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Sulfonated polynaphthalimides with benzimidazole pendant groups

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Summary

A series of new polyimides bearing simultaneously sulfonic acid groups and benzimidazole rings in different proportions has been synthesised by one pot high temperature polycondensation. The composition of the copolymers, as well as the distribution of the ionic sites along the polymer chain, has been changed systematically in order to study their relation with polymer properties. The incorporation of benzimidazole and sulfonic side groups in the structure improves the solubility in polar organic solvents. On turn, the presence of sulfonic acid moieties impairs thermal resistance. Membranes based on the synthesised polyimides were prepared by solution casting and their water uptake as well as proton conductivity were determined.

Keywords: Sulfonated polyimides; benzimidazole; Polycondensation; Ion-exchange membranes; Fuel cell.

1   Introduction

Functionalised polymers are gaining more importance in the field of advanced technologies, for instance as proton exchange materials for PEMFC (Proton Exchange Membrane Fuel Cell). [1] A fuel cell is an electrochemical system able to transform the chemical energy stored in an energy carrier (fuel) directly into electrical energy. As long as the reactants (fuel and oxidant) are provided to the fuel cell, the production of energy will continue. At present,

perfluorinated polyolefins with sulfonated side chains are almost the only commercial polymers being used as proton exchange membranes for fuel cells. Nafion® (DuPont) is used as standard in fuel cell technology, and as reference for the development of new materials. However, drawbacks are still the high price and the drying of the membrane under medium-high operation temperatures (T ≥ 90°C). This temperature range would be convenient from the point of view of kinetics, heat rejection and the catalyst's tolerance to CO. [2] [3] Therefore, in the last years, many research efforts are outlined to obtain membranes that overcome these problems.

Aromatic polymers exhibit excellent mechanical as well as thermal and chemical stability, besides relatively low production costs, especially in comparison to perfluorinated polymers. The most frequently considered polymers for this application are polyaryl ethers, polyphosphazenes, polyimides and polybenzimidazoles. [4] [5]. From the aforementioned polymers, doped polybenzimidazole is the only one considered for operation at temperatures between 130 and 200 ºC.

The annular tautomerism between both nitrogen atoms of the imidazole gives rise to an intermolecular prototropism with particularly low activation energy [6] Due to this equilibrium, and to the partially polar character of this heterocycle, a hydrogen bonding network appears. In aromatic polybenzimidazoles (PBIs) said network is extended along the whole polymer matrix in the solid state. Nevertheless, the protonic mobility through this network is not enough to use materials bearing this heterocycles as the only proton exchange unit. PBI is usually doped with acids to lead to a notable enhancement of the proton conductivity [7]. In fact, membranes based on PBI complexes with inorganic acids have shown very good performance in PEMFCs at operation temperatures above 100ºC [8],[9],[10] However, long term stability of such systems is questionable, since the continuously produced water will leach the acid-dope out of the membrane. This problem could be solved if the acidic groups were covalently bonded to the polymer.

Polyimides are high temperature polymers with outstanding properties as high performance materials [11]. In addition, the wide variety of available monomers (diamines and dianhydrides) provides a great versatility to the polyimide synthesis [12]. These qualities motivated the choice of polyimides as the polymer backbone of the polymers synthesised in this work. A disadvantage of polyimides is their low resistance to hydrolysis in acidic medium [13], [14]. To overcome this drawback we have chosen dianhydride monomer with the highest hydrolitical stability reported so far [15], [16]

Moreover, the synthesis of copolymers might be a promising strategy to join a combination of properties in a single material [16]. Many of the polymer properties can be controlled through the structure and the functional groups present in the monomers, which allows tailoring the polymer structure to fulfil specific requirements. [17]. Specifically for PEMFC application, it is claimed that structural features of the polymer such as the amount and position of acidic sites, and their distribution (random or in blocks) determine to a major extent some relevant properties of the membranes, such as their proton transport resistance and phase separated morphology [18] [19].

In this paper, we report the synthesis, characterisation and properties of a series of copolyimides containing simultaneously sulfonic groups and benzimidazole heterocycles. We examine the influence of the functional groups present, their quantity and their distribution along the polymer chain, on their properties, particularly those related to proton transport.

2   Experimental Part

2.1   Starting Materials

3,5-dinitrobenzoyl chloride, *o*-phenylenediamine, phosphorous pentoxide, hydrazine monohydrate, methanesulfonic acid, *m*-cresol and triethylamine were obtained from commercial sources and used as received. Diaminodiphenyl ether (DDE, Fluka, 98 %) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA, Fluka, 97 %) were sublimated under reduced pressure. 2,2´-Benzidinedisulfonic acid (BDSA, Alfa Aesar, 70 %) was soaked in boiling water for 5 hours and the recovered white solid was dried under vacuum. Previous to the reaction the absorbed water was determined by thermogravimetry (0.6 %). Benzoic acid (Aldrich, 90%) was recrystallized from dichloromethane. All the polymers syntheses were conducted under argon atmosphere.

2.2   Synthesis of Intermediates and Monomers

2.2.1   Synthesis of 2-(3,5-Diaminophenyl) -Benzimidazole (DABI):

2-(3,5-diaminophenyl)-benzimidazole (DABI) was prepared by the procedure previously reported (Scheme 1) [20]. First, the dinitro precursor 2-(3,5-dinitrophenyl)-benzimidazole (DNBI) was prepared from *o*-phenylene diamine and 3,5-dinitrobenzoyl chloride (Yield: 65 %; m.p.:331-332 ºC), and the diamine monomer DABI was obtained by reduction with palladium and hydrazine monohydrate (Yield: 78 %; m.p. 243-244ºC, lit. 242-243).

DNBI:

Elemental Analysis for $C_{13}H_8N_4O_4$ (284.23 g/mol): Calcd. C, 54.93%; H, 2.84%; N, 19.71%; Found C, 55.30%; H, 2.81%; N, 19.84%.

IR (KBr, cm^{-1}): 3336 ($\nu_{NH\ benzimidazole}$); 1540, 1340 ($\nu_{asym\ NO2}$, $\nu_{sym\ NO2}$).

^{1}H-NMR (DMSO-d$_6$, δ, ppm): 9.35 (d, 2H, H$_c$); 8.87 (t, 1H, H$_a$); 7.70 (dd, 2H, H$_g$, H$_{g'}$); 7.34 (dd, 2H, H$_h$, H$_{h'}$).

^{13}C-NMR (DMSO-d$_6$, δ, ppm): 148.8 (C$_b$); 147.3 (C$_e$); 139.5 (C$_f$); 133.1 (C$_d$); 125.9 (C$_c$); 123.1 (C$_h$); 118.5 (C$_a$); 115.6 (C$_g$).

DABI:

Elemental analysis for $C_{13}H_{12}N_4$ (224.26 g/mol): Calcd.: C, 69.62%; H, 5.39%; N, 24.98%; Found: C, 69.75%; H, 5.67%; N, 24.87%.

IR (KBr, cm^{-1}): 3394, 3323 ($\nu_{NH\ benzimidazole\ and\ NH2}$); 1605 ($\delta_{NH2}$)

^{1}H-NMR (DMSO-d$_6$, δ, ppm): 12.53 (s, 1H, H$_{imidazole}$); 7.57 (dd, 1H, H$_{g'}$); 7.45 (dd, 1H, H$_g$); 7.14 (dd, 2H, H$_h$, H$_{h'}$); 6.60 (d, 2H, H$_c$); 5.96 (t, 1H, H$_a$); 4.93 (s, 4H, H$_{NH2}$).

