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Chlorine dopants in plasma synthesized heteroaromatic polymers

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Abstract

This work presents a study on the simultaneous polymerization and doping by plasma of pyrrole and thiophene with chloroform. The synthesis is a hybrid combination of fragmentation, polymerization and doping processes, because some of the reagents participating in the chemical reactions are produced by the decomposition of chloroform molecules by plasma. The main objective was to study the dopant–polymer interaction, from the point of view of the electric transport along the material. The conductivity of the chlorinated polymers resulted in the 10^{-5}–10^{-3} S/cm interval, depending on the environmental humidity. This conductivity is approximately 5 orders of magnitude higher than that of the same polymers synthesized by plasma without doping. The characterization of the polymers was carried out by means of SEM, EDS, FT-IR and XPS spectroscopies.

Keywords: Dopants; Chlorine; Plasma polymers

1. Introduction

Different methods of synthesizing polypyrrole (PPy) and polythiophene (PTh), such as chemical oxidation, electrochemical and plasma polymerizations, have been studied in a continuous search for better conductive polymers. Plasma techniques, in particular, have proven to be effective in the polymerization, in the copolymerization and in the simultaneous doping in situ of pyrrole and thiophene with iodine and other compounds [1–5].

The doping of polymers occurs by the inclusion of different atoms, molecules or excited species and, depending on the electronic configuration of the dopants, these chemical species modify the electronic balance in the structure of the material. However, if sufficient energy is applied to a dopant–polymer system, reaction can be initiated between the dopant and the polymer, transforming the part of the doped material in different compounds, making the function of the dopants more complex [6,7].

Some dopants exert a significant influence on the transport of electric charges in polymers. Among them, iodine has been one of the most studied in plasma polymers, due to its high electronegativity and high vapor pressure, which facilitates the introduction of its vapor in vacuum plasma reactors.

Another electronegative element that could play a dopant role for the transport of electric charges in polymers is chlorine. However, as this halogen is more reactive than iodine, the doping has to be carefully prepared so as to avoid the undesired chemical reactions. One interesting alternative to avoid these effects is to use chemical compounds with a high proportion of Cl atoms in their structure, such as chloroform. Thus, if the energy of the plasma particles is sufficiently high, the collisions could decompose the chloroform molecules releasing fragments with chlorine atoms during the polymerization and some of these groups can be used as dopants in situ, increasing the transport of electric charges in the final material.

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With this purpose, this work presents a study on the synthesis by plasma of polypyrrole and polythiophene combined with chloroform.

2. Experimental

The synthesis was carried out within a 25 cm long tubular glass reactor with a 9 cm external diameter. The reactor has two stainless steel flanges at both ends connected to one electrode each, in order to provide a uniform electric field at the center of the reactor. The electrodes were connected to a voltage amplifier and to a 13.5 MHz radio frequency generator. The flanges contain two access ports to introduce the chemical reagents, monomers and chloroform, to the reactor. As all these components are, under standard conditions, in a liquid state and their vapor pressure is relatively high, their vapors can be introduced to the reactor using the difference of pressure between the vacuum chamber and the containers [8].

The chlorined polypyrrole (PPy–Cl) and polythiophene (PTh–Cl) were synthesized at 12 W and 7×10^{-2} torr during 300 min. Both polymers were formed as thin films adhered on the reactor walls, and removed with acetone, which washed and swelled the polymers. After that, the films were dried at room temperature and mechanically separated from the surfaces with a thin spatula.

FT-IR spectra of the polymers were taken using a Perkin–Elmer FT-IR 2000 spectrophotometer. The electron microscopy and the elemental EDS analysis were performed on a Philips XL-30 microscope. For the XPS spectra, a PH15300 ESCA spectrometer was used, sampling the polymers on glass holders at 1253.6 eV, 13 kV and 300 W with an Mg Kα X-ray source. The analysis chamber pressure was 8×10^{-9} mbar. Survey spectra were performed within the 0–1000 eV binding energy interval. High-resolution spectra were taken at a 45° angle to explore an approximately 70 Å depth. Steps of 89.45 and 35.75 eV were used to capture both, survey and high resolution spectra, respectively.

