

Final Draft
of the original manuscript:

Ponce, M.L.; Roeder, J.; Gomes, D.; Pereira Nunes, S.:
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In: Asia-Pacific Journal of Chemical Engineering (2009) Wiley

DOI: 10.1002/apj.370

Stability of Sulfonated Polytriazole and Polyoxadiazole Membranes

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ABSTRACT: The performance and stability of sulfonated polytriazoles with polymer backbones containing diphenyl ether (S-DPE-PT) and hexafluoroisopropylidene groups (S-FPT) were compared, aiming the application as proton conductive membranes for fuel cell. The chemical stability of both membranes were compared and analyzed by infrared spectroscopy after 24 h heating at temperatures up to 250°C. The superior stability of the fluorinated polytriazole was confirmed.

Keywords: polytriazole, PEMFC, proton conductivity, fuel cell

1. Introduction

The implementation of fuel cells in the automotive industry as well as in stationary applications still depends on overcoming technical hurdles, which include the development of proton conductive membranes able to operate above 120°C and at low humidity levels. The commercially available membranes like Nafion[®] dehydrate at this temperature and suffer a proton conductivity decrease. The motivations for operating at high temperatures include improved reaction kinetics, minimization of catalyst poisoning by CO, simplification of the heat and humidification management in the cell [1-3].

From the materials under investigation all over the world, amphoteric polymers like polybenzimidazole is the most discussed one for use at high temperatures [1-4]. The performance of polybenzimidazole has been investigated at temperatures as high as 200 °C. Alternative amphoteric polymers with basic nitrogens and sulfonated groups like sulfonated polyoxadiazoles and polytriazoles have been under investigation in our group [5-8]. The investigation started with focus on polyoxadiazole containing diphenyl ether groups, which are partially sulfonated during synthesis. However some degradation has been observed at long term operation. Recently fluorinated polyoxadiazoles [5] with much better chemical stability were reported. The polymer is however highly hydrophobic and the sulfonation could not be succeeded. Promising proton conductivities were measured after doping with phosphoric acid. Higher doping was however not possible due to the polymer very high hydrophobicity. A similar class of polymers, polytriazoles [6], is also under investigation with the advantage of offering additional sites for functionalization.

In this paper first the mechanism of degradation of polyoxadiazoles and polytriazoles containing diphenyl ether groups is investigated by infrared spectroscopy. More stable fluorinated polytriazoles are then for the first time synthesized and characterized as membranes for proton conduction.

2. Experimental

2.1. Materials

4,4'-dicarboxyphenyl-hexafluoropropane, HF (99%, Aldrich), 4-aminobenzenesulphonic acid (99 % Aldrich), hydrazine sulfate, HS (>99%, Aldrich), N-methyl-2-pyrrolidone, NMP (99%, Aldrich), sodium hydroxide, NaOH (99%, Vetec), phosphoric acid (85%, Aldrich), poly(phosphoric acid), PPA (Aldrich). All chemicals were used as received.

2.2 Synthesis of sulfonated poly(4,4'-diphenylether-1,3,4-oxadiazole) (S-DPE-POD)

S-DPE-POD (structure depicted in Scheme 1) was prepared according to the procedure described in previous papers [5].

2.3 Synthesis of sulfonated poly(diphenyl ether triazole) (S-DPE-PT)

The synthesis was performed following conditions previously reported for sulfonated poly(oxadiazole-triazole) copolymers [6]. The final polymer yield was always close to 100 % regarding the limiting reactant (DPE). A final N/C= 0.175 and S/C= 0.080 – 0.100 were confirmed by elemental analysis. A molecular weight higher than $6.2 \cdot 10^4$ g/mol was obtained. FTIR analysis confirmed that no rest hydrazide groups were present. The structure is depicted in Scheme 1.

2.4 Poly(hexafluor isopropylidene triazole) synthesis

Polytriazoles were prepared by adapting the procedure reported for S-DPE-PT [6] using 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (S-FPT). Oxadiazole-triazole copolymers with polytriazole conversion up to 20% was first obtained with ion exchange capacity (IEC) < 1.2 meq g⁻¹. This means that the final structure is a mixture of the structures depicted in Scheme 1

for the expected S-FPT and FPOD. The polymer was soluble in NMP, with molecular weight 10^4 - 10^5 g mol⁻¹.

2.5 Membrane preparation and characterization

A homogeneous solution containing 5 wt. % of polymer dissolved in NMP 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. Some of the membranes were doped with phosphoric acid by adding dry phosphoric acid to the membrane casting solution. 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 was around 100 μm.

2.6 Structural Characterization

The polymer structure was characterized by elemental analysis and infrared spectroscopy. Elemental analysis was conducted on a Carlo Erba Elemental Analyzer-Mod 1108. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000-400 cm⁻¹, using polymer films.