^{13}C-NMR (DMSO-d$_6$, δ, ppm): 152.8 (C$_e$); 149.4 (C$_b$); 143.7 (C$_f$); 134.8 (C$_{f'}$); 131.1 (C$_d$); 121.8 (C$_h$); 121.2 (C$_{h'}$); 118.4 (C$_g$); 111.0 (C$_{g'}$); 101.6 (C$_c$); 101.4 (C$_a$).

2.3 Synthesis of Homopolyimides and Random Copolyimides:

All homopolyimides and random copolyimides were prepared by the same method. The typical polymerisation, described hereafter for the case of NTDA-BDSA:DABI 50:50 st, was carried out as follows: Triethylamine (1.2 mol per mol of sulfonic acid, 6.00 mmol, 0.84 mL), BDSA (2.500 mmol, 0.8610 g) and *m*-cresol (10 mL) were added to a previously dried three-necked flask fitted with a mechanical stirrer, gas inlet and condenser. The mixture was stirred at room temperature under argon flow until all the solids dissolved. Then, DABI (2.500 mmol, 0.5607 g) was added and, after dissolution, NTDA (5.000 mmol, 1.3409 g), benzoic acid (1.5 mol per mol of NTDA, 7.500 mmol, 0.9159 g) and *m*-cresol (10 mL) were added. The temperature was risen to 80°C for 4 h and then to 180°C for 18 h. The reaction was cooled down and the polymer was precipitated in acetone. The fibrous polymer was filtered off, washed with methanol several times, treated with methanol in a Sohxlet apparatus and dried at 110 ºC under vacuum overnight.

2.4 Synthesis of Sulfonated Block Copolyimides:

All block copolyimides were prepared according to the literature method [21]. For example, the synthesis of NTDA-BDSA:DABI 50:50 with average block length x=9 is described hereafter. To a mixture of BDSA (2.425 mmol, 0.8352 g) and *m*-cresol (10 mL) contained in a

previously dried three-necked flask fitted with a mechanical stirrer, gas inlet and condenser, triethylamine (1.2 mol per mol of sulfonic acid, 5.8 mmol, 0.81 mL) was added and the mixture was stirred at room temperature under argon flow until all the solids dissolved. Subsequently, the dianhydride co-monomer NTDA (mmol BDSA, 2.156 mmol, 0.5781 g), benzoic acid (1.5 mol per mol of NTDA, 3.234 mmol, 0.3949 g) and m-cresol (5 mL) was added. The temperature was risen to 80°C for 4 h and then to 180°C for 14 h. After this period, the reaction was allowed to cool down to 80ºC, and DABI (2.425 mmol, 0.5439 g) and m-cresol (5 mL) was added. After complete dissolution of the diamine, the amount of NTDA needed to respect the stoichiometry of functional groups in the overall reaction (2.695 mmol, 0.7227 g) was added together with benzoic acid (1.5 mol per mol of NTDA, 4.042 mmol, 0.9159 g) and *m*-cresol (5 mL). The reaction was conducted at 80ºC for 4 h and at 180ºC for 14 h. From here on, the same procedure as above was followed.

2.5   Film Preparation

The polymers (in triethylammonium sulfonate form) were dissolved in dimethyl sulfoxide (DMSO) or *m*-cresol. The solution was filtered and cast onto a silanised glass plate heated to 70°C for solvent evaporation. The films were subsequently dried in a vacuum oven at 150 °C for 24 h, stripped off with warm water and extracted with methanol in a Sohxlet. Triethylammonium, the counter-ion of the sulfonic groups, was exchanged to proton by dipping the membranes in 0.1 M HCl (Merck Titrisol) for 20 hours, and then they were rinsed several times with deionised water.

2.6   Polymer Characterisation

The elemental analyses were carried out with a Carlo Erba EA 1080 instrument. H_2O was determined by the Karl-Fisher method. Fourier transform infrared (FT-IR) spectra were recorded in the transmission mode on a Bruker EQUINOX 55 spectrometer using KBr disks for the monomers and intermediates, and thin films for the polymers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DCX 300 spectrometer operating at 300.13 MHz and 75.47MHz respectively. The measurements were performed at 25 ºC for the monomers and at 80°C for the polymers. Gel permeation chromatography (GPC) analyses were carried out using a KNAUER device, equipped with a differential refractive index detector (Knauer RI/VISC) and a viscosity detector (Viscotek H502) and PSS GRAM columns of nominal pore sizes 100 and 1000 Å. N,N-Dimethylacetamide with 0.05 M LiCl was used as a solvent and the measurements were done at 50°C with a flow rate of 1.0 ml·min^{-1}. Universal calibration with narrow polystyrene standards was used to calculate the average molecular weights.

Thermogravimetric analyses (TGA) were conducted on a thermobalance NETZSCH TG 209 at a heating rate of 10 C·min^{-1} from 100 to 700°C under argon flow. 20-40 mg of sample were pretreated at 180ºC for 15 min to eliminate water and traces of solvent. Thermo-oxidative assays were conducted in the same manner, but under synthetic air flow. Qualitative solubility was determined at 3% wt/wt concentration, stirring for 24 h at room temperature, or heating up to the solvent boiling temperature until dissolution for those samples which were insoluble.

2.7 Membrane Characterisation

Water uptake data were obtained by drying films (in sulfonic acid form) at 90°C in a vacuum oven for 24 hours and weighing to obtain an initial dry weight. The films were then soaked in deionised water at room temperature for 24 hours, removed from the water, wiped dry and weighed. The water uptake (%W.U.) was calculated according to: $\%W.U. = (W_{wet} - W_{dry}) \cdot 100 / W_{dry}$.

Proton conductivity was determined by impedance spectroscopy. Proton conductivity values were obtained from the impedance modulus at null phase shift (high frequency side). Measurements were carried out with the membrane in contact with water vapour generated in a separated chamber as described by Alberti et al [22], at temperatures ranging from 50 to 150 ºC and at100% relative humidity. The samples were measured without pre-treatment. The impedance measurements were carried on stacks of membranes (similar cumulative thickness, around 500 μm). This procedure was performed because the resistance of a single membrane with high ionic content (IEC 1.94 meq·g^{-1}) is close to the short-circuited cell's resistance. The stacks were pressed between two Etek$^{®}$ electrodes to decrease the mass and charge transfer resistance between the membrane and the cell electrodes. The spectrometer used was a Zahner IM6 electrochemical workstation, working in the frequency range between 10 and 10^{6} Hz.