The electric conductivity was calculated through the resistance measured with an OTTO MX620 digital multimeter in a double probe capacitor array with copper electrodes. The polymers were placed between the electrodes and the whole device was located in a humidity chamber in order to modify the water content in the inner atmosphere [1]. The voltage used in the resistance measurements was approximately 5 V and the temperature was maintained approximately constant, at 20 °C. In this configuration, the electric charges have to travel through the polymer volume and the resulting electric conductivity can be considered representative of the entire material.

3. Results and discussion

3.1. Elemental analysis

Table 1
Elemental composition of PPy–Cl and PTh–Cl

Polymer	%C	%N	%O	%S	%Cl	C/X
PPy–Cl	70.8	15.9	9.3	–	4.0	4.4
PTh–Cl	70.2	–	9.4	17.1	3.3	4.1

X means N or S, depending on the polymer.

The elemental analysis of the polymers is presented in Table 1. The electric conditions in the plasma promote the formation of free radicals and ions from the monomers. These reactive species are the main polymerization agents. However, they may also affect the direction of the chemical reactions, producing fragmentation, ramification and crosslinking in the polymers due to collisions with electrons, ions, radicals and other neutral molecules in the plasma. As the whole effect is used for the decomposition of chloroform molecules to form dopants, which are used during the polymerization, it should be convenient to consider that some fragments leave the system through the vacuum system. So, the elemental balance in this section will consider only the polymers that remain within the reactor. Taking into consideration this point, the monomer ''ring'' discussed in this section was considered as formed by four C atoms and one N or S atom, depending on the polymer studied. Thus, if the polymers were constituted with the same atomic proportion as in the monomers, the atomic carbon/nitrogen (C/N) ratio in PPy and the carbon/sulfur (C/S) ratio in PTh should be 4. However, considering the additional C atoms from the chloroform in the polymerization, the C/X ratio ($X = N$ in PPy–Cl and $X = S$ in PTh–Cl in Table 1) should be slightly greater than 4. The data in Table 1 indicate that this ratio in PPy–Cl is 4.4, whereas in PTh–Cl is 4.1.

The atomic percentage of chlorine in these polymers is 4.0 and 3.3, which represents approximately 4 and 5 monomer rings per each Cl atom in the structure of PPy–Cl and PTh–Cl, respectively. This Cl atomic content induces big changes in the transport of electric charges in the polymers, as will be discussed in the following sections.

According to Table 1, oxygen has an atomic contribution of 9.3 and 9.4% in both polymers, approximately 2 monomer rings per each oxygen atom. The presence of oxygen can be attributed to two sources: the residual atmospheric oxygen at the beginning of the polymerization and the reaction of the residual radicals at the end of the reactions.

3.2. XPS of PPy–Cl and PTh–Cl

The participation of chloroform in the plasma polymerization of pyrrole and thiophene can be studied following the contribution of the individual chemical species in the final polymeric structures. Although it is not easy to distinguish atoms in single or multiple bonds by photoelectrons by using the core and not the valence orbitals, the XPS technique allows to discriminate between different oxidation states and chemical environments through slight shifts in the binding energies.

In this strategy, the energetic distribution of photoelectrons can be used to find out the chemical participation of atoms in the polymers. In this work, the binding energy of C 1s, N 1s, O 1s and Cl 2p atomic orbitals in PPy–Cl and PTh–Cl was deconvoluted according to the particular chemical environment in the polymers. The main peaks and the relative areas are presented in Table 2.

