine (aniline) should be too low to reach a high degree of cyclocondensation of polyhydrazide to polytriazole. This explains the low conversion to polytriazoles obtained for samples 8 to 11 in Table 1.

Effect of t_1 and t_T on the S/C ratio: A maximum sulfonation level (S/C ratio) of 0.400 is established here when each phenylene ring contains a sulfonic acid group and for N/C = 0.175. From elemental analysis, it was found that this one-pot synthesis of polytriazoles in poly(phosphoric acid) (PPA) using sulfonated monomers (hydrazine sulfate, HS, and sulfonated aniline, S-ANI) rendered partially sulfonated copolymers (s-POD-SPT) (Figure 2 (a)), with S/C values up to 0.094 (Table1). Contrary to our expectations to obtain polymers with high sulfonation degree when using sulfonated monomers, HS and S-ANI, only polymers with a relatively low sulfonation level were obtained. It is to consider that electron-withdrawing groups in the *ortho*- and *para*-position to the sulfonic acid group in the phenyl ring increase the hydrolytic stability of the sulfonic acid group in the aromatic ring; the opposite effect is given by electron-donor substituents like amino (-NH₂) groups in *ortho* and *para*-position to the sulfonic acid group, resulting in hydrolytically less stable aromatic sulfonic acid groups [19]. Considering the synthesis conditions here described, the desulfonation of aminobenzensulfonic acid, S-ANI, can be considered as very

probable [20] (Figure 1, mechanism E) and explains the low sulfonation levels reached when synthesizing polytriazole with high conversion using sulfonated aniline.

The ^1H NMR spectra of s-POD-SPT copolymers in DMSO- d_6 should be expected to show a singlet at 8.5 ppm for the proton adjacent to the sulfonic group in the aromatic ring of the polymer backbone [11] and another seven signals for the protons on the pendant sulfonated and non-sulfonated phenyl group and for the aromatic protons in the polymer backbone [21,22]; however only 5 NMR signals are distinguishable, indicating overlapping signals specially of that corresponding to the protons on the pendant phenylsulfonic acid groups (Figure 4). This way, it was neither possible to confirm the quantitative conversion to polytriazoles nor the sulfonation level by ^1H NMR. Although ^1H NMR spectroscopy was not a proper tool for a quantitative analysis of the copolymers, it was useful to confirm the absence of residual polyhydrazide, which can be found in the range of 10.0–10.5 ppm [22,23].

(Figure 4)

For s-POD-PT copolymers, neither the sulfonation level nor the conversion degree to polytriazole could be confirmed by NMR because of the same reasons explained above for s-POD-SPT copolymers. Also for these copolymers no residual polyhydrazide was detected.

The molecular weight is also a very important requirement for fuel cell membrane materials. High molecular weight polymers lead to better film forming properties and membranes with better mechanical properties. The short one-pot synthesis here described has rendered s-POD-SPT and s-POD-PT copolymers with average mass molecular weights (M_w) in the order of 10^5 g mol $^{-1}$ (Table 2); the obtained high molecular weights can be attributed to the formation of three-dimensional crosslinked structures [13].

(Table 2)

Despite having high molecular weight, all the polymers were soluble in organic polar solvents like NMP, DMAc, DMF and DMSO enabling the preparation of dense membranes. It was observed that for polymers synthesized under the same initial reaction time (till the addition of aniline or sulfonated aniline), an increase in the total reaction times diminishes the molecular weight (average mass molecular weights, M_w) almost one order of magnitude as a consequence of the polymer degradation mentioned before (Figure 3, Table 2).

The sulfonation level (S/C ratio) of ionomeric polymers is crucial for high proton conduction. The figure 5 shows the ionic conductivity values of s-POD-SPT copolymers with different S/C at temperatures between 30°C to 80°C.

(Figure 5)

Considering the low sulfonation level of these copolymers, the ionic conductivity values are relatively high. This seems to be due to the structure of these s-POD-SPT copolymers: the presence of the basic pyridine-like N sites in the oxadiazole and triazole rings might contribute to the ionic conduction together with the sulfonic groups present in the neighbor diphenylether groups as well in the pendant phenyl group. The effect of the polymer structure on the ion transport can be also evidenced when analyzing the ionic conductivity values of s-POD-SPT and s-POD-PT membranes with almost the same sulfonation level, like in the example shown in Figure 6 (S/C= 0.084, IEC = 1.63). Probably the presence of the sulfonic group in the pendant phenyl ring of the triazole ring in s-POD-SPT membrane, is the reason for the high ionic conductivity of these membranes compared to those of s-POD-PT.

(Figure 6)

It is also known that residual solvent molecules in the casted membrane also participate in hydrogen-bonding interactions (either as donors or acceptors) with a polymer component like the sulfonic group [24-29]. Since these interactions will have an additional effect on to the proton transport, proper solvents for these s-POD-SPT and s-POD-PT copolymers must be of dipolar nature, with good proton donor ability, and aprotic nature. Solvents with such properties are DMSO and NMP. Difference in the strength of hydrogen-bond interactions between these solvents with the –OH of sulfonic group in the polymer, are manifested in the different conductivity values measured for s-POD-SPT and s-POD-PT membranes when using DMSO as solvent instead of NMP (Figure 7).

(Figure 7)

Hydrogen-bonding interactions of both solvents with the hydroxyl group of PPA have been confirmed by the high viscosity of PPA/ NMP solutions (140000 CPs) compared to PPA/DMSO (60000 CPS) solutions with the same concentration ratio (Figure 8) [30]; for these aprotic solvents, the following order of proton donor ability has been found: DMSO >> N-methylpyrrolidone (NMP) > N,N-dimethylacetamide (DMAc) >> dimethylformamide (DMF) [31]. It can be assumed that the strong complexion ability of NMP compared to DMSO is not only due to the participation of the oxygen of the carbonyl bond but also of the hydrogen at alpha position, which is not present in DMSO [32]. Analogous effect (interaction between NMP and the acid sulfonic group in the polymer) is the reason of relatively low proton conductivity of membranes prepared using NMP as solvent, compared to those prepared from solutions in DMSO.

(Figure 8)

Taking into account the high ionic conductivity values shown in Figure 5 as well as the relative high molecular weight (Table 2), a membrane sample with S/C = 0.091 was converted into the acid form and the ionic conductivity was compared to that in the salt form. The significant difference between the ionic conductivity of polymers in salt and in acid form (Figure 9) is attributed to the fact that larger ions have lower mobility than protons [11,33]. Proton conductivity of membranes in the acid form was as high as 16 mS cm^{-1} at 50°C and 100% relative humidity.

(Figure 9)

To analyze the contribution of the pyridine-like N sites (proton acceptor) in the oxadiazole and triazole rings to the proton transport, the proton conductivity of a s-POD-SPT membrane, at 100% relative humidity and at the temperature range of 60°C to 150°C was compared to that of a sulfonated poly(ether ether ketone) with the same sulfonation level (S/C= 0.091) (Figure 10) [34]. It was observed that the s-POD-SPT membrane was much better proton conductor than the s-PEEK membrane. This makes the s-POD-SPT membrane a promising material for fuel cells applications.