2.7 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). A solution with 0.05 M lithium bromide in DMAc was used as the carrier.

2.8. Thermal and mechanical analysis

Dynamic mechanical thermal analysis (DMTA) was used for determination of glass transition temperature (T_g), storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1 Hz and 0.1 N initial static force. 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%.

Thermal gravimetric analysis was carried out using a Netzsch TGA 209, with coupled FTIR. Non-isothermal experiments were performed at 10 °C min⁻¹ from 25 °C to 900 °C. Argon or oxygen atmosphere flow was maintained at 50 cm³ min⁻¹. Before the analysis, the samples were dried in a drying oven at 80 °C for 24 hours.

2.9. Proton Conductivity

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 with 5 % of relative humidity (RH). Measurements were performed at 180°C with a flow cell purged with wet nitrogen; relative humidity was controlled by bubbling nitrogen gas in 81°C heated water. The impedance measurements were carried out on stacks containing up to five membranes (similar cumulative thickness, around 500 μ m, spherical membranes of 8 mm diameter). The spectrometer used was a Zahner IM6 electrochemical workstation.

3. Results and Discussion

Sulfonated polyoxadiazoles and polytriazoles with diphenyl ether groups in the backbone have been previously investigated in our group for application as proton conductive membranes [6-8]. When application for fuel cell is aimed, long term chemical stability under aggressive conditions is a very important aspect. Therefore the thermal degradation of membranes made of poly (diphenyl ether oxadiazole) and poly (diphenyl ether triazole) was investigated here.

3.1 Chemical Stability of the poly (diphenyl ether oxadiazoles)

First the changes in the infrared spectrum of S-DPE-POD membranes were monitored after 24 hours exposition to oxidative atmosphere at 25 and 200°C. Three membranes were compared: (1) membrane in the salt form (Na⁺), (2) membrane treated with dilute sulfuric acid solution after casting and (3) membrane immersed in a 1.6 mol L⁻¹ sulfuric acid solution for 48 hours. The results are shown in Figure 1.

The spectrum of S-DPE-POD in the salt form (Na⁺) is characterized by a decrease of absorption intensity in the range 3500-3000 cm⁻¹ related to lost of water when heated at 200°C, and practically no more modifications in the whole range of wave number. The membrane in the acid form (immersed in diluted acid solution) is also characterized by a decrease of absorption intensity at 3500-3000 cm⁻¹ due to lost of water but other slight changes start to be visible and are much more intense in the membrane immersed in more concentrated acid solution and left in oxidative atmosphere at 200°C. One visible change is quite probably related to the degradation of the ether groups. A decrease of peak intensity can be seen around 1240 cm⁻¹, which might be assigned to the C-O-C stretching of ether groups. At the same time around 1420-1430 cm⁻¹ a increase of intensity can be seen for a peak, which might be assigned to the appearance of phenol as a product of the ether degradation [9].

The pure thermal degradation of S-DPE-POD could be investigated by analyzing the gases evolved during TGA experiments. Figure 2 shows the volatile products of degradation of S-DPE-POD- Na^+ films during a TGA measurement heating from room temperature up to 900°C under (a) inert gas and (b) air flux. Up to 350°C the volatile products are mainly water (3750 - 2950 and 1775 - 1590 and 950 - 400 cm^{-1}) and small amount of CO_2 (2348 cm^{-1}). At 390°C a peak appears at 1363 cm^{-1} . This absorption becomes very strong at 550°C and disappears above 650°C . Absorption in this range is frequently assigned to O-H stretching, which might be related to the sulfonic group of S-DPE-POD, but might also come from phenol groups resulting from ether degradation. A peak starts to appear near the CO_2 absorption at 2200 cm^{-1} at temperatures above 500°C , which is probably related to the absorption of aromatic nitrile groups.

The peak related to aromatic C-H stretching and bending absorption starts to appear at temperatures above 500°C . The difference between inert and oxidative atmosphere becomes evident when the intensities of the peaks of CO_2 and $-\text{C}\equiv\text{N}$ are considered related to other absorptions. In inert atmosphere only very low absorption relative to $-\text{C}\equiv\text{N}$ can be seen compared to the CO_2 absorption. But under oxidative atmosphere the intensities of both bands are much higher than the C-H stretching absorption. It means that in oxidative atmosphere more CO_2 and $-\text{C}\equiv\text{N}$ are evolving, resulting in less solid residue, as confirmed in TGA measurements. At 700°C 55 % of char residue is left when heating the sample under argon, while only 9 % is left when heating the sample in air.

The degradation of diphenyl ether catalyzed by acid has been reported in the literature before for instance for polysulfones [11]. The ether lone pair is protonated, facilitating the nucleophilic attack by the anion and leading to a cleavage with formation of a phenoxy terminated segment, as shown in Scheme 1.