3 Results and Discussion

3.1 Monomer and Polymer Synthesis

We designed and prepared a series of sulfonated polynaphthalimides bearing pendant benzimidazole heterocycles. Within this series, the sulfonic acid content was systematically varied. For each composition, both a random distribution and a distribution in blocks of the sulfonated polymer segments were essayed

NTDA was chosen as dianhydride monomer because naphthalimide rings exhibit an improved stability towards hydrolytical degradation in comparison to phthalimide rings.[23] The

commercially available 2,2´-Benzidinedisulfonic acid (BDSA) was selected for the introduction of the sulfonic acid groups. For the non sulfonated component of the copolymers a diamine bearing benzimidazole, 2-(3',5'-diaminophenyl)-benzimidazole (DABI) was chosen. The location of the heterocycle in this structure may reduce the planarity of the polymer structure in comparison to PBI, thus hindering molecular packing. This diamine was synthesized as summarised in Scheme 1. The synthesis of the dinitro intermediate DNBI from *o*-phenylenediamine and 3,5-dinitrobenzoic acid or derivatives has been previously accomplished by different routes [20],[23],[24], We have chosen the method reported by V. Ayala et al.[18], in which a mixture of methanesulfonic acid and phosphorus pentoxide (Eaton's Reagent, PPMA) [24] is used as cyclodehydration agent for the first synthetic step, followed by reduction with hydrazine monohydrate in the presence of a metallic hydrogenation catalyst (Pd/C) in ethanol.

For comparison purposes, sulfonated polyimides without benzimidazole group were also prepared. In this case, diaminodiphenyl ether (DDE), whose ability to yield film-forming polyimides is well known, was chosen as diamine.

All of the polymers were prepared by the high temperature polycondensation method [11] [26]. In all cases, *m*-cresol was the solvent used and benzoic acid was added to the reaction as a catalyst. The homopolymers and the random copolymers were synthesised in one step, whereas the block copolymers were synthesised by the two stage one-pot method described by Genies et al. [21] By this method, diamino telechelic sulfonated oligomers of controlled average length are prepared in the first step, by condensation of the sulfonated diamine and the dianhydride. Average block lengths of 3 and 9 sulfonated repeat units (denoted as x=3 and x=9 respectively) have been essayed. In the second stage, the non-sulfonated diamine and the remains of dianhydride are added to the reaction, in the amount required to fulfil the exact stoichiometry of the functional groups. For both random and sequenced copolymers, the moles of sulfonic groups per gram of polymer, i.e. the calculated ion exchange capacity (IEC) can be easily controlled by adjusting the proportion of sulfonated to non-sulfonated diamine. To enable a more reliable comparison of the transport properties in relation to the polymer structure, the molar ratio of sulfonated to non-sulfonated diamine for the different polymer structures was calculated for each series of copolymers in the way that the theoretical ion exchange capacity (IEC_t) had the value 1.94, 1.54, or 1.14 meq·g^{-1}.

The compositions for this series are summarised in Scheme 2. The sulfonated diamines were transformed into their corresponding triethylammonium salts *in situ*, previous to the reaction, in order to solubilise them in the reaction medium and to liberate the protonated amino groups

for the polycondensation reaction. Water formed during the imidation was continuously removed with a stream of argon.

3.2   *Polymer characterisation and properties*

The polymers were characterized by elemental analyses, GPC-viscosimetry and spectroscopic techniques (FTIR and ^{1}H NMR).

Due to their strong hydrophilicity, the polymers contain non negligible amounts of absorbed water, especially those with high ionic contents. The contained moist alters the CHNS composition of the samples. Thus, the results of the elemental analyses were corrected taking into account the percentage of absorbed water. The elemental analyses were in good agreement with the proposed chemical compositions (Table 1). As it is usual for high temperature polymers such as aromatic polyimides, which cannot be completely pyrolised in normal analysis conditions, the values found for carbon percentages were slightly lower than those calculated.

The estimated MW calculated from the data of GPC-viscosimetry (Table 2) indicated the formation of high molecular weight polyimides, which was also confirmed by the fact that creasable films could be obtained by casting and solvent evaporation of copolymer solutions. The obtained values for the polydispersity were typically about 2, or even less, since the low molecular weight chains were washed out during Sohxlet extraction, and this resulted in a narrowing of the molecular weight distribution. When comparing the Mw of copolymers with identical composition, the statistical copolymers presented higher values than the parent sequenced copolymers. The cause might be that the synthesis of the sequenced copolymers was accomplished in a two stage method, and hence a stoichiometric imbalance is more probable than in the one-stage method.

Spectroscopic characterisation methods (^{1}H-NMR and FTIR) confirmed the structure of the polymers. The ratio between the integrals of the signals ascribed to the protons of methyl groups in triethylammonium and of naphthalene aromatic nucleus confirms the functionalisation degree of the polymers. The ^{1}H NMR spectra of three polymers of the DABI series with different sulfonic acid contents, together with the assignment of the signals, are shown in Figure 1.

Films (ca. 10 µm) were prepared to register the FT-IR spectra in the transmittance mode. The spectra presented absorption bands due to the asymmetrical and symmetrical stretching of the two naphthalimide carbonyl groups at 1700 and 1670 cm^{-1}, respectively, and the C-N bond at about 1350 cm^{-1}. A very broad absorption band with maximum at about 3200 cm^{-1}, typical of

absorbed water, could be observed in the spectra of all the sulfonated polymers, along with two peaks around 1225 and 1175 cm^{-1} associated to asymmetrical and symmetrical stretching of the SO$_2$ group (Figure 2). The copolymers derived from DDE showed also absorption at 1230 cm^{-1} corresponding to the CO bond asymmetrical stretching. FT-IR spectra also confirmed that imidation was essentially complete.

All of the sulfonated copolymers could be dissolved in organic polar solvents (Table 3).. In each series of sulfonated polymers the solubility is improved as the sulfonic acid contents increases. The lower regularity derived from copolymerisation respect to the corresponding homopolymers, and the bulkiness of pendant benzimidazole also have a positive influence on the solubility, since all these modifications hinder the molecular packing, i.e., lower the cohesive energy density. As a consequence, the sulfonated polymers with benzimidazole pendant groups had better solubility. In the series NTDA-BDSA:DABI, in which a systematic variation of the distribution of the sulfonated units was investigated (block or statistic copolymers), the solubility, for a given composition, decreases as the block length increases. This might be related to the presence of NTDA-DABI blocks (the NTDA-DABI homopolymer is insoluble in all the essayed solvents).

As to thermal resistance, the polymers without sulfonic groups present the onset of thermal degradation at about 550°C, the typical value for polymer chain degradation in aromatic polyimides. The sulfonated polymers showed a first degradation step with the onset temperature at about 300°C, and a second step at about 550°C (Figure 3). The first temperature corresponds to the elimination of the sulfonic side groups. The weight loss during this first step and the value calculated according to the sulfonic group contents in the corresponding polymer structure conformed fairly well. There was no significant difference in the degradation temperature, whether the sulfonic group was as the free acid or as the triethylammonium sulfonate, which indicates that the most labile bond of these polymers is actually the bond between the aromatic ring and the sulfonic group. The second decomposition step corresponds to the general degradation of the polymer chain. For polymers with identical composition and different block lengths, the differences in the TGA traces were almost negligible, as expected for polymers with the same composition of the polymer backbone. In all cases, the char yield at 700 °C was higher than 50%, as it corresponds to highly aromatic structures. The temperatures of initial decomposition in oxidative conditions, i.e. synthetic air atmosphere, were similar to those obtained under argon (Figure 3). Thus, the degradation in air seems to be merely a thermo-degradative process rather than a thermo oxidative one.