(Figure 10)

The thermal and mechanical properties of the s-POD-SPT and s-POD-PT membranes were evaluated by means of dynamic mechanical thermal analysis. Good dimensional stability and high storage modulus (E') (3 GPa at 300°C) (Figures 11 and 12) were observed. Table 2 shows the T_g taken as the maximum of $\tan \delta$ and loss modulus (E'') curves for some s-POD-SPT and s-POD-PT membranes, respectively.

(Figure 11)

(Figure 12)

The T_g values for the s-POD-SPT membranes (up to around 440°C) were higher than the T_g for the s-POD-PT membranes (up to around 400°C). The sulfonic group is bulky, making the rotation movement more difficult.

Conclusions

Sulfonated poly(oxadiazole-triazole) copolymers with high molecular weights (order of magnitude 10^5 g mol^{-1}) were obtained by one-pot synthesis method with short reaction times. The method consists of polycondensation of sulfonated hydrazine, an aromatic dicarboxylic acid and an sulfonated or non sulfonated-aniline in poly(phosphoric acid). For reaction times not longer than 5 hours, the synthesis has not only rendered polymers with a high conversion degree (up to 93%) but also with a high sulfonation degree (IEC up to 1.84 meq g^{-1}) and good mechanical properties. Sulfonated poly(oxadiazole-triazole) copolymer with high sulfonation level had high proton conductivity ($10^{-2} \text{ S cm}^{-1}$ at 150°C) making it promising for the manufacture of polymer electrolyte membranes.

References

1. R.F. Savinell, M.H. Litt, Proton conducting polymers used as membranes, US Patent 5,525,436, 1996.
2. R. He, Q. Li, G. Xiao, N.J. Bjerrum, Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors, J. Membr. Sci., 226 (2003) 169-184.

3. R. He, Q. Li, A. Bach, J.O. Jensen, N.J. Bjerrum, Physicochemical properties of phosphoric acid doped polybenzimidazole membranes for fuel cells, *J. Membr. Sci.*, 277 (2006) 38-45.
4. A. Yu. Leikin, E. G. Bulycheva, A. L. Rusanov, Yu. Likhachev, High-Temperature Proton-Exchange Membranes Based on Polymer–Acid Complexes, *Polym. Sci. B*, 48 (2006) 144-151.
5. J. A. Asensio, S. Borros, P. Gomez-Romero, Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles, *J. Polym. Sci., Part A: Polym. Chem.*, 40 (2002) 3703-3710.
6. L. Xiao, H. Zhang, T. Jana, E. Scanlon, R. Chen, E.-W. Choe, L.S. Ramanathan, S. Yu, B.C. Benicewicz, Synthesis and Characterization of Pyridine-Based Polybenzimidazoles for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications, *Fuel Cells*, 5 (2005) 287-295.
7. J. Kiefer, Method for the production of proton-conducting polymer membranes, improved polymer membranes, and the use thereof in fuel cells, Patent WO 2004,024,796.
8. S. Vetter, S. P. Nunes, Synthesis and characterization of new sulfonated poly(arylene ether 1,3,4-oxadiazole)s, *React. Funct. Polym.*, 61 (2004) 171-182.
9. D. Gomes, J. Roeder, M.L. Ponce, S.P. Nunes, Characterization of partially sulfonated polyoxadiazoles and oxadiazole–triazole copolymers, *J. Mem. Sci.*, 295 (2007) 121-129.
10. J. Roeder, D. Gomes, M.L. Ponce, V. Abetz, S.P. Nunes, *Macromol. Chem. Phys.*, 208 (2007) 467-473.

11. D. Gomes, J. Roeder, M.L. Ponce, S.P. Nunes, Single-step synthesis of sulfonated polyoxadiazoles and their use as proton conducting membranes, *J. Power Sources*, 175 (2008) 49-59.
12. M.L. Ponce, D. Gomes, S.P. Nunes, V.Abetz; Deutsche Patentanmeldung 10 2007 005 666.6
13. D. Gomes, C.P. Borges, J.C. Pinto, Study of the synthesis of poly(4,4'-diphenylether-1,3,4-oxadiazole) in solutions of poly(phosphoric acid), *Polymer*, 42 (2001) 851-865.
14. D. Gomes, C.P. Borges, J.C. Pinto, Effects of reaction variables on the reproducibility of the syntheses of poly-1,3,4-oxadiazole, *Polymer*, 45 (2004) 4997-5004.
15. G. Alberti, M. Casciola, L. Massinelli, B. Bauer, Polymeric proton conducting membranes for medium temperature fuel cells (110–160°C), *J. Membr. Sci.*, 185 (2001) 73-81.
16. J.R. Holsten, M.R. Lilyquist, Aromatic poly(phenylene)4-phenyl-1,2,4-triazoles, *J. Polym. Sci. A*, 3 (1965) 3905-3917.
17. E. R. Hensema, M. E. R. Sena, M. H. V. Mulder, C. A. Smolders, Syntheses and properties of related polyoxadiazoles and polytriazoles, *J. Polym.Sci. Part A: Polym. Chem*, 32 (1994) 527-537.
18. A.N. Pankratov, I.M. Uchaeva, S.Yu Doronin, R.K. Chernova, Correlations between the Basicity and Proton Affinity of Substituted Anilines, *J. Struct. Chem.*, 42 (2001) 739-746.
19. M. Schuster, K.D. Kreuer, H.T. Andersen, J. Maier, Sulfonated Poly(phenylene sulfone) Polymers as Hydrolytically and Thermooxidatively Stable Proton Conducting Ionomers, *Macromolecules*, 40 (2007) 598-607.

20. C. Vogel, J. Meier-Haack, A. Taeger, D. Lehmann, On the Stability of Selected Monomeric and Polymeric Aryl Sulfonic Acids on Heating in Water(Part 1), Fuel Cells, 4 (2004) 320-327.
21. K.R. Carter, R.D. Miller, J.L. Hedrick, Synthesis of 1,2,4-triazole poly(aryl ethers) via heterocyclic-activated displacement polymerization, Macromolecules, 26 (1993) 2209-2215.
22. D. Gomes, J.C. Pinto, C. P. Borges, Determination of hydrazide content in poly(oxadiazole-hydrazide) copolymers by NMR and thermal analysis, Polymer, 44 (2003) 6223-6233.
23. D. Gomes, S.P Nunes, J.C. Pinto, C.P. Borges, Synthesis and characterization of flexible polyoxadiazole films through cyclodehydration of polyhydrazides, Polymer, 44 (2003) 3633-3639.
24. S. K. Chatterjee, B. P. Singh, L. S. Pachauri, Copolymerization parameters of substituted aniline monomers, J. Polym. Sci. Polym. Chem. Ed., 21 (1983) 1165-1171.
25. S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, M. Guiver, Properties of SPEEK based PEMs for fuel cell application, Catal. Today, 82 (2003) 213-222.
26. C.C. Pereira, R. Nobrega, C.P. Borges, Membrane formation with presence of Lewis acid-base complexes in polymer solution, J. Appl. Polym. Sci., 83 (2002) 2022-2034.
27. J. Huang, X. Li and Q. Guo, Interpolymer complexes and miscible blends of poly(*p*-vinyl phenol) and poly(ethylene imine) Eur. Polym. J., 33 (1997) 659-665.
28. I. D. Brown, Structural chemistry and solvent properties of dimethylsulfoxide, J. Solution Chem., 16 (1987) 205-224.