The replacement of the electron-donor ether group by an electron-withdrawing group ($-\text{C}(\text{CF}_3)_2-$) increases significantly the chemical stability of the polyoxadiazole. It was recently

reported [5] that polyoxadiazole containing diphenyl ether groups after treatment for 1 h in lower acid concentration, 3:1 volume ratio of H₂SO₄: oleum (20% SO₃) has a significant decrease of molecular weight (from 358000 to 17000 g mol⁻¹), while for the fluorinated polyoxadiazole no changes in the molecular weight can be observed even in more drastic conditions, 19 days in 2:1 volume ratio H₂SO₄: oleum (20% SO₃).

At high temperatures protonated oxadiazole groups degrade and suffer cleavage, analogously to the mechanism proposed by Franski et al. [11]. As can be seen in Scheme 2, the decomposition mechanism explain the appearance of peaks relative to the protonated amine, carbonyl and -C≡N.

As mentioned by [12], the degradation of polymers is often triggered at “weak links” in a polymer chain or network in the form of end groups or structural moieties derived from possible by-product reactions or products of degradation initiated in other point of the chain. Once started the degradation it might propagate catalyzing the ceasing of other more stable chain parts.

3.2 Chemical Stability of the poly (diphenyl ether triazole)

According to Arnold [12], triazole rings are in general more stable than analogous polyoxadiazoles. Polytriazoles with diphenyl ether groups were doped with phosphoric acid and heated during 24 at 180°C and 5 % relative humidity, conditions similar to that used for the proton conductivity measurements. Infrared spectra were obtained before and after the heating treatment following the doping with different phosphoric acid concentrations. The results can be seen in Figure 3. Again in the case of S-DPE-PT the ether links can be considered weak points of the polymer and after heating the absorption connected to the ether groups are reduced, while phenoxy peaks increase in intensity. At high doping level when

heated at 180°C, peaks relative to the presence of carbonyl group and protonated amine can be seen. This is an indication that the degradation of other parts of the chain has been induced.

3.3 Chemical Stability of the poly (hexafluor isopropylidene triazole)

Diacids with hexafluor isopropylidene moieties instead of diphenylether were used in the synthesis of the polytriazole, aiming the achievement of products with higher chemical stability. Films of the new polymer in the acid form were heated at 250°C during 24 h and analysed by FTIR. Carbonyl groups could not be detected in opposite to what was observed for the analogous polymer with ether groups. A peak can be seen around 1500 cm⁻¹, which can be assigned to the aromatic ring C=C stretching vibrations, but no additional shoulder as indication of protonated amine was detected. Also high stability was observed for the fluorinated polyoxadiazole treated in similar conditions. These observations confirmed the higher stability of the fluorinated polyheterocycles.

3.4 Thermal mechanical characterization of polytriazoles

Polytriazoles with diphenylether and hexafluor isopropylidene were characterized by thermal mechanical analysis. The glass transition temperature of S-DPE-PT can be clearly seen at 426°C. For the fluorinated polymer, the glass transition temperature decreases to just above 300°C. Furthermore a second maximum of Tan δ is observed around 110°C. During the preparation of the S-DPE-PT, the ether group stimulates the sulfonation of the aromatic rings in the backbone, due to its electron donating capability. In the case of the S-FPT only the side ring attached to the triazole is sulfonated, while the backbone is very hydrophobic. Furthermore the polymer investigated here had a conversion of only 20 %, being a copolymer of polyoxadiazole with hydrophobic fluorinated segments and 20 % of sulfonated fluorinated

polytriazole. The sulfonated side groups tend to assembly forming clusters apart from the hydrophobic polyoxadiazole part of the chain. The presence of two microseparated phases is responsible for the detection of 2 temperature transitions in the DTMA curve, the higher transition temperature coinciding to that reported for fluorinated polyoxadiazole before [5].

3.5. Proton conductivity

The ionic conductivities of S-DPE-PT and S-FPT were measured at 180°C at 5 % R. H. with different doping levels. S-DPE-PT has a higher conductivity than S-FPT due to the fact that also aromatic rings in the polymer backbone are partially sulfonated. The S-DPE-PT membrane in the salt form without doping had a proton conductivity of $2 \cdot 10^{-4}$ S/cm, while the conductivity of S-FPT in the same conditions was 10-fold lower. When doped with 2 or 4 mol PA/monomer units S-DPE-PT had the proton conductivity increased to 8 and $20 \cdot 10^{-4}$ S/cm, respectively. The achieved doping level for the S-FPT was lower (0.5 mol PA/sulfonated monomeric unit) leading to a proton conductivity of $1 \cdot 10^{-4}$ S/cm. Higher doping levels were not performed in order to be sure that the samples are homogeneous. The more hydrophilic S-DPE-PT allows the introduction of more phosphoric acid without any detectable macrophase separation. For all the membranes investigated here doping was achieved by adding the phosphoric acid directly to the casting solution, in opposite other measurements reported by our group for polyoxadiazole and polytriazole [5, 6].