C 1s spectra in both polymers were resolved in four peaks, see Fig. 1(a) and (b). They were numbered from the lowest to the highest energy as C1 to C4, see Table 2. C1 peaks are centered in both polymers at 284.88 eV and can be identified with carbon atoms in C−C, C=C and C−H bonds [5,9]. These are the most abundant chemical states of carbon atoms in both polymers, between 56.44 and 57.73%. As the C 1s orbitals assume different conformations, the binding energy increases. The most energetic peak in both polymers was found in C4, between 288.5 and 288.46 eV, and can be associated with carbons in C=O bonds. This kind of oxidation is greater in PPy−Cl, 21.43%, than in PTh−Cl, 12.07%. The intermediate peaks, C2 and C3, have their own meaning in each polymer.

In PTh−Cl, the C2 peak was found at 285.88 eV and represents the C 1s orbital energy of carbon in C−S bonds [5]. The C3 peak was located at 286.78 eV and can be associated with carbon in C−O and C−Cl bonds. The participation of chloroform in this polymerization can be seen inside the 21.33% area of this peak, due to the C−Cl groups added to the polymers from the chloroform fragments.

In PPy−Cl, the C2 peak was found at 286.62 eV, which implies the participation of C atoms in C−N, C−O and C−Cl bonds. The area percentage of this peak is 17.43%, which is lower than that of the energetically similar C3 peak in PTh−Cl. The C3 peak was found at 287.65 eV, where the carbon atoms could be associated with slightly polarized nitrogen. The area percentage of this chemical state is small, 4.7%.

The N 1s spectra were adjusted for PPy−Cl with two contributions, N1 and N2, see Table 2. N1 was centered at 399.56 eV and includes both, N− and N=, which are part of the aromatic characteristic of pyrrole rings [10]. The relative area of this peak is 81.44%. N2 was calculated in 400.81 eV with 18.56% of relative abundance, see Fig. 2(a). This peak can be related to the overlapped contributions of N− and N+. The energetic distribution is slightly shifted to ionic species, maybe because of the presence of chlorine atoms near the nitrogen sites.

The S 2p orbitals in PTh−Cl were adjusted with only one contribution, S1 in Table 2, centered in 163.84 eV, see Fig. 2(b). This binding energy is in the interval of sulfur bound to carbon [5,11] and has been found before, in an unresolved doublet, in 2-iodothiophene polymerized by plasma [12].

The O 1s signal was adjusted with only one contribution in both polymers. The energies are approximately the same, with a slight difference due to the particular chemical environment in each polymer. In PPy−Cl the O1 energy is centered at 532.33 eV belonging to overlapped −O− and =O configurations in bonds like N−O, C−O and C=O, see Fig. 3(a). In PTh−Cl the O1 peak was calculated at 532.57 eV, see Fig. 3(b). This energy is greater than in their equivalent orbitals in PPy−Cl due to the influence of O−S bonds instead the O−N bonds in the total energy distribution.

The Cl 2p orbitals produce a fairly complex binding energy distribution that can be resolved into two spin-orbit doublets belonging to anions and covalent atoms in both polymers. The first doublet in PPy−Cl was centered at approximately 197.1 and 199.1 eV with a relative area of 54.4%, see Fig. 4(a), and corresponds to chlorine anions [13]. The other doublet was fitted at 200.7 and 202.2 eV with a relative area of 45.6% and corresponds to covalent chlorine in C−Cl bonds [13,14].

In PTh−Cl, the Cl 2p signal is less complex than in PPy−Cl and was calculated also with the same two doublets slightly shifted to higher energies, see Fig. 4(b). The first one was located at 197.4 and 199.7 eV with relative area of 46.0%. The second doublet was centered at 201.1 and 202.3 eV with relative area of 54%. These signals suggest that the chlorine atoms participate in the polymers with chemical bonds and as dopant agents. The participation of chlorine anions in PTh−Cl is not as strong as in PPy−Cl.

3.3. Infrared analysis of PPy−Cl and PTh−Cl

Fig. 5 shows the FT-IR transmission spectra of PPy−Cl and PTh−Cl. Each spectrum is composed basically by wide absorption bands which suggest the existence of complex interactions in the plasma polymers.

