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Molecular simulation of plasma polymerized polyaniline–iodine compounds

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Abstract

This work presents a molecular simulation study of plasma-polymerized polyaniline–iodine compounds. The simulation is focused on the *ortho*, *meta* and *para* substitutions of aniline benzene rings where the polymers can grow into the maximum and partially reduced and oxidized states of polyanilines. This simulation offers the possibility of visualizing the spatial conformation of polyanilines while interacting with iodine atoms with and without chemical bonds between them. Such cases are often found in plasma polymerization and doping processes.

Keywords: Molecular simulation; Plasma polymerization; Polyaniline

1. Introduction

The study of conducting polymers deserves a great interest in the research of polymers obtained by plasma due to their considerable potential applications in the electronic industry. The most common types of plasma semiconducting polymers are, among others, polypyrrole (PPy) and polyaniline (PAn). The PAn synthesis has been studied under varying dopants, reaction time and plasma conditions leading to improved electrical conductivity in the materials [1–6]. The importance of the dopant depends on the influence that its atoms exert to modify the arrangement of the entire structure, lengths and rotation of the segments in the polymers, which in turn modifies the final properties of the material. One of the dopants that has produced outstanding results in increasing the electric conductivity of PAn is iodine. The PAn doped with iodine (PAn/I) has reached conductivity values up to six orders of magnitude higher than that of not doped PAn, depending on the interaction with the environment [7].

Although the synthesis of PAn by radio frequency (RF) plasmas has been studied before, and the main macroscopic semiconducting properties of its products have been analysed, very little is known about the molecular structures formed in plasmas. In a plasma, a great number of reactive species can be formed due to the collisions among particles, molecules, atoms, electrons and radicals, which produce complex structures given the high energy involved in the collisions, usually exceeding the atomic bond energy levels in most organic compounds, 3–10 eV [8]. This energy can be higher than the one involved in other syntheses.

The molecular simulation of PAn under this kind of synthesis has not been previously studied, mainly because of the complicated structures found, since the polymers can grow in each propagation step for three different ways that are the possible substitutions in the aniline rings. Additionally, depending on the oxidation state, the benzene rings of PAn can change the electronic distribution from benzoidal to quinoidal forms, and this modification has a great impact on the electric properties of the polymer.

The present molecular simulation study of polyaniline interacting with iodine atoms (PAn/I) considers the three substitutions (*ortho*, *meta* and *para*) of the benzene rings found in previous works on plasma PAn/I [7,8]. Our study was made by means of the molecular mechanics module of the Cerius 2 program [9]. In it, the molecules can be

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recreated on the basis of the atomic geometry. Once the molecules are constructed, extreme conditions are applied in order to obtain one of the minimum energy states associated to the geometric configuration. This task was carried out through the UNIVERSAL module [10–13] that also belongs to the Cerius database.

2. Molecular simulation

Our fundamental assumption about the molecular mechanics is that the experimental and calculated data for small molecules, such as bond lengths and angles, can be extrapolated to bigger molecules. Thus, molecules are considered as collections of atoms joined by springs or by the typical harmonic forces of classical mechanics. The forces are defined as functions of the potential energy expressed in terms of the internal molecule coordinates. Electrons in the molecule are not explicitly treated, but they are considered as contributors to the total potential of that molecule.

Usually, the collective forces in the molecules are called potential forces (force field, FF). The force field method has been developed to reproduce the structural geometry with relation to the involved energies, formation heats, crystalline arrangements and other properties. The total energy of the molecule is numerically minimized by altering the atomic coordinates and then the energy is once more calculated. Each energy is updated and summed to all the interactions in the molecule. The objective is to obtain a stable structural conformation. Therefore, the force field method generates structures with minimal energy.

2.1. Aniline

The aniline molecule is formed by a benzene ring bonded to an amine group. When aniline is polymerized, the electronic cloud of the polymer can be a continuous surface where the electrons move in response to an external electric field. Consequently, some oxidation states of the polymer are more accessible than others as to transporting electric charges [14–20].