In a previous work [5] the proton conductivity of fluorinated polyoxadiazoles was low for the non protonated plain polymer (in the order of magnitude of 10^{-5} S cm⁻¹ at 120°C and 100 % R. H.). The F-POD is a very hydrophobic polymer. The sulfonation is not possible due to the electron withdrawing effect of the hexafluoroisopropylidene group linked to the aromatic rings. However the amphoteric character of the oxadiazole groups is quite convenient for the formation of hydrogen bonds when the polymer is doped with phosphoric acid, stimulating the proton transport. When the polyoxadiazole membrane was doped by immersion in

concentrated phosphoric acid (0.34 mol of phosphoric acid per polyoxadiazole monomeric unit, 11.6 wt.% H₃PO₄) proton conductivities in the order of magnitude of 10⁻² S cm⁻¹ at 100 % R. H. were obtained. . Proton conductivity in the order of magnitude of 10⁻³ S cm⁻¹ at room temperature has been reported [13] for polybenzimidazole with a higher doping level (40 wt.% H₃PO₄). Conductivity values of 0.2 S cm⁻¹ at higher temperature (200°C) have been reported for PBI doped with 20 mol of phosphoric acid per polymer repeating [4]. Due to the very high hydrophobicity of the fluorinated polyoxadiazole the doping level could only be increased by the incorporation of functionalized silica, while when S-FPT is used the sulfonic side group improves the hydrophilicity and can allow higher doping levels.

A significant difference between the measurements described here for polytriazoles and results reported before is that pure phosphoric acid as doping agent was added directly to the membrane casting solution. This avoids the excessive contact with water and assures that water is not kept inside the membrane before measurement. The only water comes from the contact to the atmosphere, which in this paper had just 5 % R. H. The presence of water inside the membrane favors more the vehicle mechanism of proton transport, while at real low levels of humidity the proton transport occurs more due to Grotthuss mechanism, practically without the influence of water [14].

4. Conclusions

Polytriazoles prepared with diphenyl ether and with diphenyl hexafluor isopropylidene moieties were compared as far as the thermal and chemical stability and proton conductivity are concerned. The higher chemical stability of the fluorinated polymer could be confirmed by infrared spectroscopy, after subjecting the membranes to heating in the presence of acid. The ether links seems to be weak points after protonation. The degradation of oxadiazole and triazole rings starts at temperatures much higher than those convenient for fuel cell application. The hydrophilicity of membranes with diphenyl ether is higher, since also the

aromatic rings in the polymer backbone are partially sulfonated. Also the proton conductivity of the diphenyl ether polytriazole doped with phosphoric acid was higher when measured at very low humidity levels, down to 5 % R. H and at 180°C. Values of up to 2 mS/cm could be measured at this conditions.

Acknowledgments. The authors thank H. Böttcher for the dynamic mechanical thermal analysis and Dr. N. Scharnagl for the infrared coupled thermogravimetric analysis.

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Figure captions

Figure 1. Infrared spectra of S-DPE-POD membranes after 24 h at 25 and 200°C under O₂ atmosphere.

Figure 2. Volatile products of S-DPE-POD-Na⁺ thermal degradation in (a) inert gas and (b) oxidative atmosphere.

Figure 3. Infrared spectra of S-DPE-PT films in the acid form (---) without heating and films doped with phosphoric acid ((---) 2 and (---) 4 mol PA per monomeric unit) after 24 hours at 180°C and 5 % RH.

Figure 4. Infrared spectra of S-FPT films in the acid form after heating at 250°C during 24 h.

Figure 5. DTMA curves with E', E'' and Tan (δ) as a function of temperature for (a) S-DPE-PT and (b) S-FPT

Scheme 1. Structures of polytriazoles and polyoxadiazole

Scheme 2. Mechanism of degradation of diphenyl ether group initiated by protonation

Scheme 3. Mechanism of degradation of oxadiazole ring initiated by protonation

Figure 1. Infrared spectra of S-DPE-POD membranes after 24 h at 25 and 200°C under O₂ atmosphere.

