

Research Article

XPS Study of the Chemical Structure of Plasma Biocopolymers of Pyrrole and Ethylene Glycol

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An XPS study about the structure of plasma biocopolymers synthesized with resistive radio frequency glow discharges and random combinations of ethylene glycol, pyrrole, and iodine, as a dopant, is presented in this work. The collisions of molecules produced structures with a great variety of chemical states based in the monomers, their combinations, crosslinking, doping, fragmentation, and oxidation at different levels in the plasma environment. Iodine appears bonded in the copolymers only at high power of synthesis, mainly as C–I and N–I chemical bonds. Multiple bonds as C≡C, C≡N, C=O, and C=N were found in the copolymers, without belonging to the initial reagents, and were generated by dehydrogenation of intermediate compounds during the polymerization. The main chemical states on PEG/PPy/I indicate that all atoms in pyrrole rings participate in the polymerization resulting in crosslinked, partially fragmented, and highly oxidized structures. This kind of analysis can be used to modify the synthesis of polymers to increase the participation of the most important chemical states in their biofunctions.

1. Introduction

Polymers formed with oxygenated and/or nitrogenated chemical groups, such as polyethylene glycol (PEG) and polypyrrole (PPy), are studied as biomaterials to be implanted in the central nervous system to reduce possible side effects in the spinal cord after a severe injury. PEG is an oxygenated polymer with the potential to influence or repair the membrane permeability caused by injuries or diseases [1, 2] and PPy is one of the most studied nitrogenated biocompatible polymers used as a biosensor, cell growth supporter for nerve cells, and substrate for junction between neurons and microelectrodes [3, 4]. The PPy potential for transferring electric charges is related to the alternated multiple-single chemical bonds in the rings of its structure.

The chemical structure for random plasma combinations of ethylene glycol (EG) and pyrrole (Py) copolymers

(PEG/PPy) is studied in this work to produce polymers capable of interacting with neuronal cells. Other components can be added to the mix, for example, iodine with the aim of increasing the conductive properties [5]. In the spinal cord, many polymers have caused rejection due to their noncompatible physicochemistry or to the residues of solvents, catalysts, or other reagents used in the synthesis which irritate the delicate tissues causing adverse reactions that destroy healthy nerve cells. The polymers of this work reduce this problem because the plasma synthesis only uses the monomers and dopants involved in the process, without any other foreign material, producing clean and sterile polymers.

The structure of similar random plasma copolymers of EG and allylamine has been studied before using IR spectroscopy finding OH, NH and multiple bonds originated during the plasma polymerization. These copolymers also showed signals of electrical charge transference important in

the ionic processes within the human body [6]. In the field of semiconductor materials, plasma random copolymers of Py and aniline have been studied finding that the electrical properties of the copolymers are between the levels of both homopolymers [7].

Morphological, hydrophilical, and electrical studies of random plasma Py and EG copolymers have also been studied obtaining porous and rough layers [8]. It has been also reported that these plasma combinations of Py and EG can be used as implants in the spinal cord of rats after a severe injury to prevent secondary destruction in the spinal cord tissues and to partially recover the lost motor functions [9, 10]. In view of this important use, in this work, the main atomic chemical states of plasma PEG/PPy/I copolymers are studied by XPS considering the energetic distribution of Cls, O1s, N1s, and I3d atomic orbitals with the purpose to identify and quantify the structure in the copolymers. This work goes beyond the study of individual chemical bonds because it includes the whole atomic bonding.

2. Experimental

The copolymers were synthesized in a vacuum glass tubular reactor with 9 cm diameter and 26 cm length. The central tube has stainless steel flanges at the ends with three access ports each. On the central ports two stainless steel electrodes were inserted with a diameter of 7 cm and a separation of 6 cm between them. The electrodes were connected to a RFX-600 Advanced Energy power supply. In another port, a pressure gauge, an Alcatel Pascal 2010C1 vacuum pump, and an Alcatel LNT 25S condenser for residual vapors were collocated.

The monomers used in the polymerization were EG (Tec-siquim, 99.5%) and Py (Aldrich, 98%) in separate containers connected to the reactor through individual entrances. During the synthesis, EG was maintained at 50°C to produce vapors that entered the reactor, while Py and iodine were supplied at room temperature. All vapors mixed freely inside the reactor to produce random copolymers. The synthesis conditions were 0.1 mbar, 13.5 MHz, and 80 W during 180 min.