Table 2
Binding energies in PPy−Cl and PTh−Cl

	PPy−Cl			PTh−Cl		
	Peak (eV)	Area (%)	Chemical state	Peak (eV)	Area (%)	Chemical state
C 1s	C1 = 284.88	56.44	C−C, C=C, C−H	C1 = 284.88	57.73	C−C, C=C, C−H
	C2 = 286.62	17.43	C−N, C−O, C−Cl	C2 = 285.88	8.87	C−S
	C3 = 287.65	4.70	C−N[a]	C3 = 286.78	21.33	C−O, C−Cl
	C4 = 288.50	21.43	C=O	C4 = 288.46	12.07	C=O
N 1s	N1 = 399.56	81.44	−NH−, −N=	−	−	−
	N2 = 400.81	18.56	−NH−, N+	−	−	−
S 2p	−	−	−	S1 = 163.84	100.00	S−C, −S−
O 1s	O1 = 532.33	100.00	O−N, O−C, O=C	O1 = 532.57	100.00	O−S, C−O, C=O
Cl 2p	197.1, 199.1	54.4	Cl−	197.4, 199.7	46.0	Cl−
	200.7, 202.2	45.6	C−Cl	201.1, 202.3	54.0	C−Cl

[a] Indicates excited states.

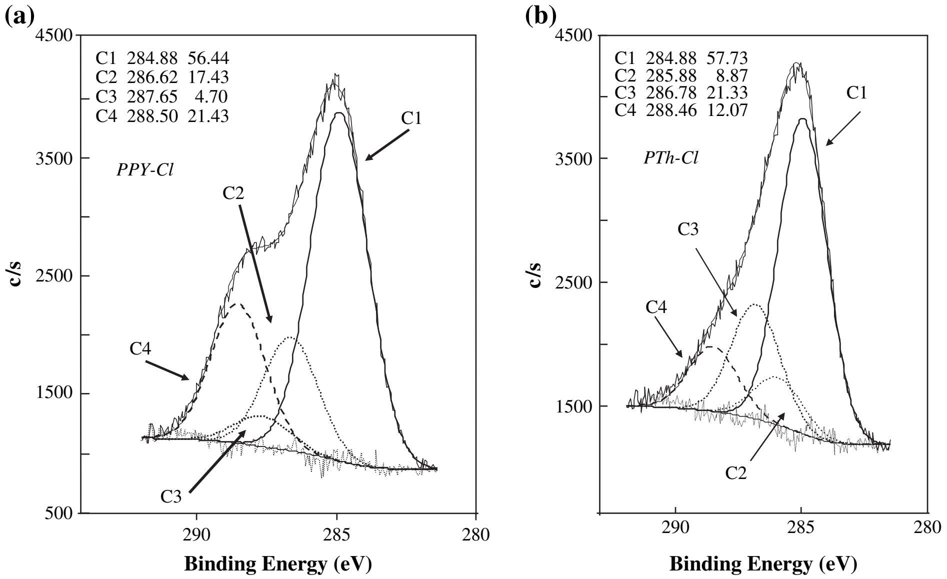


Fig. 1. C 1s binding energy of: (a) PPy–Cl and (b) PTh–Cl.

The C–H aliphatic bonds are found between 2925 and 2970 cm^{-1}. These groups can originate from the chloroform fragments or from the breaking of some pyrrole or thiophene rings due to the high energy plasma discharges. The absorption around 3035 cm^{-1} indicates the presence of C–H bonds in the heteroaromatic rings. In both polymers, the aliphatic and aromatic absorptions of C–H groups have approximately the same magnitude, indicating, by analogy, that the polymers could be composed with approximately the same proportion of C–C and C=C groups, C–C coming from the aliphatic fragments and C=C coming mainly from the aromatic rings. In a small absorption, another peak with a small intensity at 2203 cm^{-1} corresponds to C≡N groups which are related to the partial fragmentation of the pyrrole rings mentioned before [15].