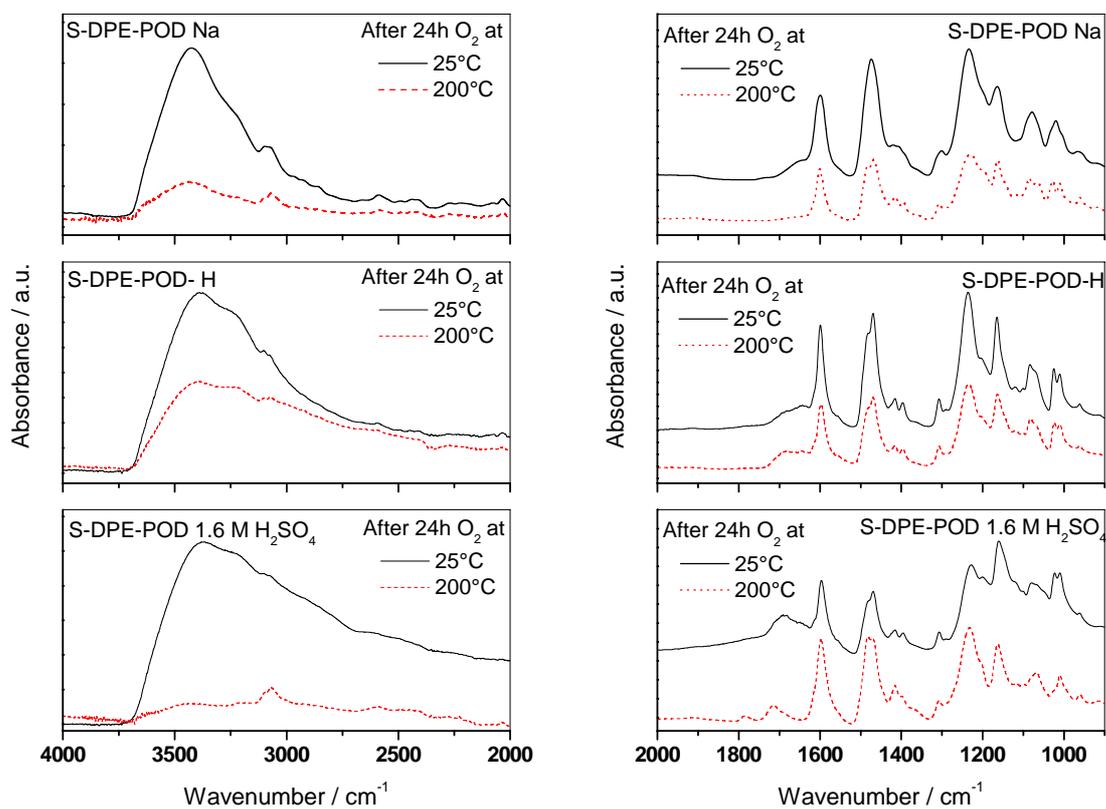
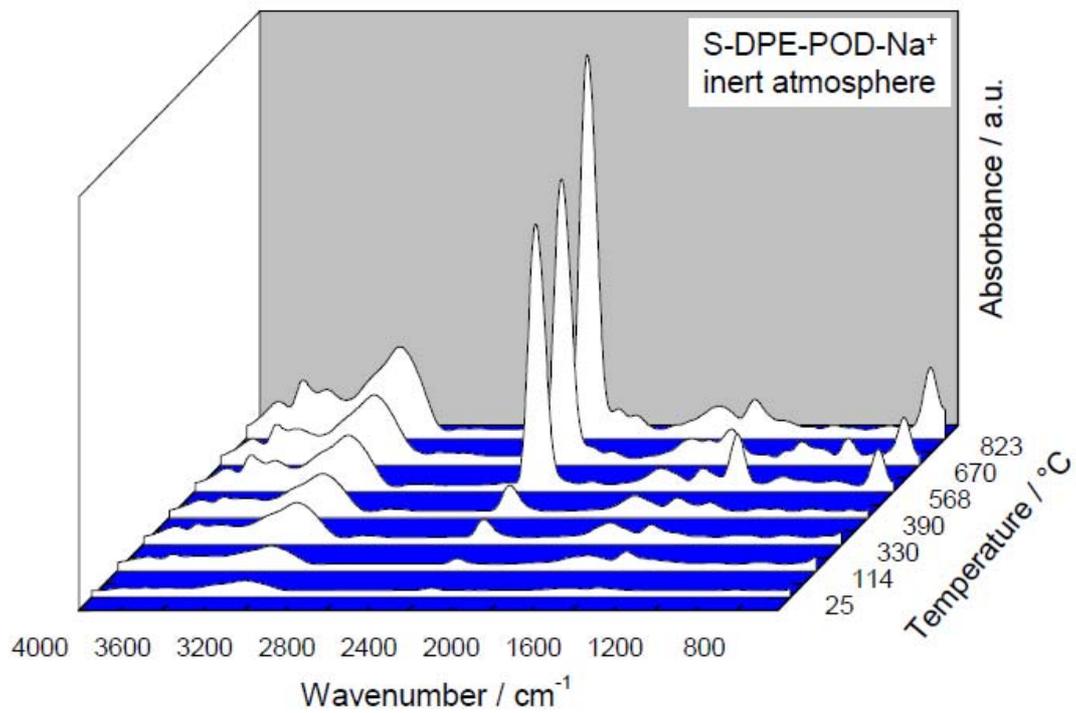
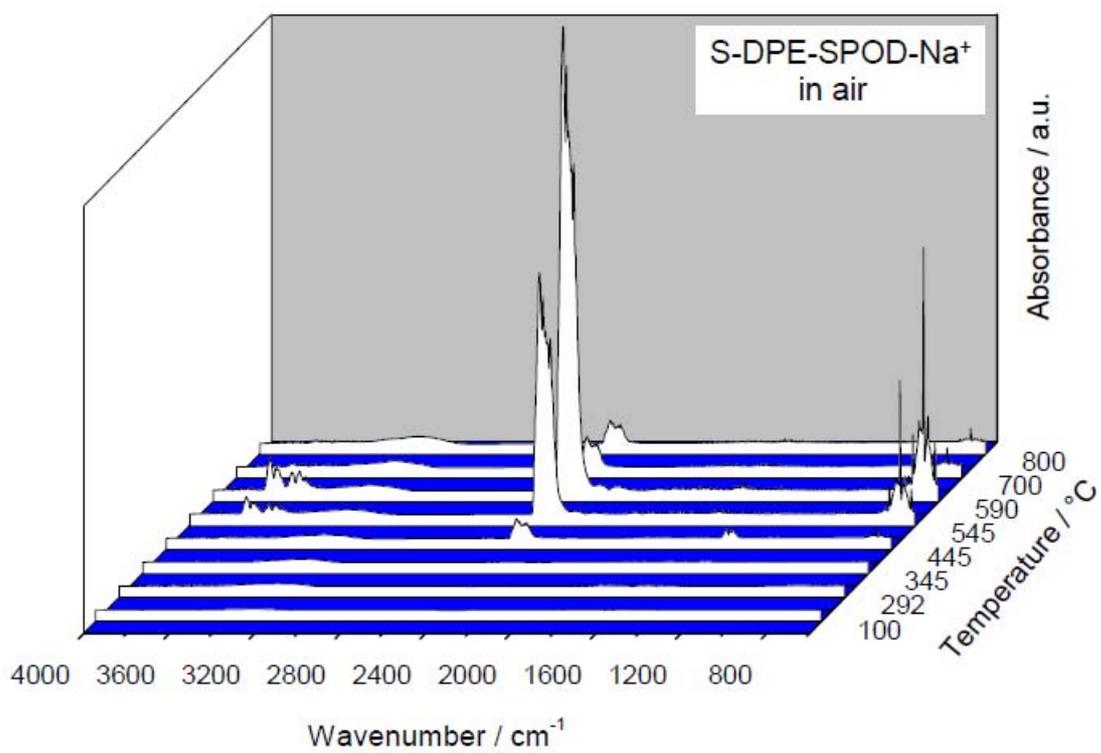