The resulting PEG/PPy/I copolymers were obtained as thin films attached to the reactor walls and electrodes. To detach the material it was necessary to apply distilled water, ethanol or acetone on the walls and dry the films and if they were released from the surface, remove them carefully with a spatula. If not, another cycle of wetting and drying was applied until the film was released from the surface. The films had an average thickness of 20 μm .

The structural chemical analyses of the bulk copolymers were performed on an infrared (IR) spectrophotometer Thermo Scientific Nicolet iS5 on ATR mode using 64 scans. Superficial X-ray photoelectron analyses (XPS) were done on a Thermo K-Alpha photoelectron spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). The diameter of the analysis area was 400 μm . The base pressure of the analysis chamber was 10^{-9} mbar; however, a beam of Ar ions was applied to the samples to reduce the electrostatic charges that increased the pressure up to 10^{-7} mbar in which the analyses were performed. The copolymers were located

in Al tapes on stainless steel sample holders, which remained in a preanalysis chamber for approximately 1 hr at 10^{-3} mbar before entering the analysis chamber. The step energy of the survey mode was 1 eV, but in the Cls, N1s, O1s, and I3d orbital scans, the energy step was adjusted to obtain approximately 200 points per each distribution, unimodal 200, bimodal 400, and so on. This means energy steps between 0.05 and 0.02 eV, depending on the element and the energetic region. Once the total energetic distribution of the orbitals in study is obtained, the specific energetic atomic states were evaluated adjusting the main distribution with internal Gaussian curves.

3. Result and Discussion

3.1. Chemical Structure of PEG/PPy/I Copolymers. Figure 1 shows the IR spectra of PEG/PPy/I synthesized between 40 and 100 W. The data were taken in ATR mode directly from the copolymer films, which show basically the same absorption, indicating that at this level of power the chemical structures do not have great differences. The widest band is located between 3750 and 3000 cm^{-1} centered approximately at 3269 cm^{-1} , which includes O–H, N–H and =C–H bonds [7, 11]. These groups are part of both monomeric structures used in the copolymers. The peak at 2944 cm^{-1} corresponds to –C–H aliphatic groups of EG and to some saturated fragments of Py rings. The wide absorption centered in 733 cm^{-1} indicates also the presence of –C–H and =C–H groups in different combinations.

In 2212 cm^{-1} , a signal of multiple bonds is found, which may be combinations of C \equiv C, C \equiv N, C=C, C=O, and C=N [12]. Triple bonds are not part of the monomeric structures and may originate from strong dehydrogenation and fragmentation caused by the high kinetic energy of particles in the plasma [13]. This absorption has a medium intensity and appears in many plasma polymers.

The most intense absorption is centered in 1613 cm^{-1} in all copolymers belonging to C=C double bonds of Py molecules; however, as this absorption becomes wider, more complex interactions occur in the structure. In this way, although the center belongs to the C=C bonds of the Py structure, at higher wavenumbers in the same curve, C=O and C=N chemical groups appear. C=O may form with the dehydrogenation of two neighboring atoms of EG molecules; however, C=N needs two consecutive effects, the breaking of Py molecules and the dehydrogenation of such fragments in similar process of C=O groups. Oxygen in the copolymers can also be observed at 1421 and 1029 cm^{-1} with the absorption of C–O groups.

All the discussed data indicate that the copolymers have hydrogenated groups, such as C–H, O–H, and N–H that survived the energy of the discharges, and multiple bonds such as C \equiv C, C \equiv N, C=O, and C=N, created as a consequence of the dehydrogenation produced by the plasma.

3.2. Superficial Elemental Analysis. The bulk and superficial structures of any material are different, because on the surface there is a complex balance of forces due to the end of the solid phase and the starting of another, usually the atmospheric gas. As a consequence, the contact with the environment

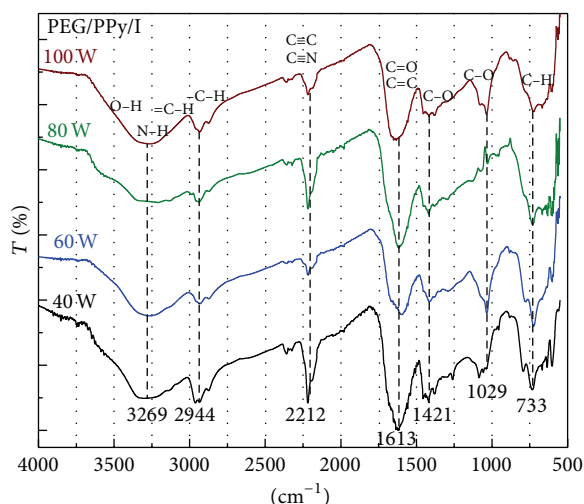


FIGURE 1: IR spectra of plasma PEG/PPy/I synthesized between 40 and 100 W.