In Fig. 1, a simulation of aniline recreates the molecular volumetric conformation along with its calculated bond lengths and angles. Six carbon atoms (in grey) form a ring which one nitrogen atom is linked to. The whole structure forms a plane. The white semicircles surrounding the structure represent the hydrogen atoms. The equivalent angles and lengths have small differences among them due to the convergence in the calculation. The C–C and C=C distances are approximately 1.4 Å. These distances are approximately the same due to the conjugation of the benzene ring. The C–N bonds are 1.34 Å, N–H is 0.99 Å and C–H is 0.95 Å.

2.2. Polyaniline

Polyaniline chains can grow from three different points apart from the nitrogen position in the monomer. These are the *ortho*, *meta*, and *para* substitutions shown in Fig. 2. The nitrogen atom is another point where the polymer grows. Combinations of such substitutions in polyaniline ordinarily appear when the polymer is synthesized by plasmas. However, when the monomer is oxidized, the hydrogen atoms bonded with the nitrogen atoms are removed and double bonds C=N can appear. This effect may change the electronic distribution in the monomers producing quinoidal rings along the polymers.

The maximum content of quinoidal rings in polyanilines is one quinoidal (Q) per each benzoidal (B) ring. In this way, the Q/B ratio varies from 0 to 1, 0 at the maximum reduced state and 1 at the maximum oxidation state. In this study, both cases are considered: the maximum reduced (benzoidal) and oxidized (quinoidal) states. The molecules in the benzoidal cases were constructed with benzoidal rings only. However, in order to compare the three structures in the same conditions, the molecules in the quinoidal cases were constructed with alternated benzoidal and quinoidal rings.

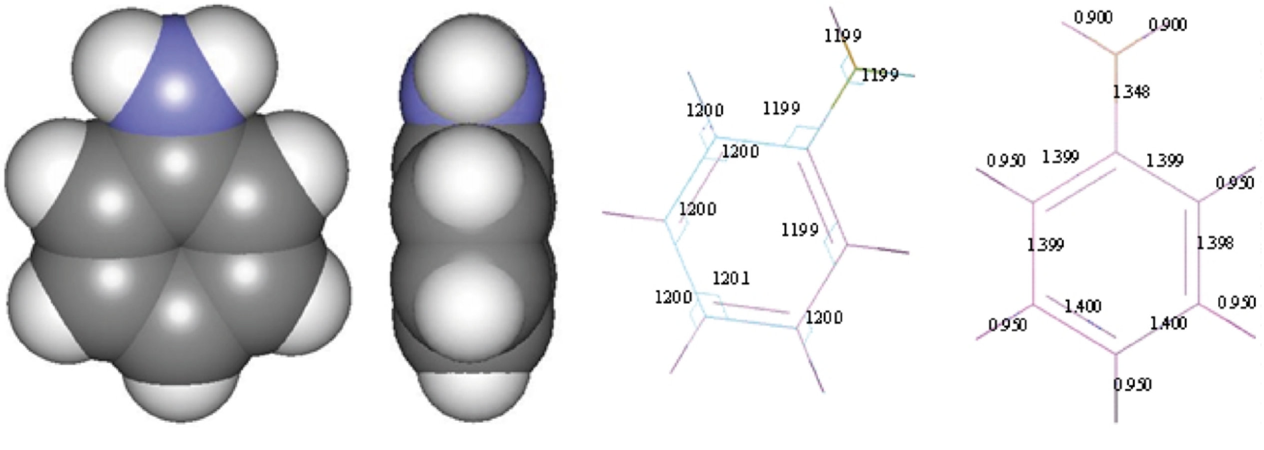

Fig. 1. Molecular simulation of the aniline molecule.