29. T. J. Baker, Formation and reactions of methylol cellulose, Ph.D. Thesis, Lawrence University, Appleton, Wisconsin (1979).
30. D. Gomes, Synthesis of Poli(diphenyl ether oxadiazole) seeking the Preparation of Anisotropic Hollow Fibers by Co-Extrusion for Gas Separation, Ph.D. Thesis, COPPE/UFRJ, Rio de Janeiro, Brazil (2002).
31. M. M. Bastos, J. P. Barbosa, A. C. Pinto, W. B. Kover, Y. Takeuchi, N. Boechat, Reductive Debromination of 1-Methyl-2,4,5-tribromoimidazole Mediated by Dry Tetramethylammonium Fluoride in Aprotic Solvents, J. Braz. Chem. Soc., 12 (2001) 417-421.
32. X. Fu, C. Zhang, D. Zhang, S. Yuan, Theoretical evidence for the reaction of *N*-methyl-2-pyrrolidinone with carbon disulfide, Chem. Phys. Letters, 420 (2006) 162-165.
33. T. Okada, H. Satou, M. Okuno, M. Yuasa, Ion and Water Transport Characteristics of Perfluorosulfonated Ionomer Membranes with H⁺ and Alkali Metal Cations, J. Phys. Chem. B., 106 (2002) 1267-1273.
34. D. Gomes, I. Buder, S.P. Nunes, Sulfonated silica-based electrolyte nanocomposite membranes, J. Polym. Sci. Part B: Polym. Phys., 44 (2006) 2278-2298.

Figures Caption

Figure 1. Proposed main and side reaction mechanisms for the one-pot synthesis of polytriazole polymers.

Figure 2. Proposed copolymer structures.

Figure 3. Effect of the total reaction time (t_T) on the conversion degree (N/C ratio), sulfonation degree (S/C ratio) and the weight average molecular weight (M_w) for a constant initial time reaction ($t_i = 1$ h). The insert shows the proposed N/C ratio for the hypothetical case of polytriazole with 100 % conversion (N/C= 0.175) as well as for pure polyoxadiazole (N/C= 0.167).

Figure 4. $^1\text{H-NMR}$ spectrum of an (s-POD-SPT) in DMSO-d_6 .

Figure 5. Proton conductivity of s-POD-SPT membranes with different sulfonation level (S/C) as a function of the temperature at 100% relative humidity.

Figure 6. Effect of the polymer composition: proton conductivity of s-POD-SPT and s-POD-PT membranes (in salt form) with similar sulfonation level (S/C= 0.084-0.86), as a function of temperature.

Figure 7. Solvent effect: proton conductivity as a function of temperature, for s-POD-SPT membranes prepared from solutions in DMSO and NMP.

Figure 8. Solvent effect on to the viscosity of PPA/ NMP and PPA/ DMSO solutions.

Figure 9. Cation size effect: proton conductivity as a function of temperature for s-POD-SPT membrane with S/C= 0.091 in the salt and acid form.

Figure 10. Proton conductivity of s-POD-SPT and s-PEEK membranes with same sulfonation level ($S/C= 0.091$) as a function of the temperature and 100% relative humidity.

Figure 11. DMTA plot of a s-POD-SPT membrane.

Figure 12. DMTA plot of a s-POD-PT membrane.

Table Titles

Table 1. Proposed composition of copolymers according to elemental analysis.

Table 2. Average mass molecular weights (M_w), T_g taken as the maximum in the $\tan \delta$ and loss modulus (E'') curves.

Figure 1

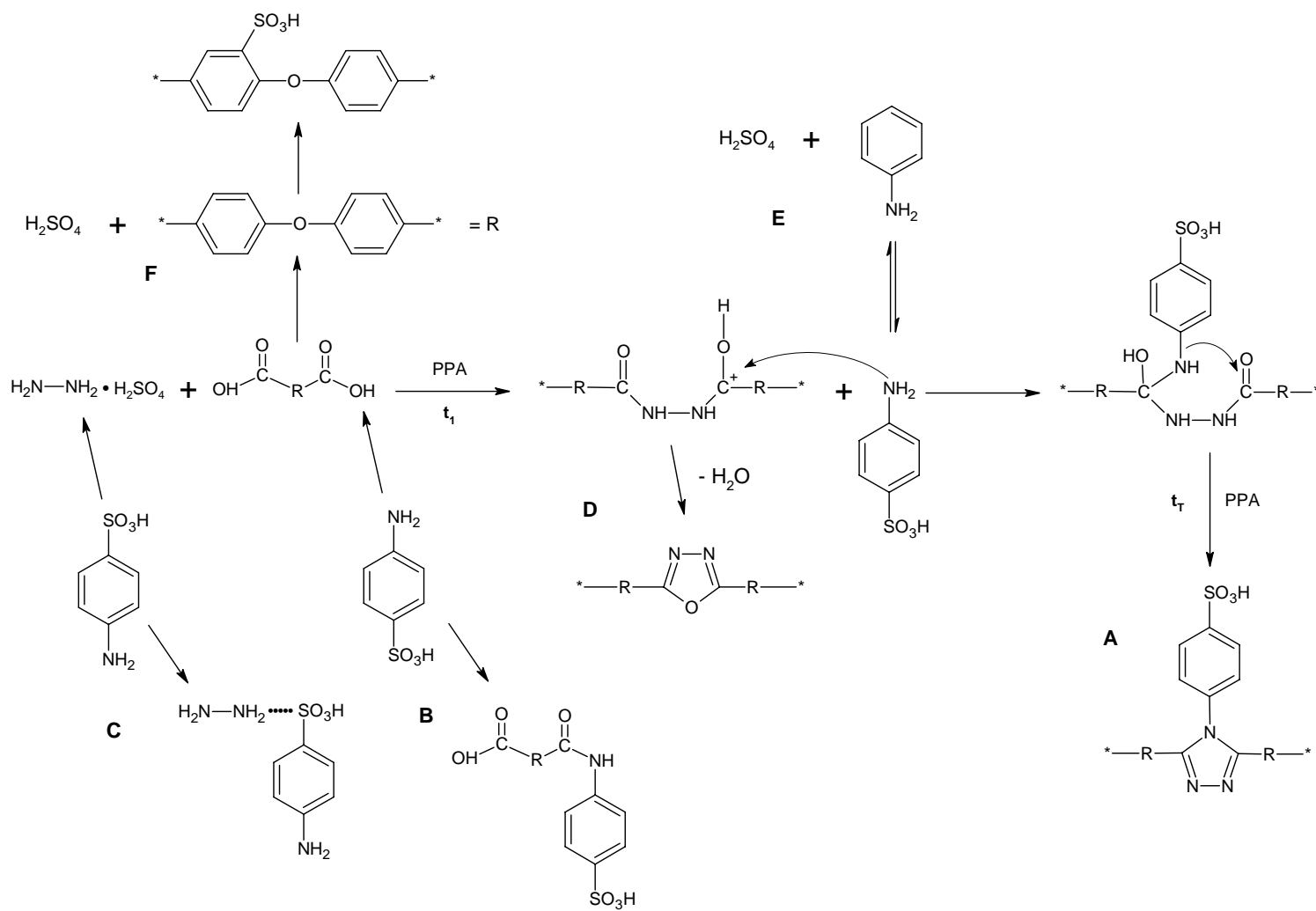
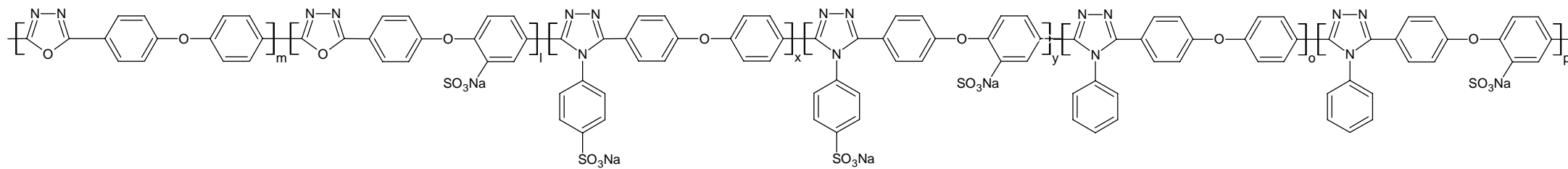