produces characteristics that depend not only on the structure of the material, but also on the surrounding fluids. In biomaterials, the surface is especially important because it is the face exposed to cells. In the following sections, the structure of PEG/PPy/I surface is studied with XPS techniques.

The survey spectra of PEG/PPy/I synthesized at different power are presented in Figure 3 in which C1s, N1s, O1s, I3d, and Si2p orbitals can be observed representing the content of their respective elements. The atomic percentage is included in the graph. As Si is not part of the copolymers, it was considered superficial contamination.

Extending the atomic ratio in the monomers to the respective homopolymers, PPy would have $N/C = 0.25$ with $O/C = 0$, because it does not have oxygen in its structure. For similar reasons PEG would have $N/C = 0$ with $O/C = 1$; see Figure 2. Thus, in plasma PEG/PPy/I, N/C should be between 0 and 0.25 and O/C should be between 0 and 1; and in a random copolymer with 1/1 combination of both monomers, both ratios would be $N/C = 0.17$ and $O/C = 0.33$.

The experimental N/C in the copolymers synthesized at different power is between 0.1 and 0.2 suggesting that both monomers participate in approximately the same proportion. However, O/C has values between 0.03 and 0.2 which indicates that Py has much more participation than EG in the copolymers. Considering the analyses of both ratios, Py participates with at least half of the content in the copolymers. On its part, I/C has very low values, from 0 to 0.0005, because it has participation of a dopant, however, at low power, this ratio has so small value that could not be measured. In some way, I/C indicates that the dopant needs power of synthesis higher than 80 W to survive in the copolymers.

3.3. Superficial Chemical Structure. To obtain the chemical composition of a solid surface, the electronic binding energy (BE) of each element on the surface was used. This is the electronic energy of the orbital in study before a perturbation, for example, the energy in 1s orbitals for C, N, and O elements.

BE can be calculated if the kinetic energy (KE) of some released electrons is known, as a consequence of an incident X-ray with carefully measured energy ($h\nu$). The relationship among these variables is an energy balance in the released electrons; see (1), where W is a work function that depends on the level of energy reached. XPS spectrometers calculate these variables in different ways giving whole distributions of BE of each element on the surface as the most valuable information. With these data, the chemical atomic environment on the surface can be studied [14]

$$BE = h\nu - KE - W. \quad (1)$$

Figures 4, 6, 8, and 10 show the energetic distribution of BE in the C1s, N1s, O1s, and I3d orbitals, respectively, to study the main superficial chemical states of PEG/PPy/I copolymers, where x -axis represents BE and y -axis represents its intensity. Each orbital curve was adjusted with several interior Gaussian curves that represent at least one atomic chemical state per curve. The maximum point of each curve is used to identify energetic state. Figures 5, 7, and 9 show the maximum position of each curve and the associated % area, which can be identified as the percentage of that state.

The curve fitting was done considering the full width at half maximum (FWHM) parameter based on the Crist work for advanced fitting of monochromatic XPS spectra [15]. The baseline of each BE distribution was set manually with the trend of data. Each energetic state was associated with a specific atomic chemical state involving all bonding orbitals shared in the atoms. For example, C shares 4 suborbitals, N shares 3, O shares 2, and I shares only 1 which can be associated with their respective valencies, but although the valence orbitals are in the exterior electronic shell and the orbitals analyzed in XPS are further inside the atomic structure (1s in C, N, and O and 3d in I), any modification in the valence orbitals modifies the energetic equilibrium of the entire atom, modifying the interior orbitals studied in the XPS analysis.

In many atoms, the energetic changes in the valence orbitals are less than 1 eV when the atom bonds with another one. However, this small modification is reflected in different magnitude in the interior orbitals which are hundreds of eV higher. Neighboring atoms also exert influence on the energetic distribution of the surrounding atoms, although they are not directly bonded. Thus, in analyzing the energetic distribution of orbitals, the whole chemical environment has to be considered and each case is different.