The peaks at 1654 and 1685 cm^{-1} belong to C=C bonds in PPy–Cl and PTh–Cl, respectively. Both absorptions are partially overlapped by the C–N and C–S groups. The N–H and/or O–H groups are located in the wide band involving the 3353 and 3216 cm^{-1} regions.

The absorption at 1041 cm^{-1} can be attributed to the oxidation of the last free radicals with the atmospheric oxygen at the end of the polymerization. The oxygen groups can recombine with hydrogen atoms to form alcohols, C–O–H.

The absorption at 613 cm^{-1} belongs to C–Cl bonds in both polymers. This absorption is part of a wide band involving also the C–S bonds in PTh–Cl and the substitutions of C–H bonds in the heteroaromatic rings because of the growing of the polymers.

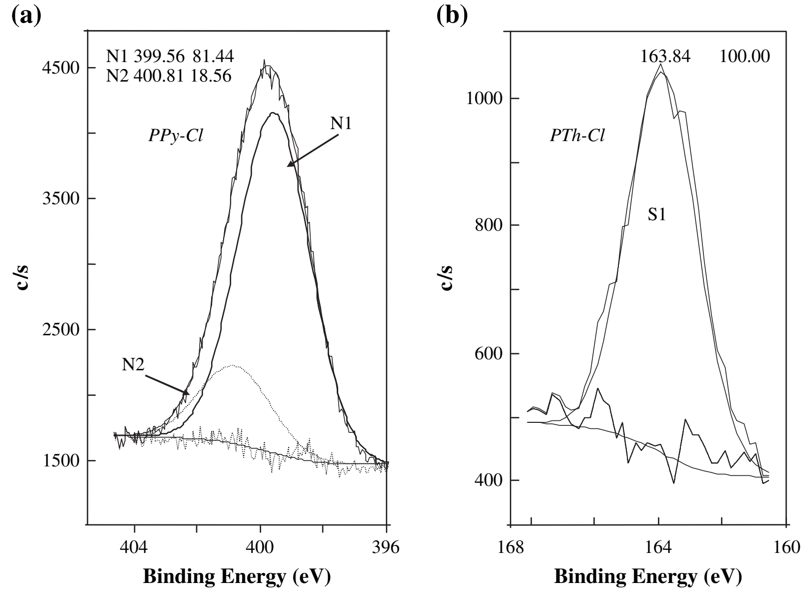


Fig. 2. (a) N 1s binding energy of PPy–Cl. (b) S 2p binding energy of PTh–Cl.

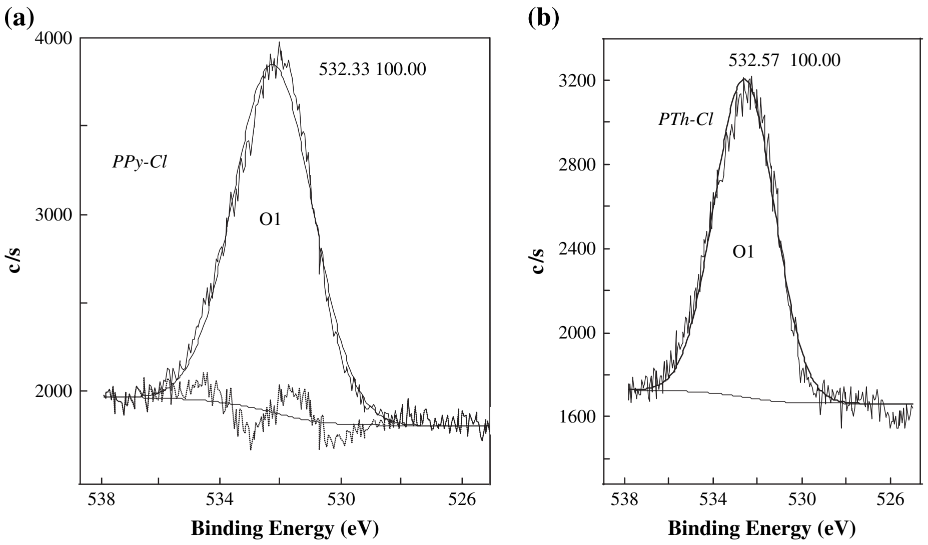


Fig. 3. O 1s binding energy of: (a) PPy–Cl and (b) PTh–Cl.

