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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

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.

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 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