No thermal transitions were detected below 400ºC under the conditions applied for DSC. The reason might be the rigid structure of naphthalimides, which notably reduces chain mobility. For the sulfonated polyimides, in addition, the ionic groups will contribute to increase the value of the T_g, since they will favour intermolecular interactions. Moreover, as it has been reported in the previous paragraph, splitting-off of sulfonic groups in these polymers starts at about 300 ºC; in consequence, this process might hide any thermal transition taking place above that temperature.

3.3   Membrane Characterisation

The results of the water uptake measurements (*%WU*), and the number of water molecules per sulfonic acid group (λ_{H2O}) calculated from those values, are presented in Table 4. The values of λ_{H2O} are fairly the same for the different sulfonated polymers. Due to the strong hydrophilicity of the sulfonic acid groups, the sulfonated polymers present very high values of water uptake, which seems to depend mainly on the content of sulfonic acid groups in the structure. The influence of other factors like the presence of benzimidazole, or the distribution of the sulfonated segments (in blocks or random) seems negligible (Table 4).

In general, the conductivity increases with the sulfonic acid content, i.e. IEC (Figure 4-6). Comparing polyimides with and without benzimidazole having the same IEC, the conductivity is higher for the polymers without heterocycles (Figure 4 and Figure 5). This is due to strong interactions between imidazole and sulfonic acid groups. [27], [28]. Nevertheless, when the sulfonic acid content is high (1.94 meq.g^{-1}), the values are quite similar at higher temperatures (*ca.* 37 mS·cm^{-1} at 130 ºC, Figure 6b).

Figure 6 shows the influence of the distribution of the acidic sites along the polymer chain on the conductivity.In the series of the polymers with IEC: 1.54 meqg^{-1}, an average block length of 3 repeat units results in the highest conductivity. When the degree of functionalisation is increased up to IEC: 1.94 meqg^{-1}, a high value of ionic content, the proton conductivity of the statistical copolymer and the copolymer with average block length x=3 turn to be essentially the same. With this high IEC, overall water uptake of the material dominates the structural effects caused by hydrophobic domains.

In both cases– NTDA-BDSA:DABI 39:61 and 50:50 – an average block length of 9 repeat units appears toinhibit proton transport. This is described by Mercier and co-workers for sulfonated polyimides analogous to the ones described here [29]: an increase in the average length of the sulfonated block implies an increase of the non-sulfonated block, which offers a major resistance to proton transport. Above a certain average block length, domains of

hydrophobic blocks reach a critical value and the the resistance becomes too high and cannot be compensated by the ease of transport within the hydrophilic domains.

The effect of the casting solvent on the proton conductivity is illustrated in Figure 7 and 8. The reason for the differences between DMSO and *m*-cresol appears to be the membrane's structure (Figure 8), that is heterogeneous and microporous for the membranes cast from *m*-cresol solutions. The last has been already observed by others [30], who also pointed out that an increase in porosity is related to a decrease in proton conductivity.

In the case of NMP, the values are much lower than those of the membranes cast from DMSO or *m*-cresol (Figure 7). An interaction between amidic solvents, which are basic, and the acid groups has been previously proposed as the reason for this decrease in the proton conductivity [31].

4   Conclusions

A series of polyimides with pendant heterocycles where syntesised and characterised with respect to the application as fuel cell materials. The pendant groups introduced in the polyimides led to an improvement of the solubility in polar organic solvents. The introduction of functional groups in the polymer structure has an influence in the thermal properties. The thermal lability of the sulfonic groups is evidenced by their degradation temperature (300-350ºC), which is much lower than the degradation temperature of conventional aromatic polyimides (at least 500ºC). The hydrophilic character of these polyimides, which can reach water uptake values of 50%, can be chiefly attributed to the sulfonic acid groups. For the sulfonated polymers this property is mainly related to the amount of sulfonic acid groups per gram of polymer, remaining thus the number of absorbed water molecules per repeat unit as almost constant and independent of the other substituents present in the polymer structure. The proton conductivity of the polyimide membranes at 100 % relative humidity was evaluated by impedance spectroscopy at temperatures ranging from 50 to 150 ºC. It can be concluded that the combination of imidazole and sulfonic groups in the same polymer leads to a higher resistance to proton transport if the proportion sulfonic acid/benzimidazole is less than 2/1. Thus, for or a polymer with a proportion 2/1 s/b and a high IEC (Fig5), proton conductivities suitable for fuel cell applications above 100°C were reached.

Captions of Figures and Schemes

Scheme 1: Synthesis of the diamine 2-(3',5'-diaminophenyl)-benzimidazole (**DABI**)

Scheme 2: General scheme of the synthesis of the copolyimides and chemical structures of the copolymer series **NTDA-BDSA:DABI** and **NTDA-BDSA:DDE**

Figure 1: ^{1}H-NMR spectra of NTDA-BDSA:DABI A) 28:72st; B) 39:61 st; and C) 50:50 st.

Figure 2: FT-IR spectrum of **NTDA-BDSA:DABI 39:61 st.**

Figure 3: Thermogravimetric traces (%TGA and %DTG) for **NTDA-BDSA:DABI 50:50 (IEC$_{th}$=1.94 meq·g^{-1})** under inert and oxidative atmosphere (sulphonic groups as free acid).

Figure 4: Proton conductivity as a function of temperature for **a) Nafion$^®$112**; and the series **NTDA-BDSA:DABI b) 50:50 st (IEC$_{th}$=1.94 meq·g^{-1}); c) 39:61 st (IEC$_{th}$=1.54 meq·g^{-1}); d) 28:72 st (IEC$_{th}$=1.14 meq·g^{-1})**, cast from m-cresol.

Figure 5: Proton conductivity as a function of temperature for: **a) Nafion$^®$112;** and the series **NTDA-BDSA:DDE b) 49:51 (IEC$_{th}$=1.94 meq·g^{-1}); c) 37:63 (IEC$_{th}$=1.54 meq·g^{-1}); d) 27:73 (IEC$_{th}$=1.14 meq·g^{-1})**, cast from m-cresol.

Figure 6: Proton conductivity as a function of temperature for the series **NTDA-BDSA:DABI a)) 39:61 st (IEC$_{th}$=1.54 meq·g^{-1}); b) 50:50 st (IEC$_{th}$=1.94 meq·g^{-1}),** cast from DMSO. Influence of the average block length.

Figure 7: Proton conductivity as a function of temperature for **NTDA-BDSA:DABI 50:50, x=3 (IEC$_{th}$=1.94 meq·g^{-1}).**– Influence of the casting solvent.

Figure 8: Proton conductivity as a function of temperature for two membranes **NTDA-BDSA:DABI 50:50 st (IEC$_{th}$=1.94 meq·g^{-1})** cast from **a)** DMSO; **b)** m-cresol, and correspondent SEM-Micrographs of the lyophilised samples.

Tables

Table 1: Elemental analysis of the copolymers in salt form (values for the acid form in brackets).