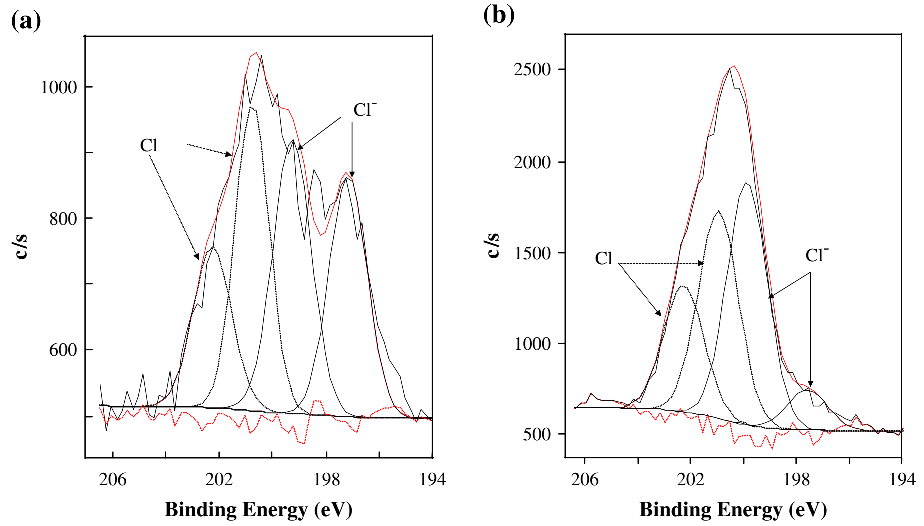


Fig. 4. Cl 2p binding energy of: (a) PPy–Cl and (b) PTh–Cl.

Both, XPS and IR analyses suggest that the energy of the plasma is sufficient to break the chloroform molecules and that the fragments combine with the polymers in progress to form chains with aliphatic fragments bonded to them. The fragments come from chloroform and from some pyrrole and thiophene rings that break during the polymerization. Both techniques suggest the presence of oxygen in the polymers which could belong to alcohol groups.

3.4. Electric conductivity

Fig. 6 shows changes of the electrical conductivity of PTh–Cl, PPy–Cl, PTh and PPy as a function of relative humidity (RH). PTh and PPy were synthesized by plasma without doping and their conductivity was included in the plot only to estimate the increase in conductivity reached with the inclusion

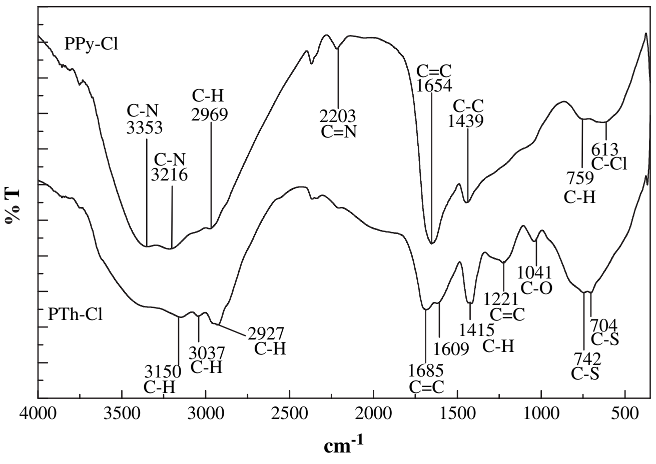


Fig. 5. FT-IR transmission spectra of PPy–Cl and PTh–Cl.