The atomic chemical states in this work were constructed including most of the possible bonding combinations in the copolymers. The notation indicates that the atom in bold face is bonded with all atoms in the formula. For example, the most common chemical state of C atoms in polyethylene is $C-CH_2-C$, in which the central C atom is bonded with two C and two H atoms in their specific spatial distribution. Thus, the previous configuration could also be expressed as C_2-C-H_2 with the same meaning.

3.4. Carbon Chemical States. Figure 4 shows a detailed analysis of the energetic distribution of C1s orbitals in PEG/PPy/I synthesized at 80 W. This copolymer was used as a case of study; however, the other copolymers synthesized at different

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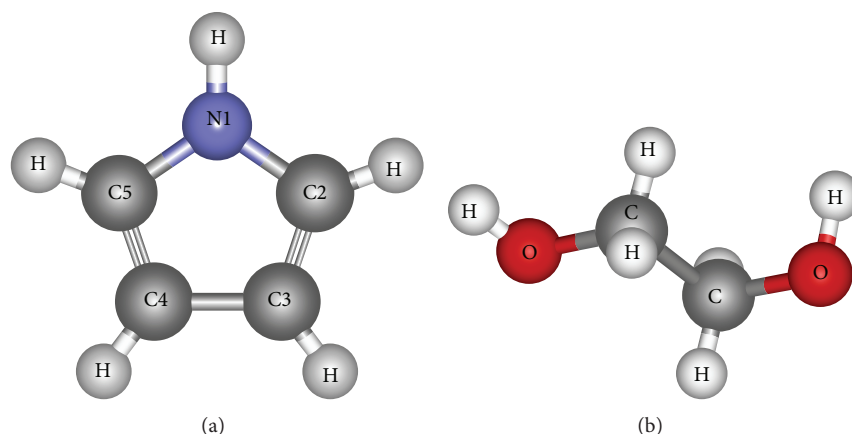


FIGURE 2: Atomic structure of pyrrole (a) with N/C = 0.25 and ethylene glycol (b) with O/C = 1. See the positions in the pyrrole ring and the respective chemical state: N1 (C-NH-C), C2 (C=CH-N), C3 (C=CH-C), C4 = C3, and C5 = C2. In ethylene glycol, C and O have only one chemical state, which are C-CH₂O and C-O-H, respectively.

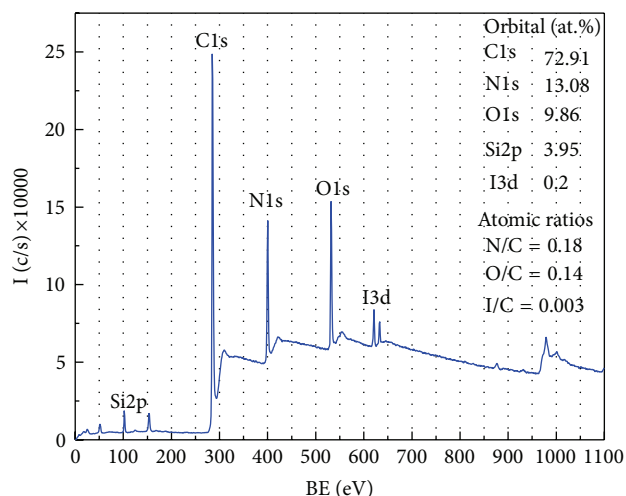


FIGURE 3: XPS survey scan of PEG/PPy/I synthesized in the 40–100 W interval with elemental content and atomic ratios.

power were analyzed in the same way, but as the data generated is huge, their most important condensed data is presented in a comparative way in Figure 5. The legends inside the curves indicate the probable chemical state with its respective approximated formation energy in eV. The area percentage of each curve and its maximum BE is also presented in the graph. The molecular formula in Figure 4 represents a possible union of three Py and three EG molecules in PEG/PPy/I and contains most of the chemical states associated with the curves.