Polymer		**Elemental Analysis**				
		%C	**%H**	**%N**	**%S**	**%H$_2$O**
NTDA-BDSA:DABI 28:72	**Calc.**	67.56	3.43	10.85	2.30	
		(66.32)	(2.50)	(10.20)	(3.11)	
st	**Found**	67.13	2.75	9.92	3.70	9.75
		(65.47)	(1.71)	(9.52)	(3.95)	(14.07)
x=3	**Found**	65.32	3.23	10.51	3.13	8.98
NTDA-BDSA:DABI 39:61	**Calc.**	66.19	3.74	10.29	3.21	
		(64.47)	(2.44)	(9.39)	(4.34)	
st	**Found**	65.34	2.79	9.48	4.63	8.86
		(62.27)	(1.12)	(8.68)	(4.78)	(13.32)
x=3	**Found**	65.97	3.77	9.87	4.48	5.56
		(61.42)	(2.06)	(8.66)	(5.26)	(12.41)
x=9	**Found**	65.30	3.81	9.67	4.49	3.96
		(62.25)	(1.95)	(9.08)	(4.50)	(9.24)
NTDA-BDSA:DABI 50:50	**Calc.**	64.83	4.05	9.74	4.12	
		(62.61)	(2.38)	(8.57)	(5.56)	
st	**Found**	64.05	3.89	8.73	5.70	9.30
		(61.52)	(1.67)	(8.58)	(6.06)	(13.32)
x=3	**Found**	62.82	3.86	8.97	5.40	8.21
		(60.45)	(1.52)	(7.86)	(6.38)	(14.40)
x=9	**Found**	61.94	4.07	9.00	5.24	4.07
		(60.59)	(1.82)	(7.81)	(6.07)	(13.21)
NTDA-BDSA:DDE 27:73	**Calc.**	68.54	3.51	6.67	2.22	
		(67.35)	(2.01)	(6.04)	(3.00)	
	Found	66.51	3.09	6.62	3.47	5.40

		(66.27)	(2.04)	(6.37)	(4.00)	(10.33)
NTDA-BDSA:DDE 37:63	**Calc.**	67.18	3.78	6.74	3.05	
		(64.80)	(2.45)	(5.88)	(4.11)	
	Found	66.54	3.33	6.83	4.72	6.54
		(64.13)	(2.10)	(5.90)	(5.01)	(11.37)
NTDA-BDSA:DDE 49:51	**Calc.**	65.55	4.09	6.83	4.03	
		(63.38)	(2.46)	(5.69)	(5.45)	
	Found	62.10	2.45	5.93	6.11	8.63
		(61.01)	(2.08)	(5.50)	(5.87)	(12.15)

Table 2: GPC results for the sulfonated copolymers

Polymer	M_n. g·mol^{-1}	M_w. g·mol^{-1}	M_w / M_n	$[\eta]$. dL·g^{-1}
NTDA-BDSA:DABI 28:72 st	26200	53100	2.03	0.75
NTDA-BDSA:DABI 39:61 st	32100	83100	2.59	1.15
NTDA-BDSA:DABI 39:61 x=3	20100	52300	2.60	0.89
NTDA-BDSA:DABI 39:61 x=9	19100	33800	1.77	0.92
NTDA-BDSA:DABI 50:50 st	36600	85700	2.34	1.18
NTDA-BDSA:DABI 50:50 x=3	29200	63500	2.17	0.97
NTDA-BDSA:DABI 50:50 x=9	21100	45000	2.13	1.05
NTDA-BDSA:DDE 27:73*	—	—	—	—
NTDA-BDSA:DDE 37:63*	—	—	—	—
NTDA-BDSA:DDE 49:51	39900	94200	2.36	1.39

*Insoluble.

Table 3: Solubility of the polyimides

Polymer	Solvent			
	m-cresol	DMSO	NMP	DMAc
NTDA-DDE	−	−	−	−
NTDA-DABI	−	−	−	−
NTDA-BDSA	+	++	+	+
NTDA-BDSA:DABI 28:72 st	±	+	±	±
NTDA-BDSA:DABI 28:72 x=3	±	±	−	−
NTDA-BDSA:DABI 39:61 st	+	++	±	±
NTDA-BDSA:DABI 39:61 x=3	+	+	−	−
NTDA-BDSA:DABI 39:61 x=9	±	±	−	−
NTDA-BDSA:DABI 50:50 st	+	++	+	±
NTDA-BDSA:DABI 50:50 x=3	+	++	+	±
NTDA-BDSA:DABI 50:50 x=9	+	+	+	±
NTDA-BDSA:DDE 27:73 st	+	±	−	−
NTDA-BDSA:DDE 37:63 st	+	±	−	±
NTDA-BDSA:DDE 49:51 st	+	+	+	+

++: soluble at room temperature; +:soluble upon heating; ±: partially soluble or swollen; −:not soluble

Table 4: Values of water uptake (*%WU*), and the number of water molecules per sulfonic acid group (λ_{H2O}) for the cast membranes

Polymer	Solvent	IEC_t	%WU	λ_{H2O}
NTDA-BDSA:DABI 28:72 st	*m*-cresol	1.14	28	14
NTDA-BDSA:DABI 39:61 st	DMSO	1.54	43	15
NTDA-BDSA:DABI 39:61 st	*m*-cresol	1.54	42	15
NTDA-BDSA:DABI 50:50 st	NMP	1.94	53	15
NTDA-BDSA:DABI 50:50 st	DMSO	1.94	52	15
NTDA-BDSA:DABI 50:50 st	*m*-cresol	1.94	46	13
NTDA-BDSA:DABI 50:50 x=3	NMP	1.94	52	15
NTDA-BDSA:DABI 50:50 x=3	*m*-cresol	1.94	57	16
NTDA-BDSA:DABI 50:50 x=9	NMP	1.94	55	16
NTDA-BDSA:DABI 50:50 x=9	DMSO	1.94	56	16
NTDA-BDSA:DDE 37:63 st	*m*-cresol	1.54	40	14
NTDA-BDSA:DDE 49:51 st	DMSO	1.94	53	15

Figures and schemes
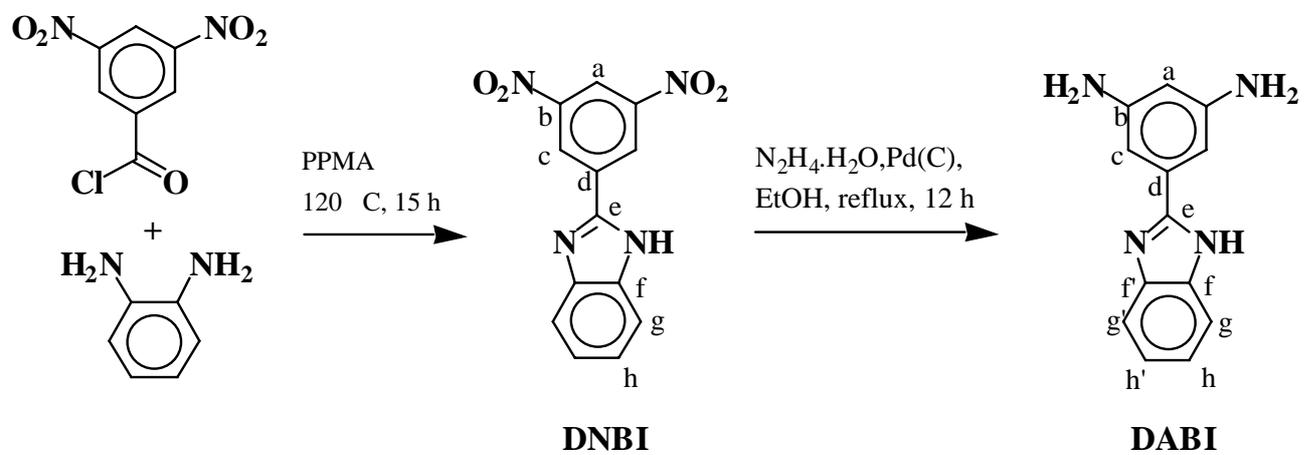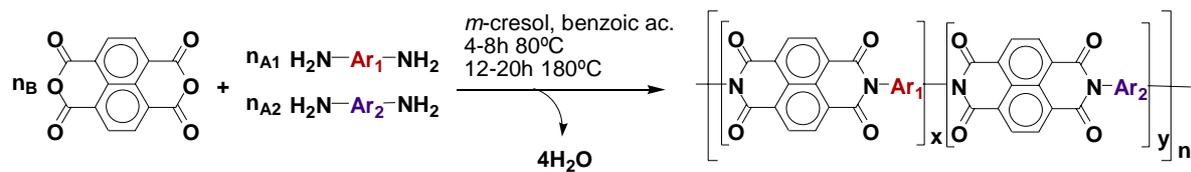
Scheme 1