Figure 2. Volatile products of S-DPE-POD-Na⁺ thermal degradation in (a) inert gas and (b) oxidative atmosphere.



(a)



(b)

Figure 3. Infrared spectra of S-DPE-PT films in the acid form (---) without heating and films doped with phosphoric acid ((---) 2 and (---) 4 mol PA per monomeric unit) after 24 hours at 180°C and 5 % RH.

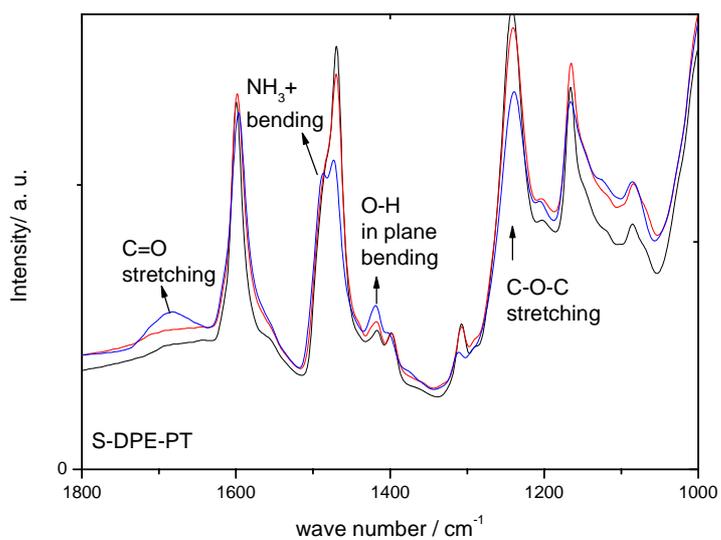


Figure 4. Infrared spectra of S-FPT films in the acid form (--) before and (--) after heating at 250°C during 24 h; (--) FPOD after heating under the same conditions.