C1s was fitted with 6 curves with FWHM = 1.0 ± 0.1 eV, where each curve is represented by its maximum BE in the discussion. The association between the energetic curves with the most probable chemical states was done considering the formation energy of each state calculated with the sum of all atomic bonding energies [16–18] which varies according to the oxidation level. The association started with the most hydrogenated, or least oxidized, state in the copolymers

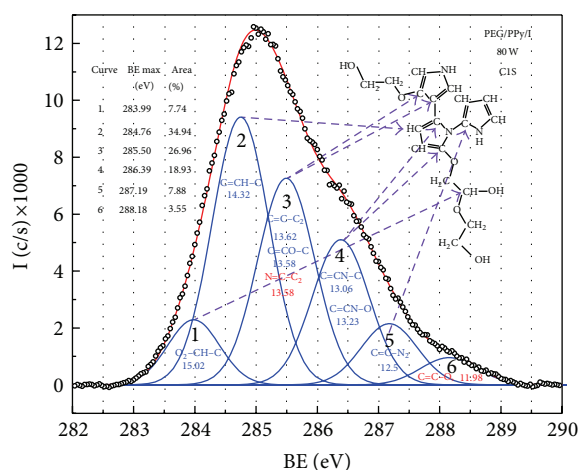


FIGURE 4: High-resolution C1s scan. The chemical formula represents the possible union of three pyrrole and three ethylene glycol molecules in PEG/PPy/I. The legends indicate the probable chemical states with their approximated formation energy in eV. The red legends indicate chemical states that do not belong to the monomers.

located in the lowest BE region, and as the hydrogen atoms are gradually substituted for other elements, more oxidized states appear towards higher BE zones reaching combinations of double and/or triple bonds.

The first fitted curve (7.74%) with the lowest BE and peak at 283.99 eV was identified with the main C state of PEG, O₂-CH-C, which is the union of two EG molecules; see Figure 4. The second curve has the maximum area of C1s (34.94%) with center at 284.76 eV and can be assigned to C=CH-C. This configuration is part of the Py structure in carbons in C3 and C4 positions; see Figure 3. In PPy, chains grow preferentially substituting hydrogen atoms in C2 and C5 leaving C3 and C4 almost untouched, which is the configuration associated with curve 2. Curve 3 with maximum BE at 285.5 (29.96%) can be assigned to C=C-C₂ and C=CO-C, both with approximately the same formation energy, 13.6 eV, originated from the union

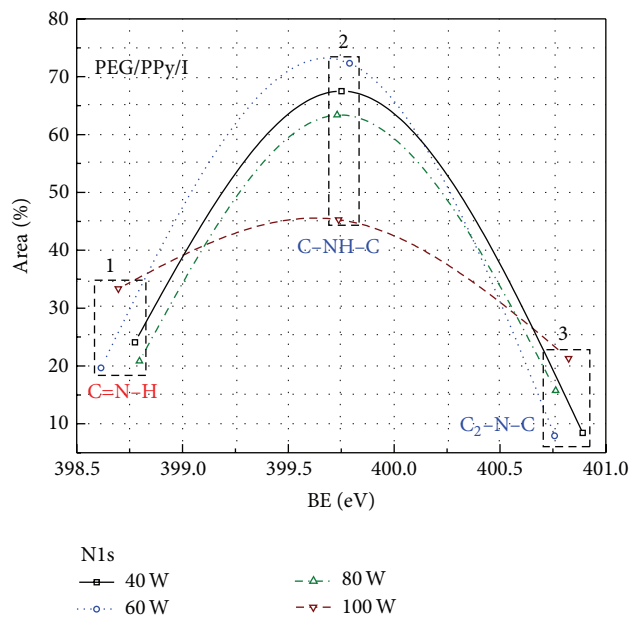
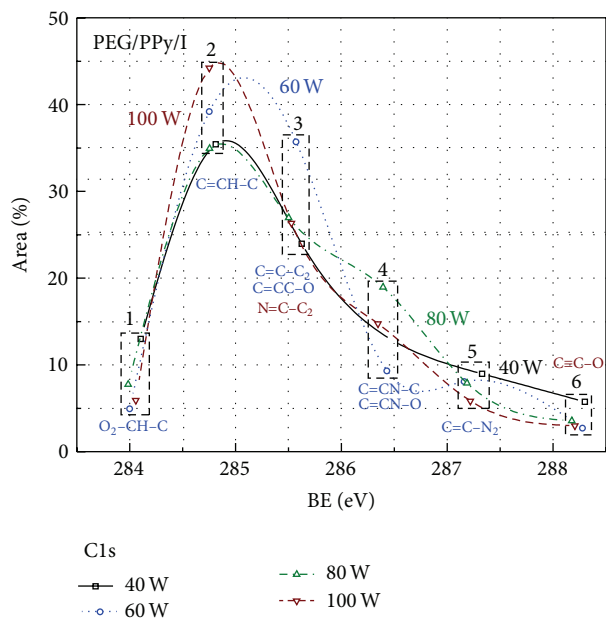


FIGURE 5: Cls orbital energy distribution comparison of copolymers synthesized at 40, 60, 80, and 100 W. The points enveloped in each box represent the same chemical state.