NTDA-BDSA:DABI
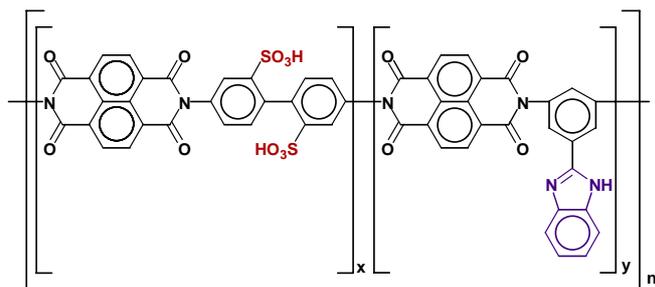
x:y	IEC$_t$	SO3H:BI
28:72	1.14	0.78
39:61	1.54	1.28
50:50	1.94	2.00

NTDA-BDSA:DDE
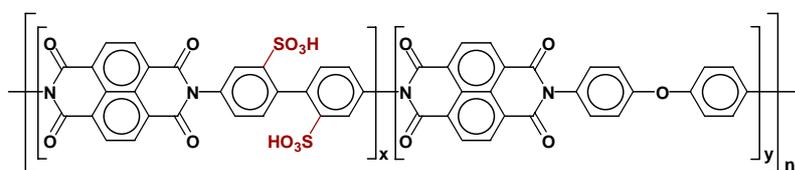
x:y	IEC$_t$
27:73	1.14
37:63	1.54
49:51	1.94

Scheme 2

Figure 1

Figure 2

NTDA-BDSA:DABI 50:50 (1.94 meq·g-1), sulfonic ac.