Figure 2.

(a)



(b)

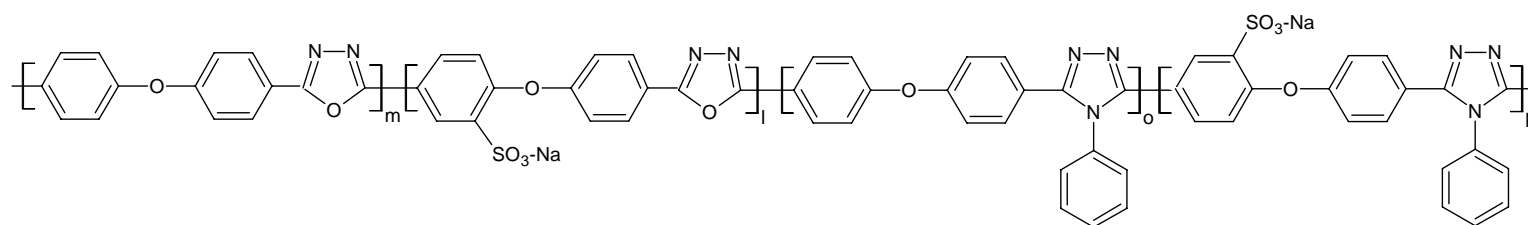


Figure 3.