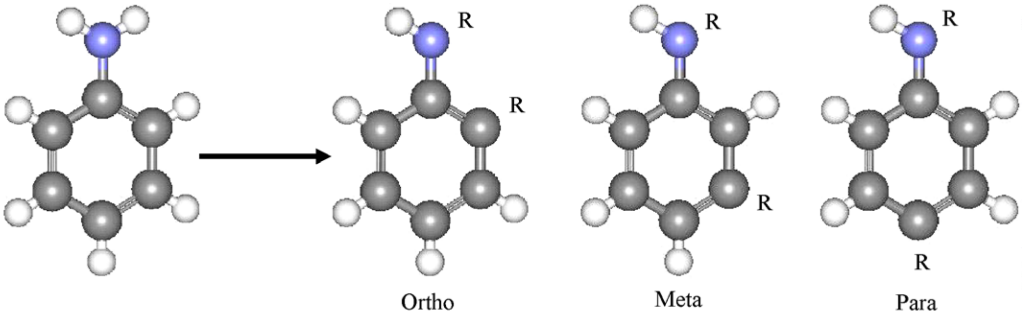

Fig. 2. Substitutions in aniline where the polymer can grow.

The quinoidal rings were given a *para* configuration and the benzoidal rings were assumed to be in the three substitutions.

In the next sections, polymers with the three growing patterns are simulated in order to observe the conformation of the polymer in each case. The polymers were represented with segments of 20 monomers. It is important to note that the aniline rings maintain their planar formation in all the structures. However, in contrast to the aniline molecule without interactions, the rings in the polymer rotate keeping the nitrogen atoms as points of rotation.

The big dark atoms in the next figures correspond to the iodine atoms. The molecules have been calculated with different angles between planes until they reached a minimum energy state for that configuration. The numbers obtained in the extremes of the molecules were not considered in the averages, since the border effects in the molecules modify the values respect to the central rings.

When the polymers are synthesized and doped simultaneously in plasma, the position of the dopant in the polyaniline chains is not easy to define as the very energetic conditions developed in the reactor can lead to a great variety of possibilities. When the polymer is synthesized and doped using the traditional methods, hydrogen interaction with the iodine atoms can appear in the chains. This behavior is also a possibility in the polymers synthesized by plasma. Another possibility is that the iodine atoms replace some hydrogen atoms from the monomers appearing C–I bonds in the polymers. One last possibility is that the iodine atoms remain trapped among the polymer chains, without chemical bonds, in the layer by layer deposition found in many plasma syntheses. This case is called ‘free iodine’ in the next sections.

The simulation presented here considers the two last alternatives with the three substitutions in the benzene rings found in plasma polyanilines: free iodine as dopant in the polymer and C–I bonds in the benzene rings. To simulate the free iodine interaction, the polymer is constructed first and later, the interaction of the iodine atoms and the polymers are calculated.

Each of the next figures contains three images of the computer conformations of polyanilines: a space-filling representation, another image with the angles between the benzenic planes, and a scheme with the interatomic distances and bond angles in the central monomers.

3. Results and discussion

3.1. para-Benzoid PAn with free iodine atoms

Fig. 3 shows a simulation of the *para*-benzoid PAn (*p*-BPAn) interacting with free iodine. The volumetric image shows pronounced rotations in the benzene rings caused by the short interatomic distances compared with the large volume occupied by the atoms. These distances in the polymer have small variations with respect to the calculated distances of the aniline molecules. In the polymer, the C–C bond is 1.404 Å, the C=C is 1.400 Å, the C–N is 1.436 Å, the C–H is 1.082 Å and the N–H is calculated as 1.044 Å.

In spite of the fact that PAn and iodine are not bonded, when the molecule relaxes, the iodine interaction modifies the conformation of the nearest monomer. The smallest angle is 55.1° and the largest one is 59.8° namely, difference of 4.9° between these two values. The differences between the angles can be seen as an approximation to a state of free rotation between consecutive benzene planes. Therefore, when a monomer is added to the chain, the freedom of rotation of that segment is approximately 4.9°. Thus, the next benzene planes are added in angles of approximately 57.3°, which is the average angle in the molecule respect to the previous plane.