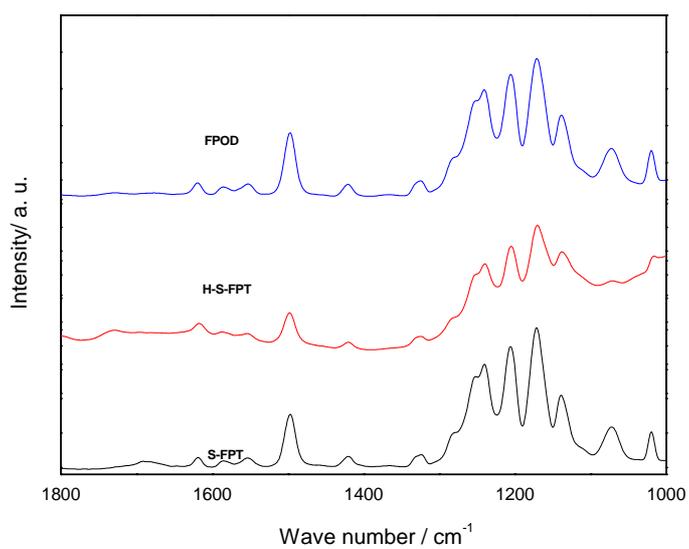
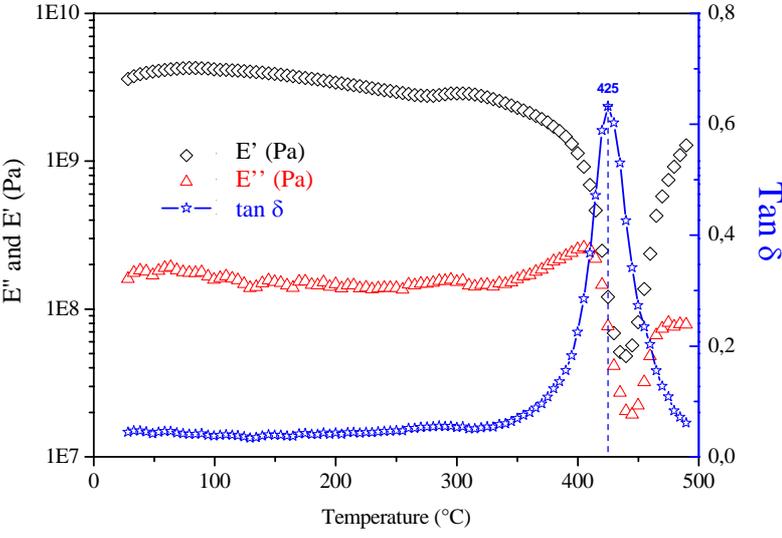
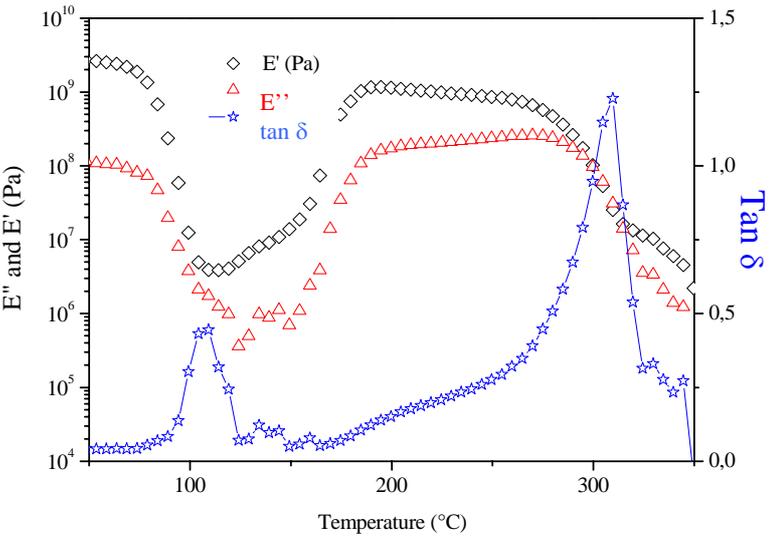


Figure 5. DTMA curves with E' , E'' and $\text{Tan}(\delta)$ as a function of temperature for (a) S-DPE-PT and (b) S-FPT