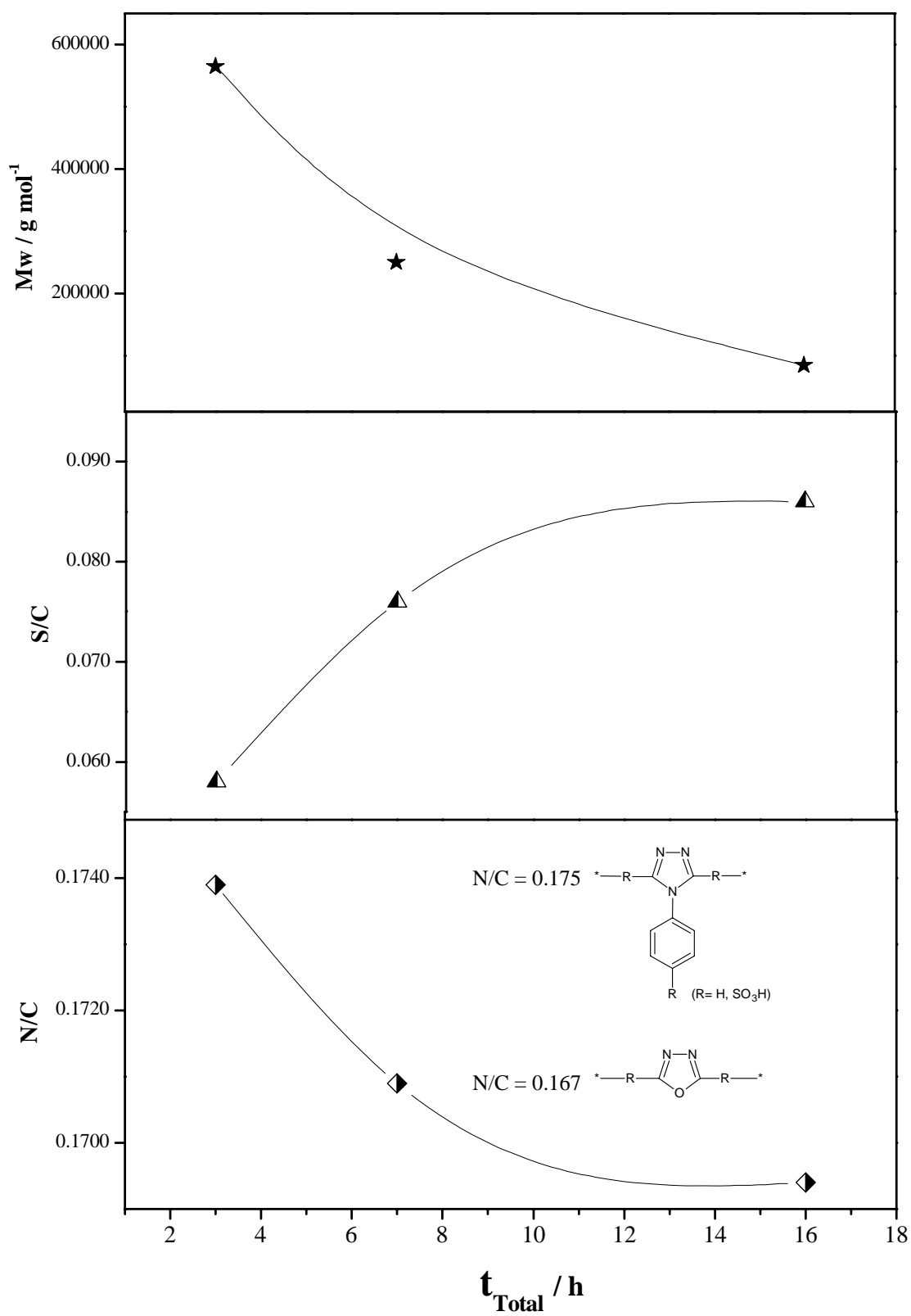


Figure 4

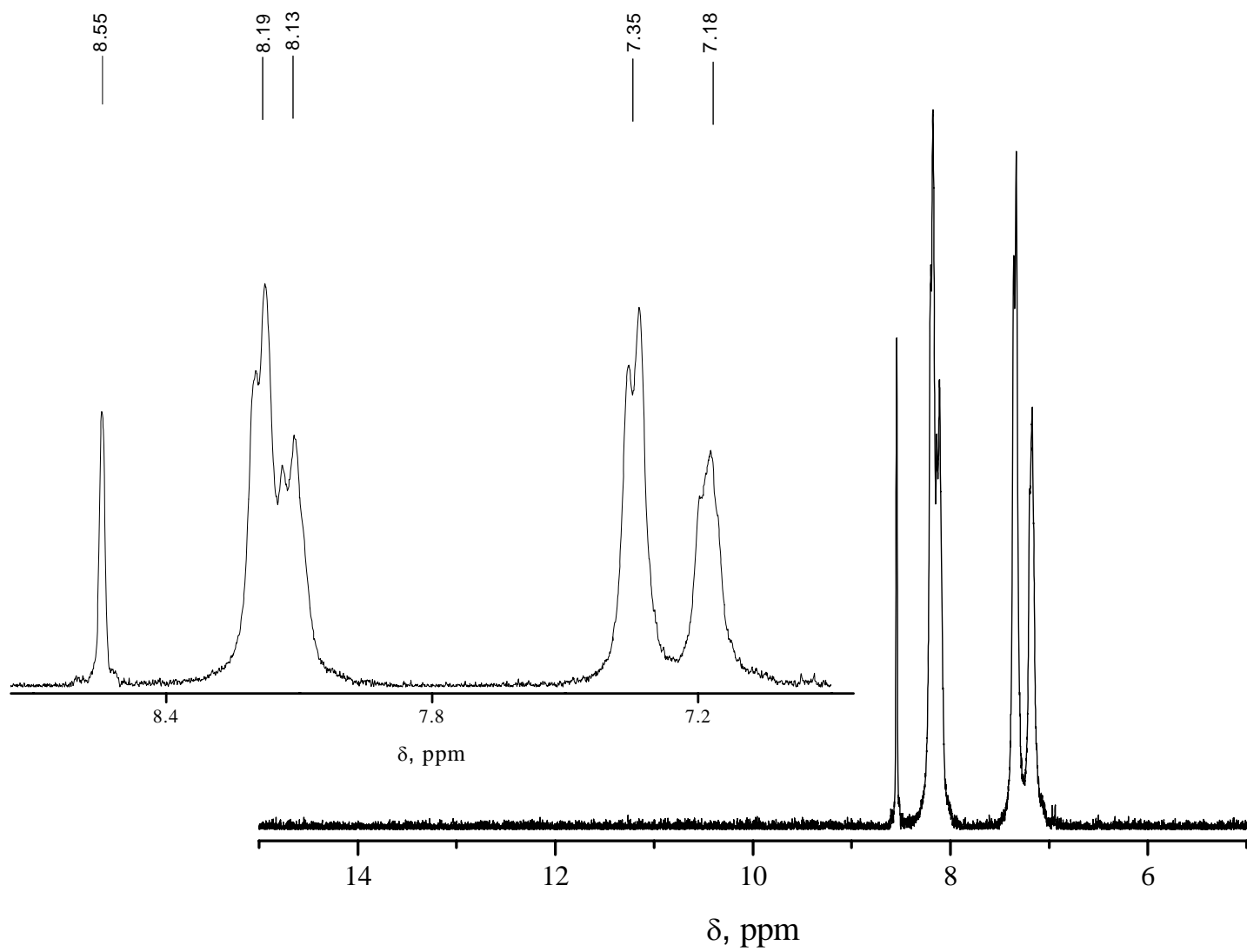
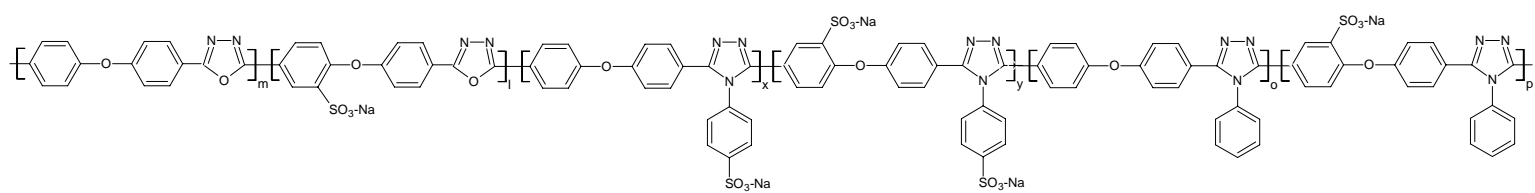


Figure 5.

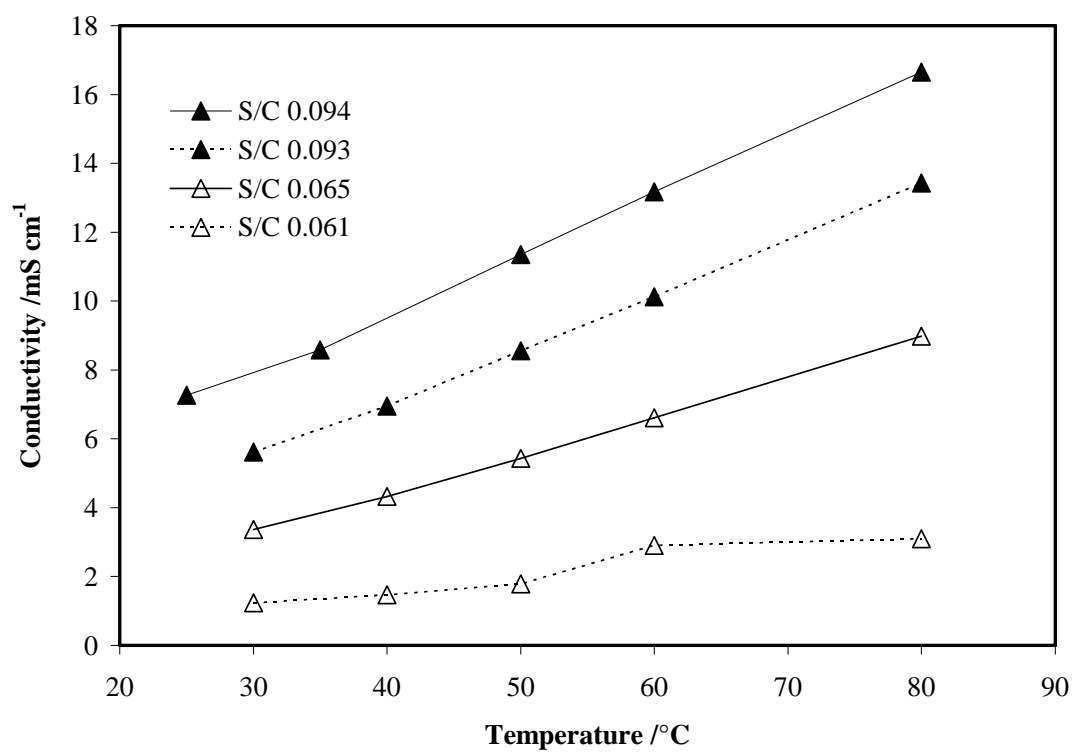


Figure 6.