The space-filling model shows the iodine atoms very near to the polymer, as if they were chemically bonded with it. In the left section of the image, the distance between carbon and iodine atoms is 4.169 Å and the nitrogen to the same iodine atoms is 3.903 Å. In the right section, the distance between the other iodine and the nearest carbon atoms is 4.105 Å, the distance from the nitrogen to iodine is 4.773 Å, and the largest carbon–iodine distance is 6.662 Å.

According to this calculation, the iodine atoms can approach very near to the polyaniline chains. The shortest distance between iodine and carbon without a chemical bond is approximately twice that obtained in the true C–I bonds. This approximation of iodine atoms and PAn chains can be found in doping processes.

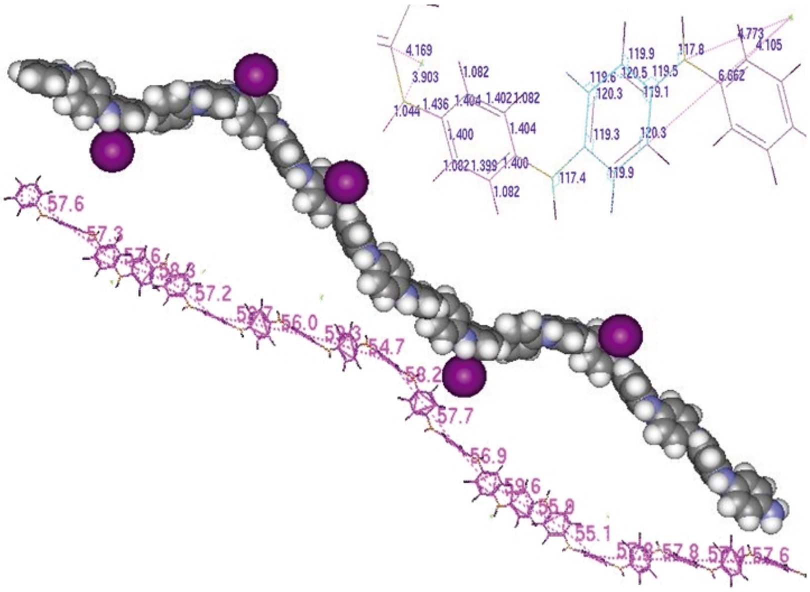

Fig. 3. Simulation of *para*-benzoid PAn with free iodine atoms.

3.2. meta-Benzoid PAn with free iodine atoms

The *meta*-benzoid PAn (*m*-BPAn) with free iodine simulation is shown in Fig. 4. This image presents the same rotation tendency in the rings, as the *p*-BPAn. There is not sufficient space for the hydrogen atoms around the rings. Therefore, in order to keep the integrity of the benzene planes, the aniline segments have to rotate, using the nitrogen atoms as points of rotation. The iodine atoms are also very near to the molecule giving the appearance of a true chemical bond.

The average angle between planes is 56.09°. This indicates that the *m*-BPAn could be flatter than the similar *p*-BPAn. The rotation freedom in this arrangement is 11.6°, higher than the *p*-BPAn. The bond that presents the highest difference is C–N with 0.09 Å. An angle of 118.1° is formed between the C–N and the N–H bonds, over which the benzene rings rotate. The most interesting distance is that of iodine and carbon atoms, which can be as short as 4 Å. This value indicates that the iodine atoms are not far to the polymer.