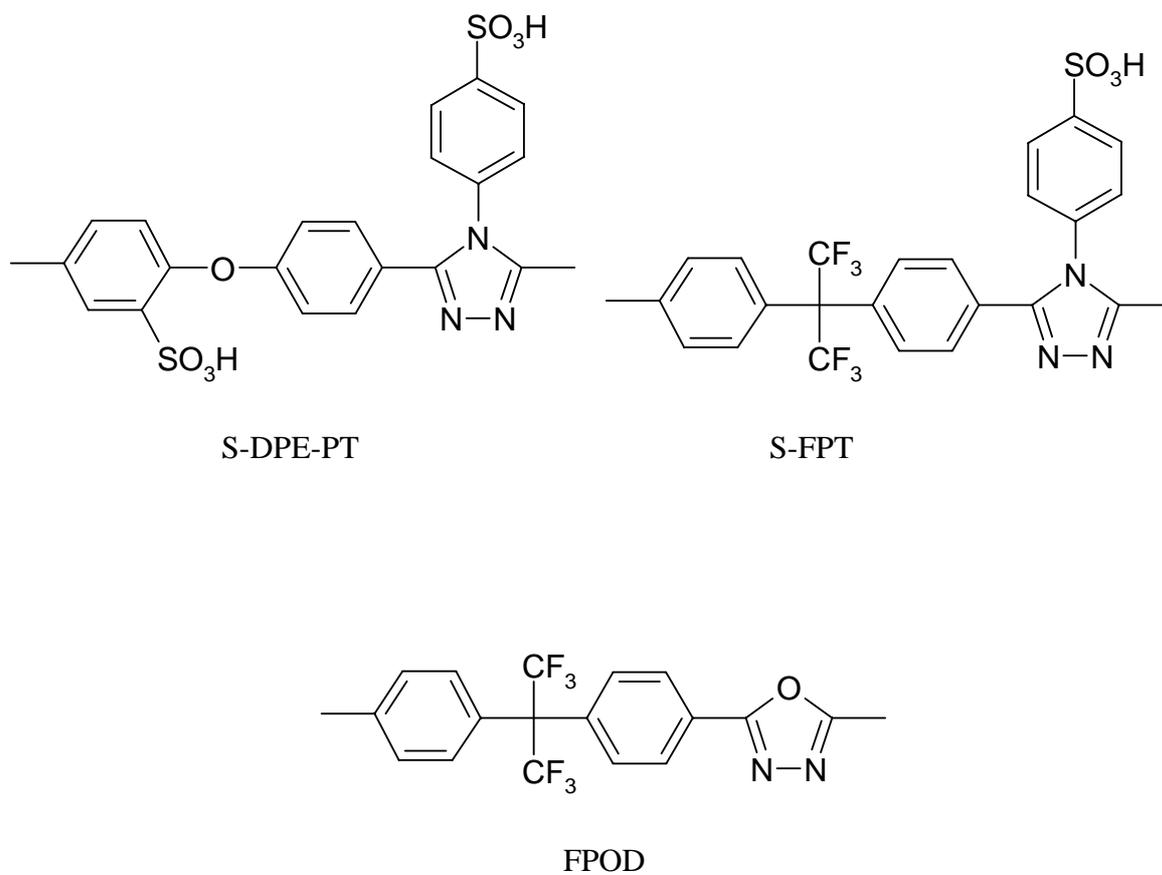


(a)

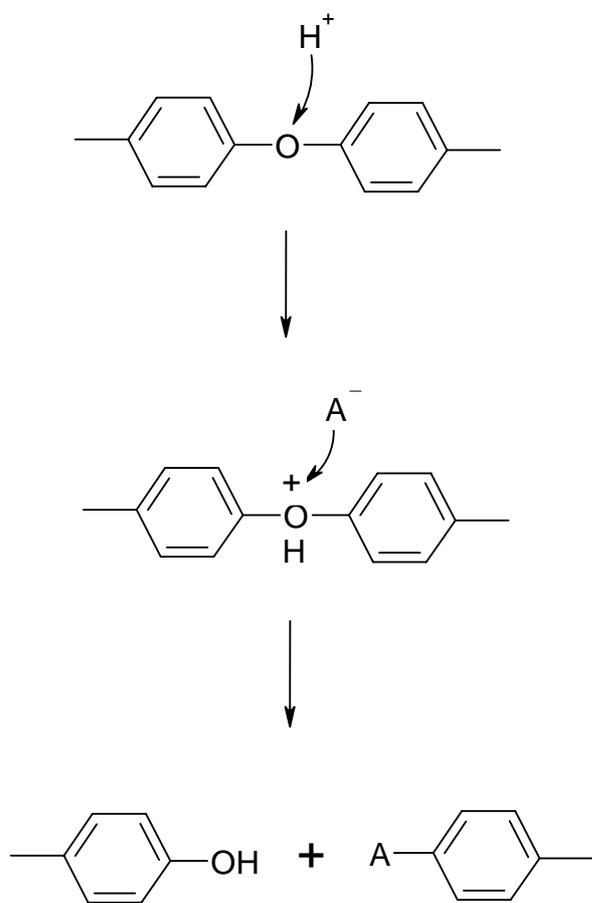


(b)

Scheme 1. Structures of polytriazoles and polyoxadiazole



Scheme 2. Mechanism of degradation of diphenyl ether group initiated by protonation



Scheme 3. Mechanism of degradation of oxadiazole ring initiated by protonation