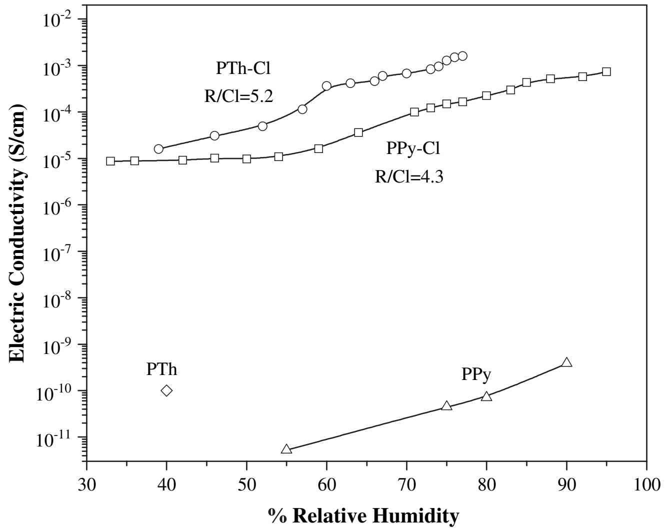


Fig. 6. Conductivity of PTh−Cl and PPy−Cl.

of chloroform in the polymers. The interaction of water with polypyrroles and polythiophenes is important because these semiconducting polymers can be used as biosensors or in biocompatible materials, and inside the body fluids; the polymers are immersed in an aqueous medium [16].

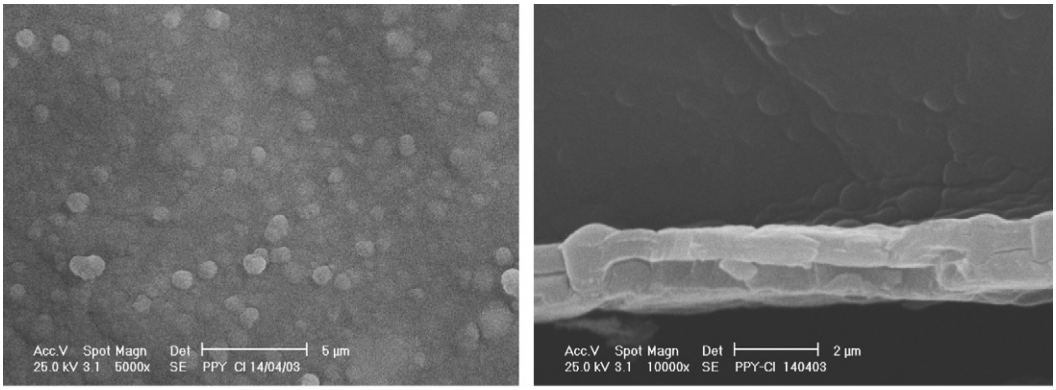
PTh without doping has conductivity of approximately 10^{-10} S/cm at 40% RH. PTh−Cl shows a 10^{-5} S/cm conductivity at 40% RH and reaches up to 10^{-3} S/cm at 75% RH. Although it has only an increase of 2 orders of magnitude as a consequence of humidity, its tendency suggests only one conduction mechanism.

Plasma PPy without doping has conductivity in the 10^{-11}–10^{-9} S/cm interval, from 55 to 90% RH. PPy−Cl presents an approximately constant electric conductivity of 10^{-5} S/cm from 35 to 50% RH and after that, increases continuously up to 10^{-3} S/cm at 95% RH. This behavior suggests two conduction mechanisms. The first one at low humidity could be predominantly electronic and the second, at high humidity, could be a combination of electronic and ionic transferences of charges [1].