FIGURE 7: Comparison of nitrogen chemical states in copolymers synthesized at 40, 60, 80, and 100 W. The red legend shows a chemical state that does not belong to the monomers.

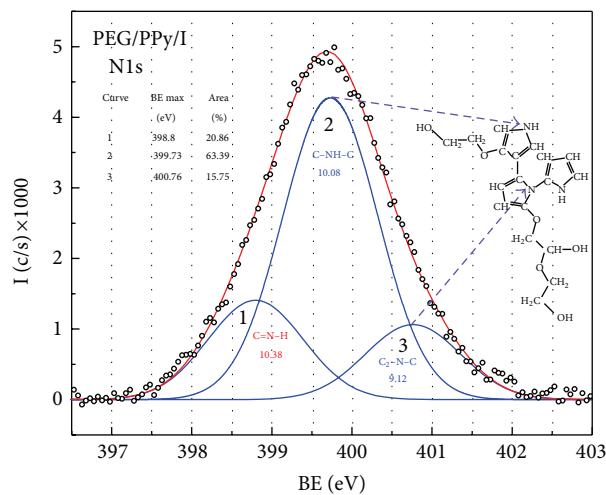


FIGURE 6: High-resolution N1s scan. The legends indicate the probable chemical state with its respective formation energy in eV. The red legend shows a chemical state that does not belong to the monomers.

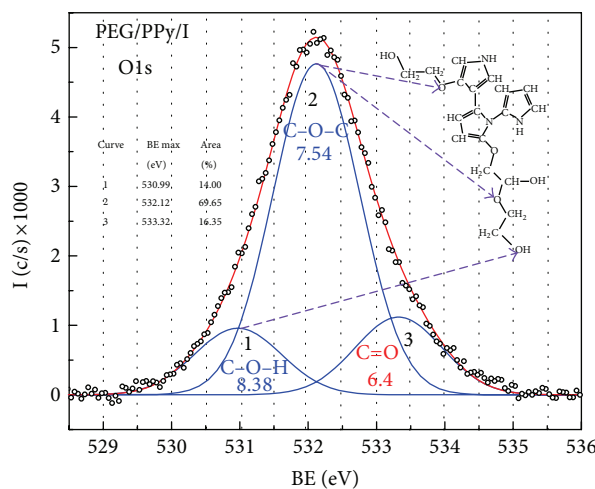


FIGURE 8: High-resolution O1s scan. The legends indicate the probable chemical states with their respective formation energy in eV. The red legend shows a chemical state that does not belong to the monomers.

between two pyrrole rings in C4 position, and with the union of Py and EG in the copolymers, respectively. There is another chemical state in red with approximately the same formation energy identified with the N=C-C2 configuration that may appear in oxidized fragments of Py. At 286.39 eV curve 4 (18.93%) has its maximum with the C=CN-C and C=CN-O possible states which are the bonds of Py-Py and Py-EG, respectively, both involving C2 position in Py. This is typical growing configuration of polypyrroles. The fifth curve with maximum at 287.19 eV (7.88%) was assigned to C=C-N₂ which is part of the Py-Py bond through the nitrogen atoms

and is another combination of a crosslinked polymerization of pyrrole. The last curve (3.55%) has its maximum at 288.18 eV and can be assigned to combinations of double and triple bonds with the possible chemical states: C≡C-O and N≡C-N. Triple bonds are undoubtedly expressions of maximum oxidation in PEG/PPy/I and can be created in complex structures or in molecular fragments of the polymers in progress. As these chemical states do not belong to the structure of the monomers, they are not included in the structure of the copolymers discussed in Figures 4, 6, and 8.