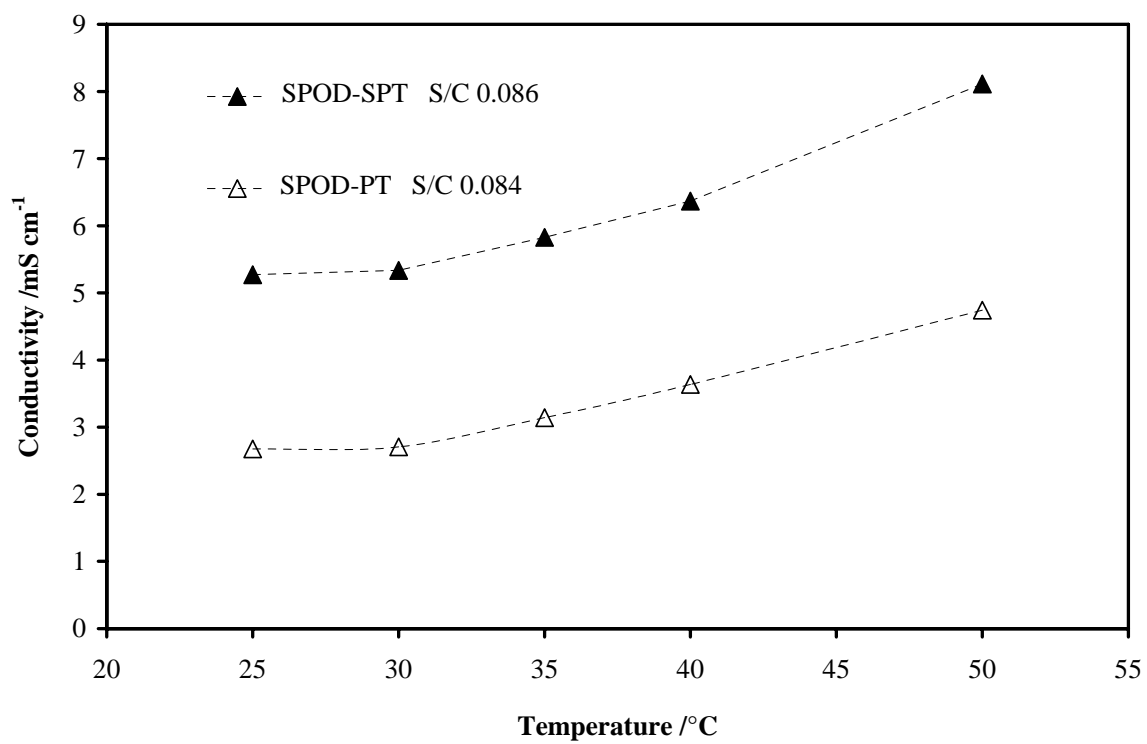


Figure 7.