Figure 3

NTDA-BDSA:DABI, m-cresol

Figure 4

NTDA-BDSA:DDE, m-cresol

Figure 5

NTDA-BDSA:DABI 39:61, DMSO

, mS.cm-1

- st
- x=3
- x=9

T,°C

a

NTDA-BDSA:DABI 50:50, DMSO

, mS.cm-1

- st
- x=3
- x=9

T, °C

b

Figure 6

NTDA-BDSA:DABI 50:50 x=3
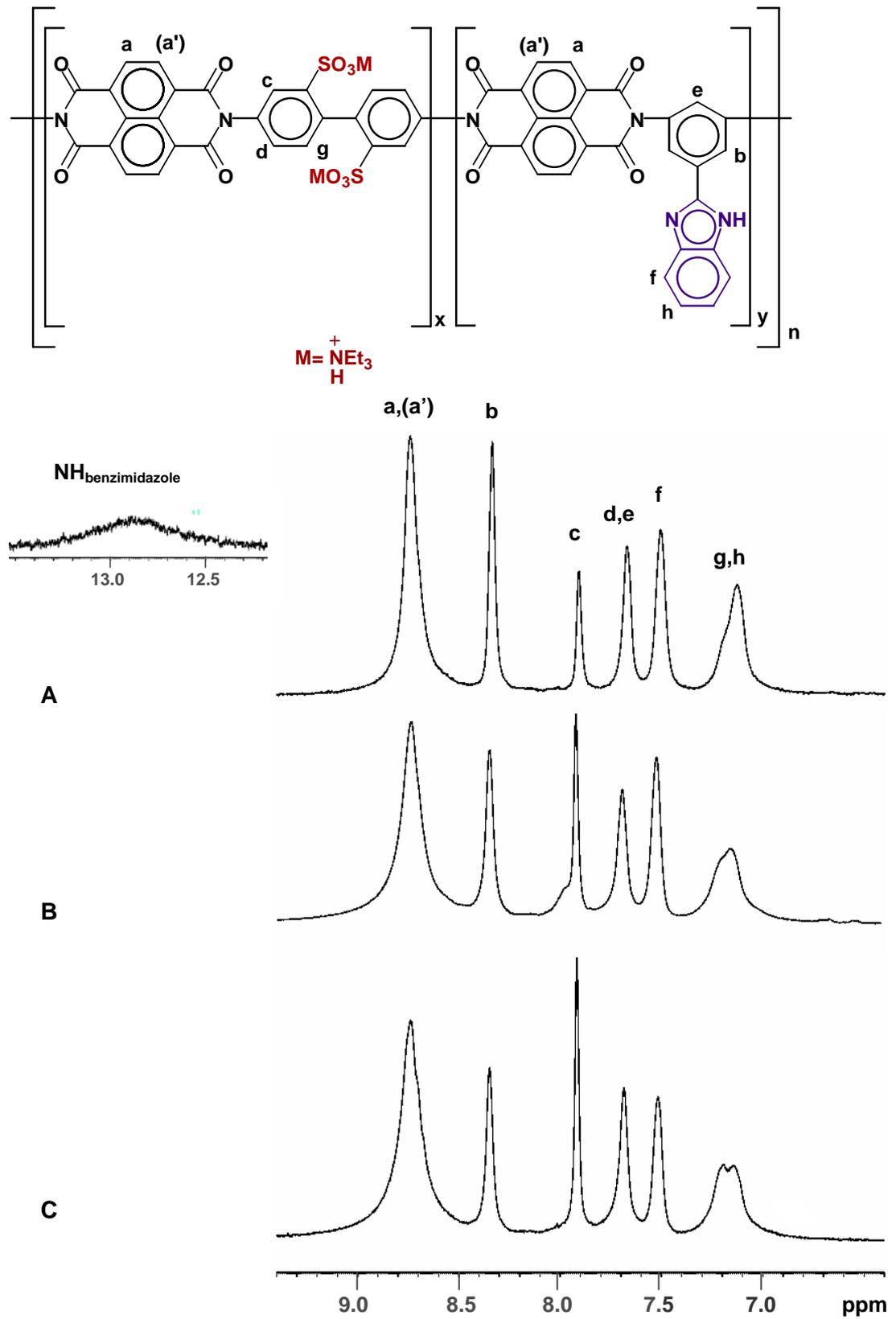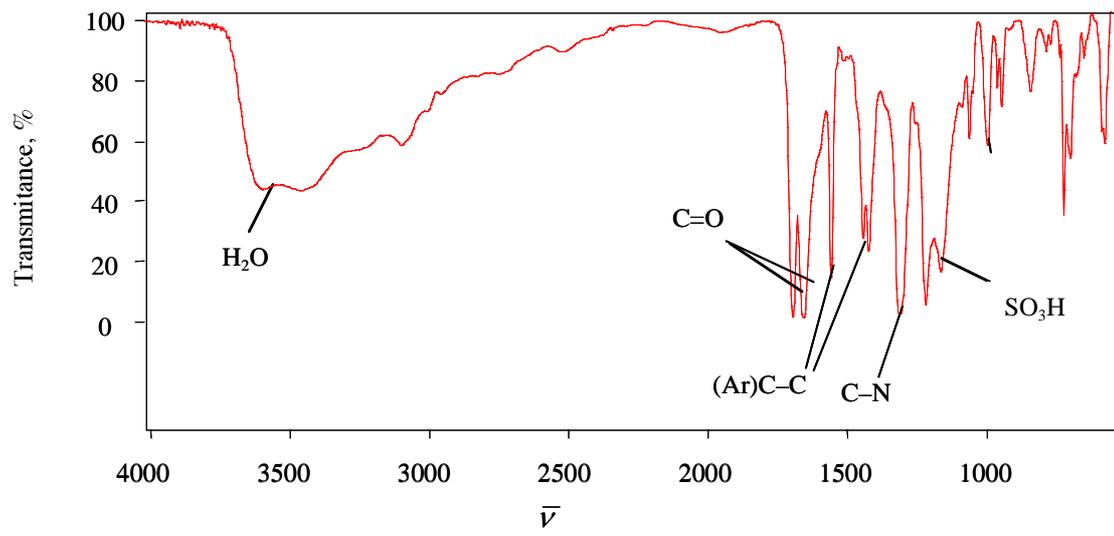