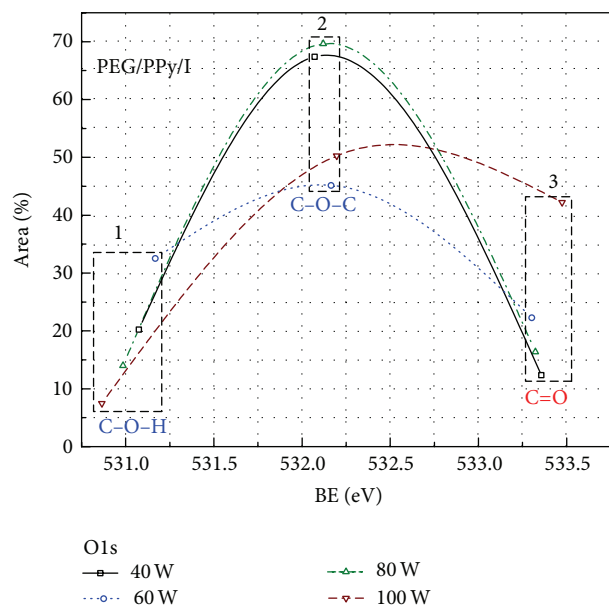


FIGURE 9: Comparison of oxygen chemical states in the copolymers synthesized at 40, 60, 80 and 100 W. The red legend shows a chemical state that does not belong to the monomers.

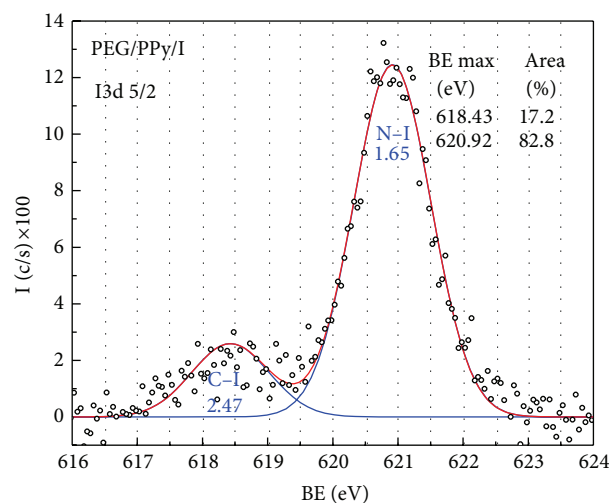


FIGURE 10: High-resolution I3d 5/2 scan. The legends indicate the probable chemical states with their respective formation energy in eV.

The sum of Py or EG percentages of their respective chemical states would give their participation in the copolymers. In the curves involving both monomers, the percentage can be divided equally between them. In this scheme, the percentages of Py and EG in the copolymers are 65.76% and 30.69%, respectively. This means that Py doubles the participation of EG. This is another indicative that Py has more participation in the copolymers than EG, as discussed in the superficial elemental analysis section. The molecular fragmentation belongs to the last curve and is 3.55% in the copolymers synthesized at 80 W.

Figure 5 condenses the C1s data in copolymers synthesized at different power to study the evolution of chemical

states. The graph shows the maximum BE of each chemical state in x -axis and the area percentage of that state in y -axis. There are 4 curves, one for each power of synthesis. The points in the same box indicate that they belong to the same chemical state. Note that the differences in BE of all chemical states in the same box are small indicating that the power does not change substantially the chemical states; it only modifies the participation of them in the copolymers without a specific pattern respect to the power.

3.5. Nitrogen Chemical States. The energetic distribution of N1s orbitals is studied in Figure 6, which was adjusted with 3 Gaussian curves using $\text{FWHM} = 1.3 \pm 0.1$ eV. The transformation of energetic states to chemical states in this orbital was done following similar dehydrogenation criteria to those in C1s. The first curve with peak at 398.8 eV (20.86%) with the lowest oxidation can be assigned to C=N-H (10.38 eV) originated in hydrogenated fragments of Py molecules formed during the collisions of particles during the synthesis.

The second curve, with maximum at 399.73 eV (63.39%) and the maximum area, represents the typical chemical state of nitrogen in Py, C-NH-C (10.08 eV). The third curve with maximum at 400.76 eV (15.75%) was assigned to C₂-N-C (9.12 eV) and probably with triple bonds C≡N (9.11 eV) of highly oxidized nitrogen in the copolymers; both have approximately the same formation energy and cannot be differentiated in this analysis. The first chemical state belongs to tertiary amines and it is a signal that the N1 positions of Py also participate in the chemical reactions to crosslink the copolymers, EG may also join Py through this position. The second state is a fragment of Py with maximum oxidation of N atoms; this kind of bonds was also found in the IR spectra. Near this curve another chemical state has been found in melamine (C₃N₆H₆), C=N-C (9.42 eV) [19], with energy that could be partially located between the second and third curves. According to these data, N states show that N bonds preferably with C in the copolymers, avoiding bonding with oxygen and that there are signals of fragmentation and crosslinking in the copolymers.