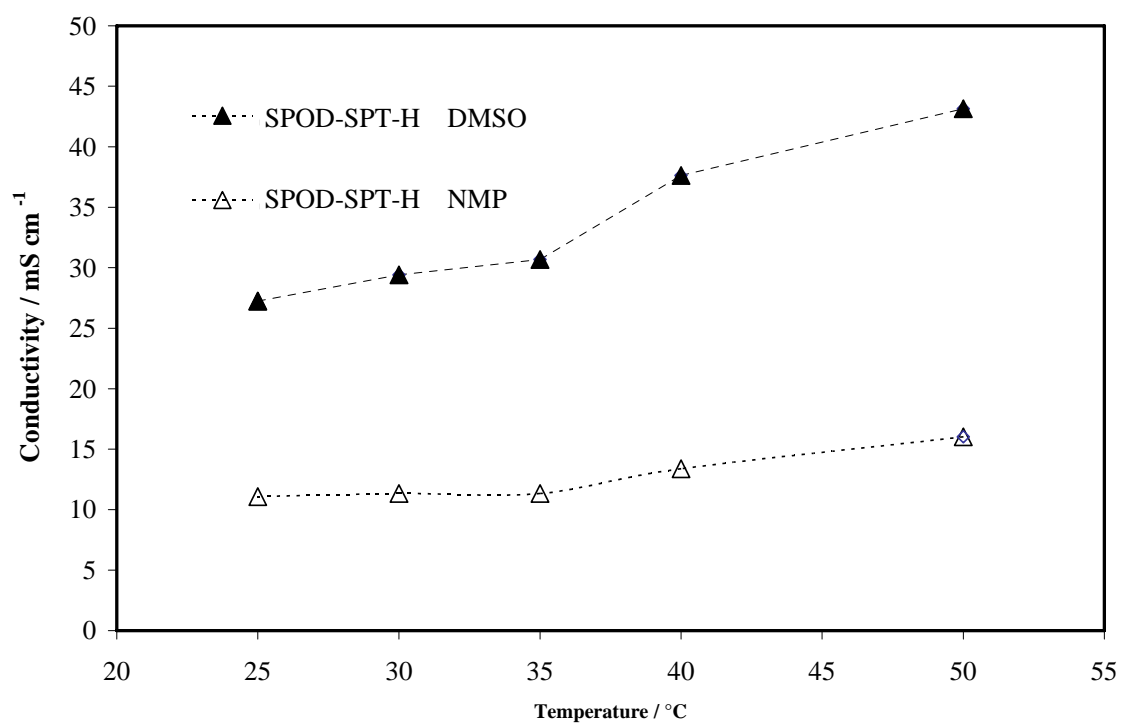


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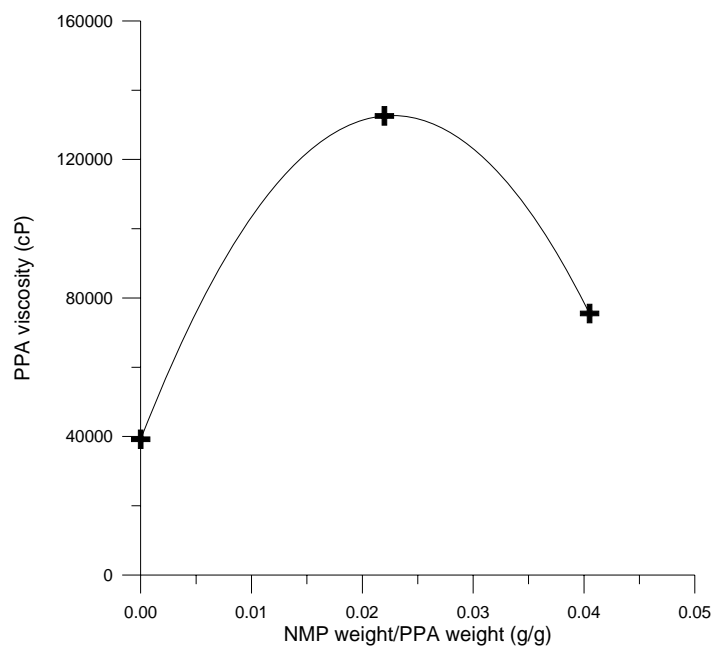
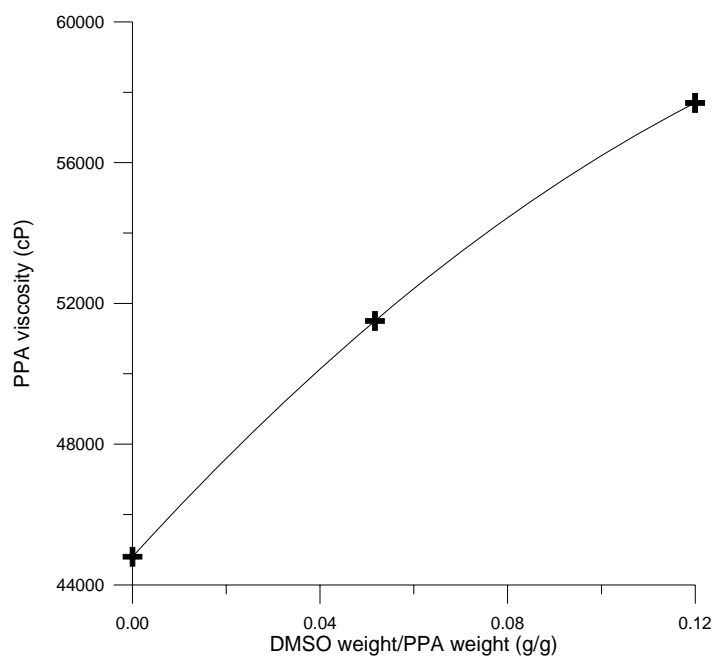
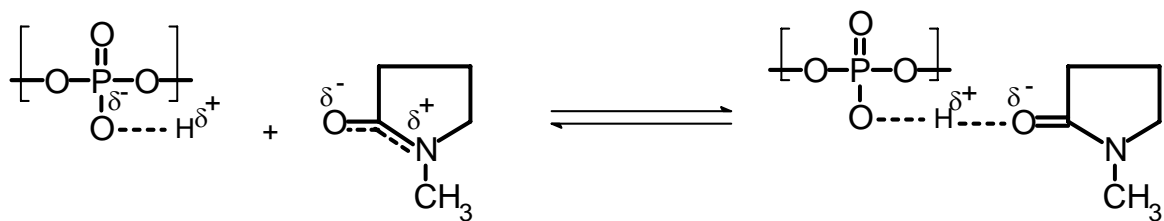


Figure 9.

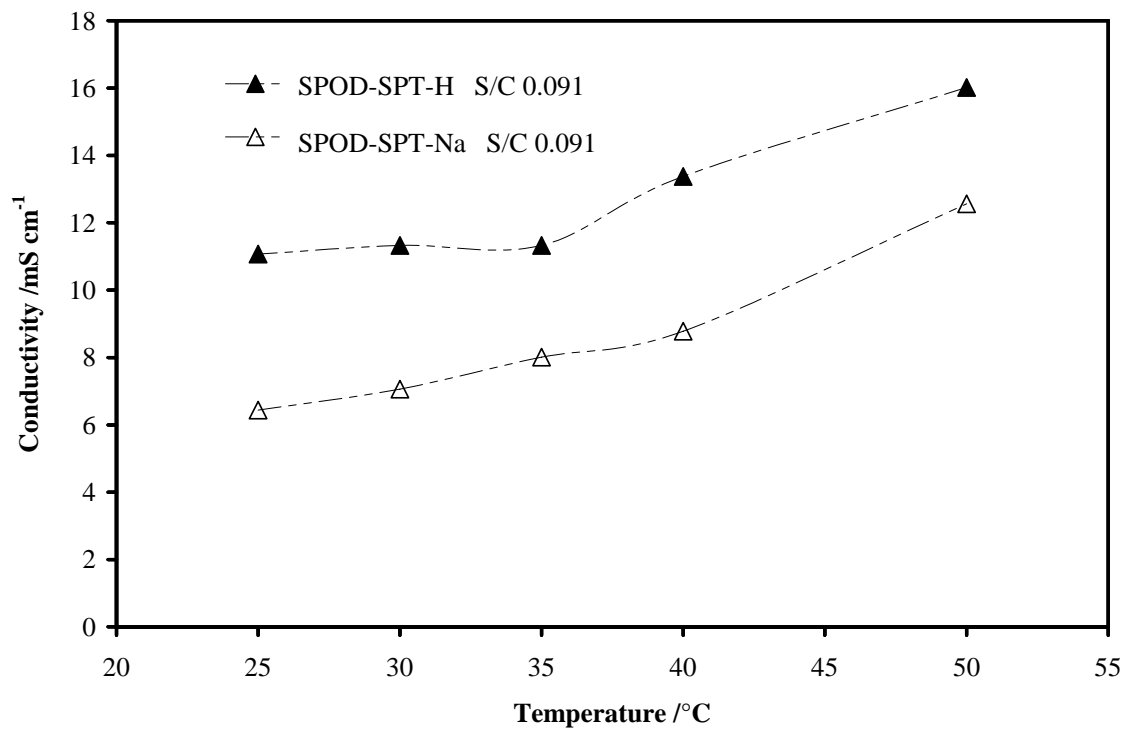


Figure 10.