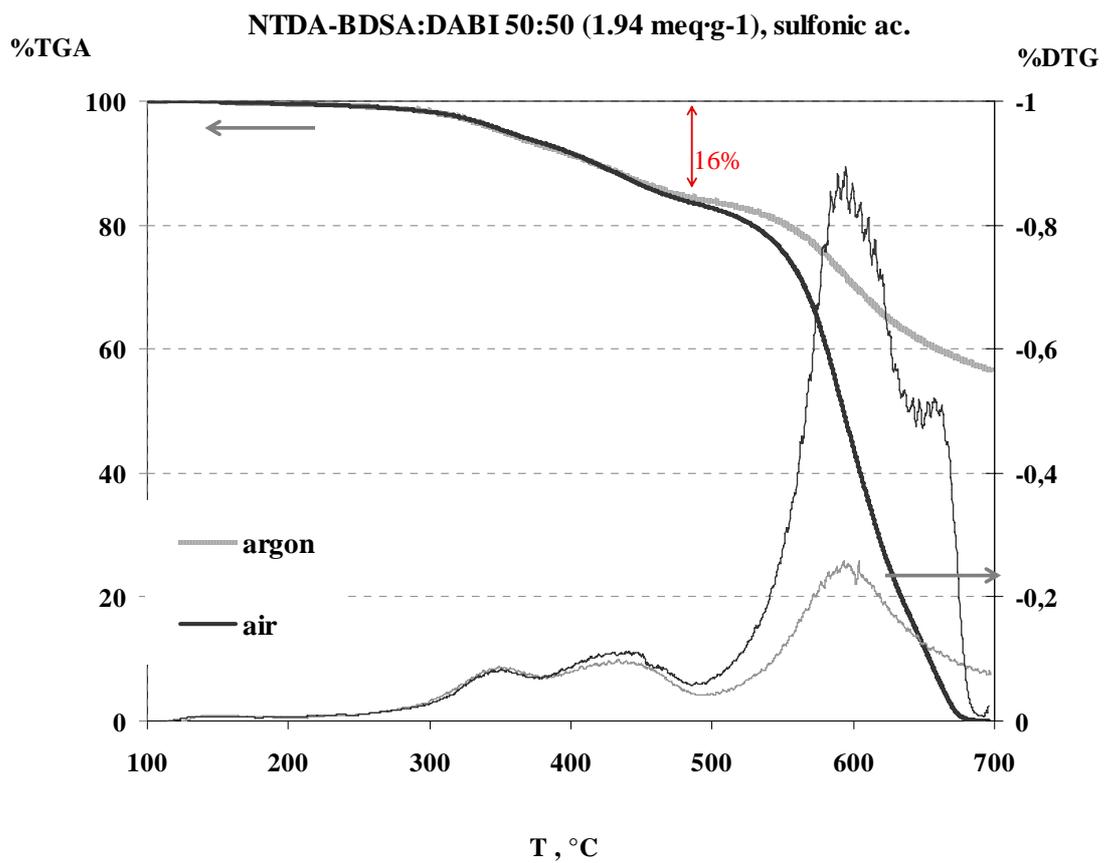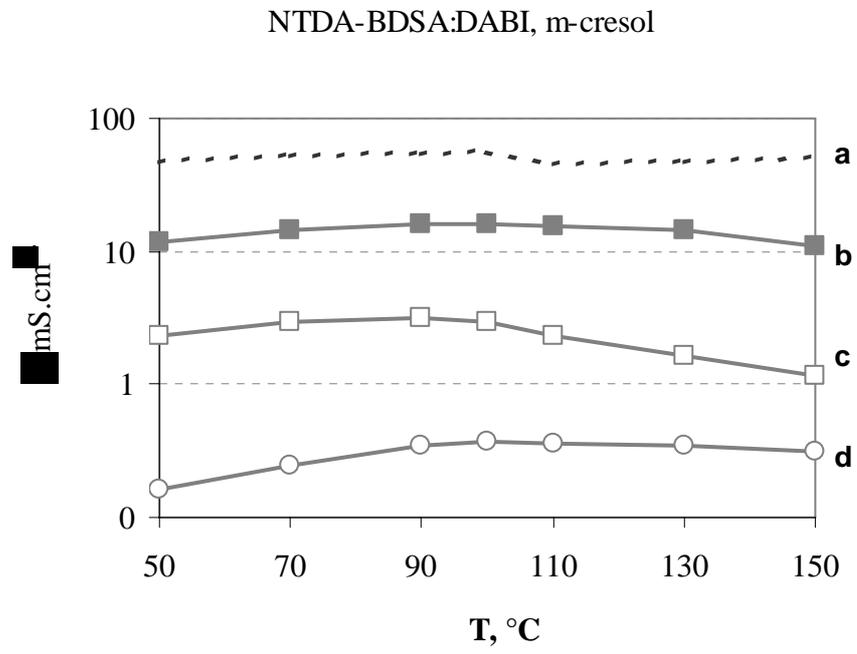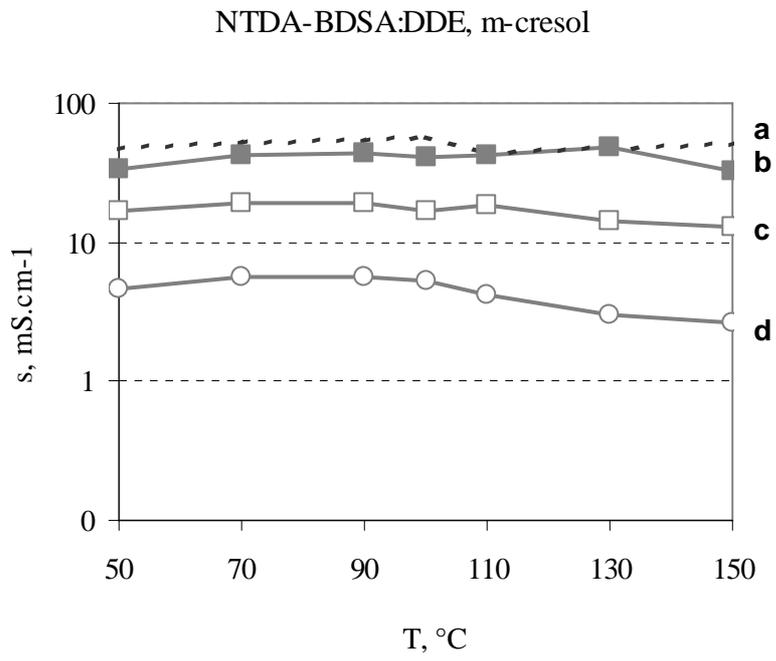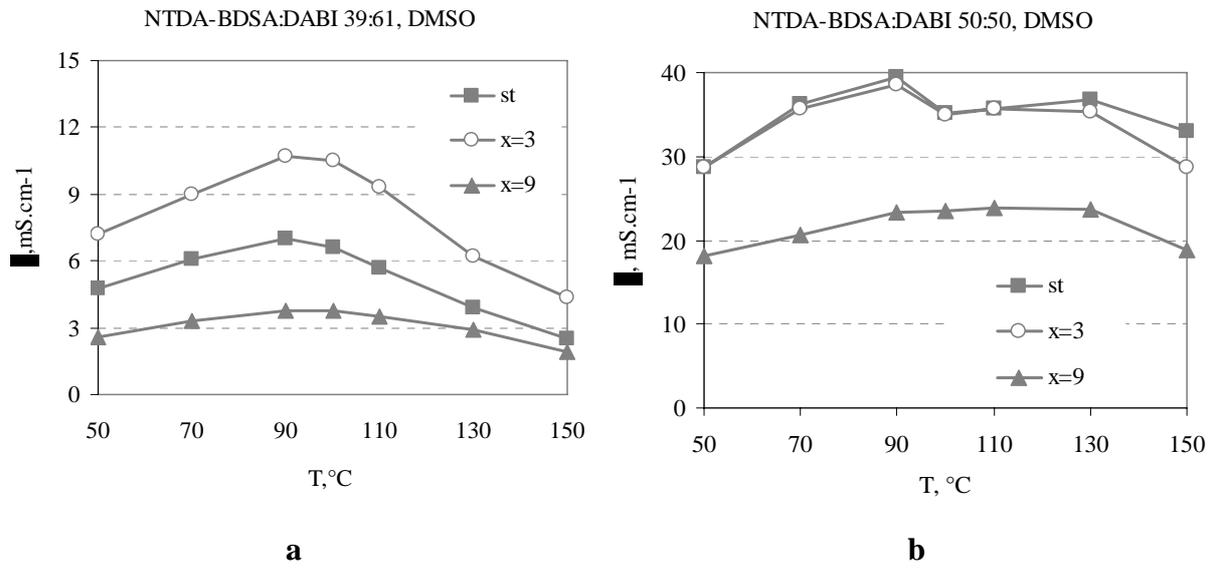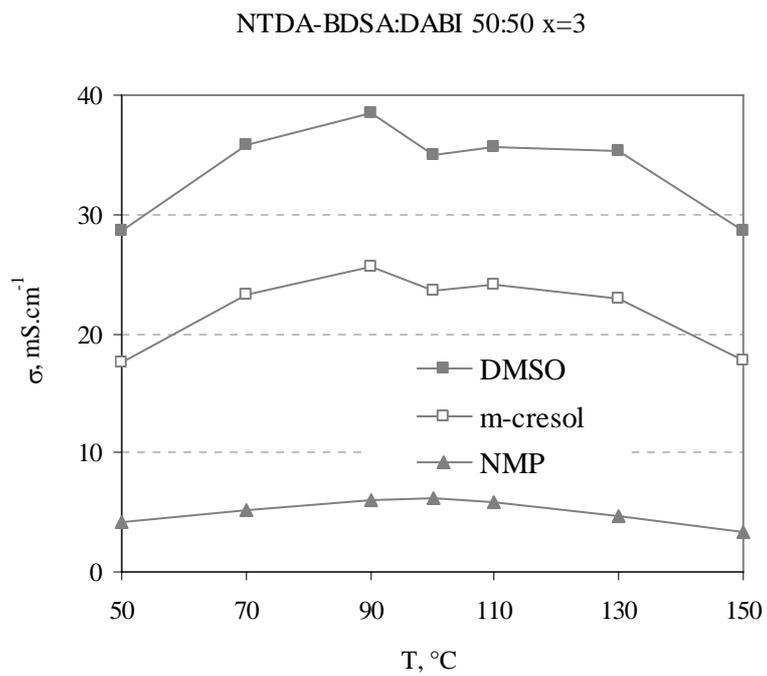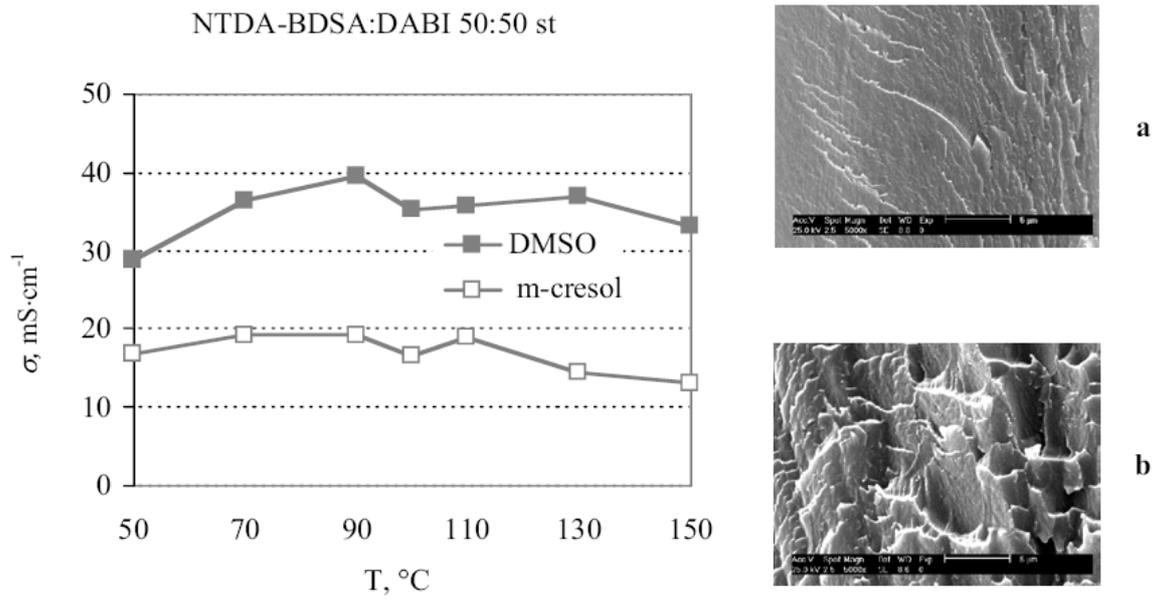
Figure 7

Figure 8

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