Figure 7 shows a comparison between N1s chemical states in copolymers obtained at different power. As in C1s, the power of synthesis does not change the chemical states, only the percentage of their participation. From 40 to 80 W the percentages of chemical states are similar, but at 100 W the percentage of C-NH-C state is much lower than in the other syntheses suggesting that C-NH-C dehydrogenates in a greater extent as the power of synthesis increases. This effect is reflected in the participation of tertiary amines, C₂-N-C and/or triple bonds C≡N, which also increase with the power.

3.6. Oxygenated Chemical States. Figure 8 shows the high resolution scan for O1s orbitals of PEG/PPy/I. The first peak is located at 530.99 eV (14%) and was assigned to the C-O-H (8.38 eV) state which is part of EG structure. The greatest curve (69.65%) with peak located at 532.12 eV was assigned to C-O-C (7.12 eV) groups. This state may appear from at least two sources, the union of two EG molecules and from the union of EG with Py. Both are part of the copolymerization

[20]. The third curve, located at 533.32 eV (16.34%), can be assigned to C=O (6.4 eV) with possible origin in the dehydrogenation of C–O–H groups discussed in the first curve.

Figure 9 presents a comparison among the adjusted O1s orbitals for each copolymer synthesized at different power. There are 3 chemical states in each curve, although with different percentage showing that oxygenated states are more sensitive to the power of synthesis than to N and C groups. However, the lack of a specific tendency suggests that the superficial interaction influences the participation of O and N chemical states in the study due to the additional oxidation and nitridation of the copolymers. This is usually observed in the chemical states with the highest oxidation.

3.7. Iodine Chemical States. Figure 10 shows a high-resolution BE scanning of I3d 5/2 orbitals in the 616–624 eV interval. As iodine was used as a dopant, its content was very small, 0.02% in the copolymer synthesized at 80 W, and the data was collected with noise, but 2 Gaussian curves can be clearly adjusted to the data with FWHM in the 1.35–1.4 eV interval. The first curve has a maximum at 618.43 eV (17.2%) and was assigned to C–I (2.47 eV). The second curve has a maximum at 620.92 eV (82.8%) and was assigned to N–I (1.65 eV), which indicates some affinity to form N–I bonds under the energetic conditions in plasmas. This effect can be seen at 80 W or higher power of synthesis. No signals of iodine could be measured in the copolymers at lower power.

4. Conclusions

The structure of plasma random bio-copolymers of ethylene glycol and pyrrole doped with iodine is studied in this work; the aim is to reduce possible side effects in the spinal cord after a severe injury. The structure of such copolymers has not been studied at the light of the XPS energetic orbitals to identify and quantify the main chemical states. The N/C and O/C atomic ratios indicate that pyrrole has more participation than ethylene glycol in the copolymers. On its part, the content of iodine indicates that the dopant appears in the copolymers at 80 W or higher power of synthesis, mainly as N–I chemical bonds.

The chemical states of PEG/PPy/I copolymers can be associated with the structure of the traditional homopolymers of polypyrrole and polyethylene glycol, with the combination of pyrrole and ethylene glycol, and with a big variety of other additional states due to crosslinking, doping, fragmentation, and oxidation at different levels. Multiple bonds not present in the typical homopolymers of pyrrole and ethylene glycol were formed by dehydrogenation and oxidation caused by the constant collisions of accelerated particles in plasmas where the syntheses occurred. With this information, the synthesis of PEG/PPy/I copolymers can be modified to increase the participation of the most important chemical states in their biofunctions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

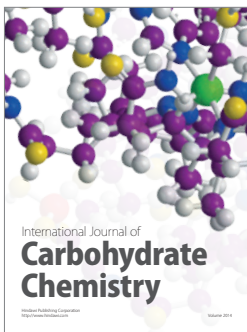
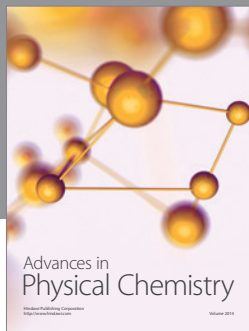
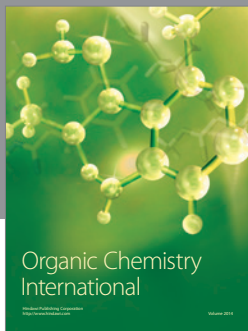
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