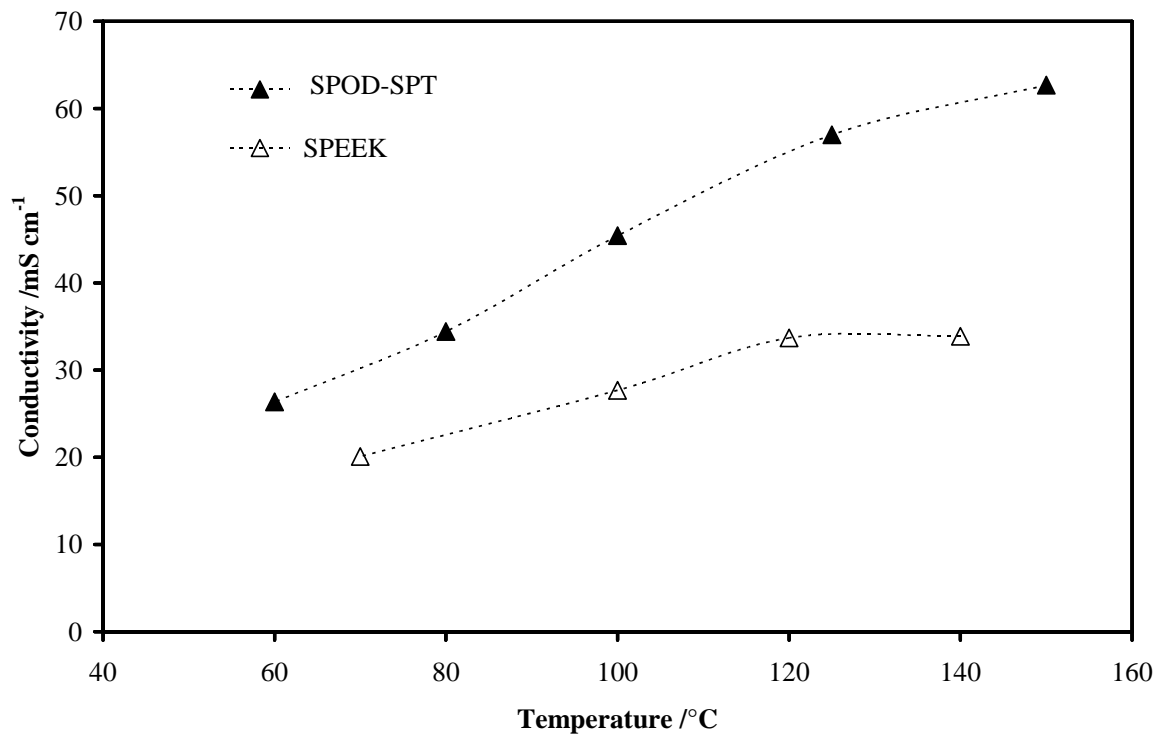


Figure 11

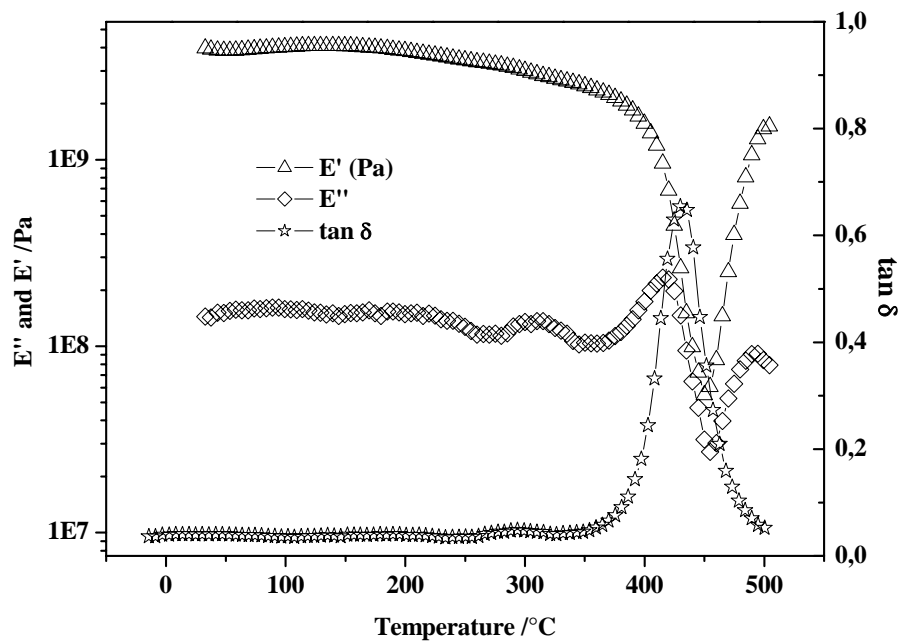


Figure 12

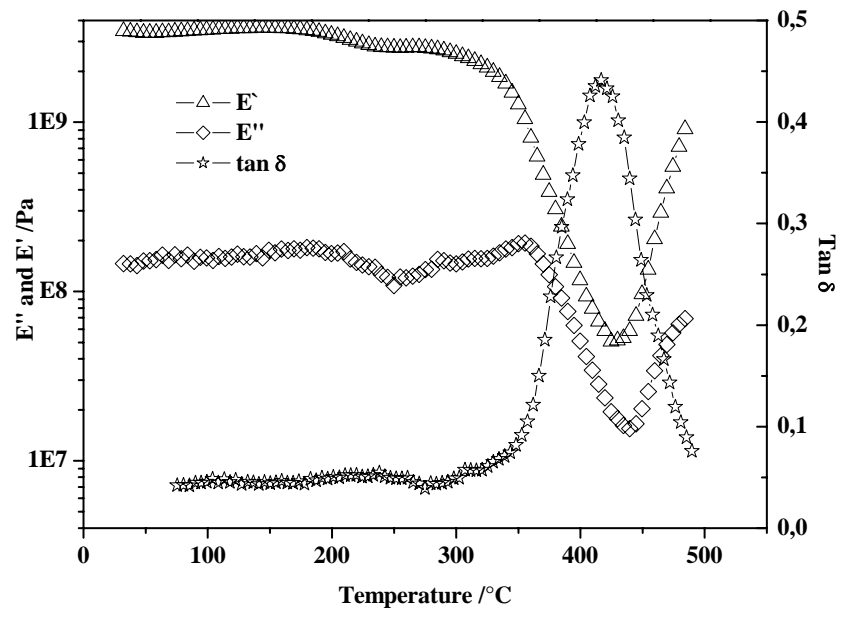


Table 1.

Sample	Composition (POD:SPT:PT) ¹	t ₁ (h)	t _T (h)	N/C _{calc.}	S/C _{calc.}	N/C _{found}	S/C _{found}	IEC (meq. g ⁻¹)	%PT	Yield (%)
1	0.18:0.15:0.67	1	3	0.1739	0.058	0.1739	0.058	1.20	86	82
2	0.54:0.16:0.30	2	4	0.1712	0.091	0.1712	0.091	1.71	53	95
3	0.28:0.18:0.54	3	5	0.1732	0.095	0.1732	0.094	1.84	78	87
4	0.58:0.20:0.22	1	7	0.1709	0.076	0.1709	0.076	1.49	48	86
5	0.75:0.15:0.10	1	16	0.1694	0.086	0.1694	0.086	1.63	30	95
6	0.36:0.13:0.51	3	7	0.1726	0.077	0.1726	0.077	1.48	69	93
7	0.10:0.17:0.73	2	5	0.1744	0.058	0.1744	0.058	1.17	93	83
8	0.84:0:0.16	1	3	0.1684	0.084	0.1685	0.084	1.58	18	95
9	0.72:0:0.28	1	4	0.1696	0.083	0.1696	0.083	1.63	32	95
10	0.72:0:0.28	1	5	0.1696	0.084	0.1696	0.084	1.63	32	98
11	0.81:0:0.19	1	7	0.1688	0.060	0.1688	0.060	1.21	23	97

¹POD (m,l):SPT (x,y):PT (o,p) in Figure 2

Table 2.

Sample	Mw (g mol ⁻¹)	T _{g, E''} (°C)	T _{g, tan δ} (°C)
1	565000	419	437
2	438000	420	435
3	45600	-	-
4	250000	390	420
5	85000	395	420
7	176000	395	420
6	330000	375	420
8	478000	355	390
9	386000	360	404
10	374000	350	400
11	51500	350	395