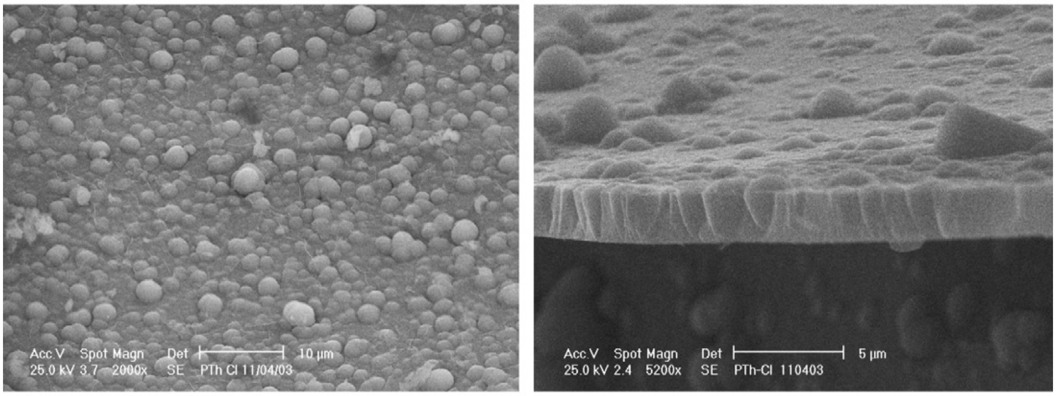
The plot indicates that PTh−Cl has higher electric conductivity than PPy−Cl in the RH range studied. According with these results, chlorine atoms, combined with water, give better conditions for the transport of electric charges in polypyrroles and polythiophenes [17]. Other dopants, such as 4-ethylbenzenesulfonic acid, have increased the conductivity of plasma PPy up to 4.8×10^{-4} S/cm using non-plasma doping processes [18].

3.5. Morphology

Fig. 7 contains micrographs of PPy−Cl and PTh−Cl films taken from two different perspectives, front and cross-section views. Fig. 7(a) and (b) corresponds to PPy−Cl and Fig. 7(c) and (d) to PTh−Cl. Both polymers have a homogenous



(a) PPy-Cl surface **(b) PPy-Cl cross-section**



(c) PTh-Cl surface **(d) PTh-Cl cross-section**

Fig. 7. Morphology of PPy−Cl and PTh−Cl.

smooth surface with tiny spheres of different sizes inserted on the surface. The spherical agglomerates on the surface indicate that both films are formed by a process of gas phase polymerization followed by deposition on the internal walls of the reactor. This type of film is characteristic of some polymers synthesized by plasma [3]. The thickness of these films is around 2−4 μm, although the PPy−Cl film looks as formed by more than one layer.

4. Conclusions

PTh−Cl and PPy−Cl have been synthesized by plasma in a doping process that involves chloroform molecules decomposed in chlorined derivatives by the plasma energy and these fragments are simultaneously incorporated to the polymers in formation. The results indicate that the Cl atoms are combined with the structure of both polymers in a proportion of 4 or 5 equiv monomer rings per Cl atom. The presence of each chlorine atom in the polymers modifies the electronic configuration in its neighborhood, because of the high electronegativity of Cl, in such a way that those sites could be negative to other parts of the chains. This slight polarization effect, multiplied along the polymers, enhances the conductivity of PTh−Cl and PPy−Cl in approximately 5 orders of magnitude, compared with the same polymers without doping.

The final polymers contain aliphatic and aromatic C−H groups in approximately the same proportion. This indicates that there are double bonds C═C in the structure of the polymers which most probably belong to the aromatic rings that survive to the polymerization. The possibilities of transporting electric charges along the polymers are closely linked to the presence of C═C bonds in similar patterns as those found in the heteroaromatic rings.

The mechanism of charge transference exhibits two tendencies in PPy−Cl; one that predominates up to 55% RH and another that rules above that point. The transference of charges in PTh−Cl has a unique linear tendency along the RH interval studied. The morphology of both polymers consists of tiny spheres on the surface for both polymers. This morphology has also been observed in polypyrrole doped with iodine [3].

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