3.3. ortho-Benzoid PAn with free iodine atoms

In the same scheme, Fig. 5 shows the *ortho*-benzoid PAn

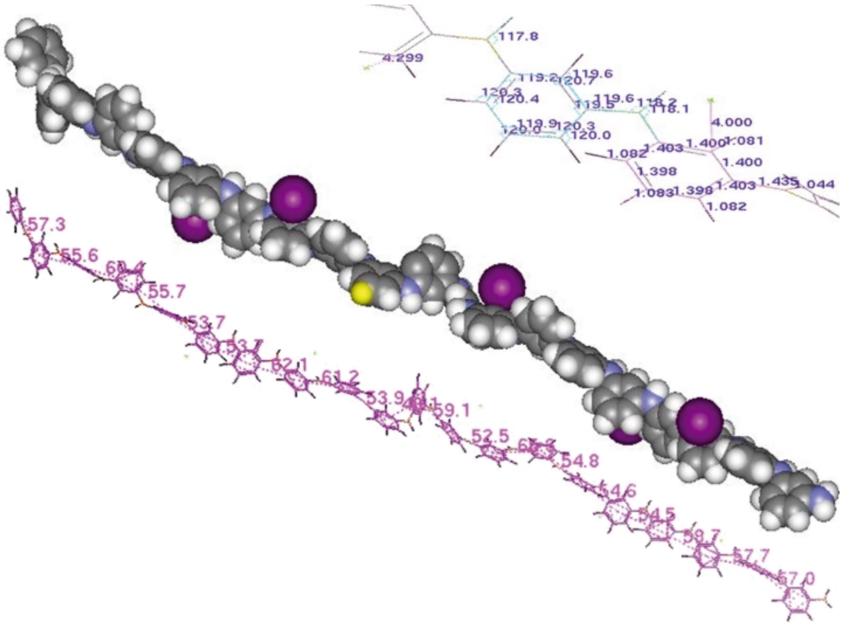

Fig. 4. Simulation of *meta*-benzoid PAn with free iodine atoms.

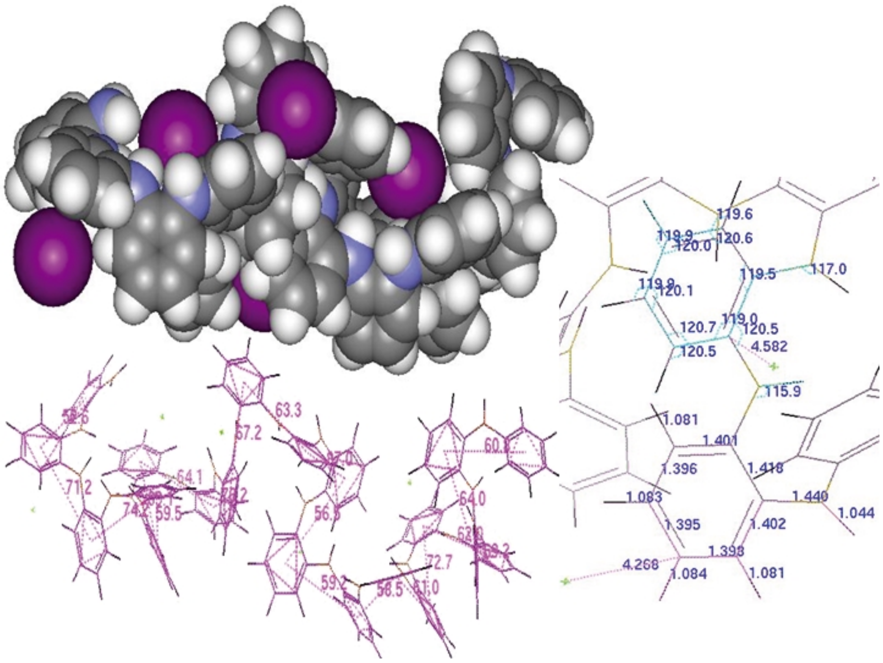

Fig. 5. Simulation of *ortho*-benzoid PAn with free iodine atoms.

(*o*-BPAn) with free iodine simulation. In this arrangement, the molecule has a tendency to grow in different directions simultaneously because the benzene rings have to rotate in more than one axis to accommodate due to the proximity of the positions in the benzene rings. This configuration displays important variations among all monomer angles. The smallest angle in the chain is 56.5° and the greatest angle is 74.2°, the freedom of rotation in this arrangement is 17.7° and the average angle is 64.6°.

Something important to note in this arrangement is that the iodine atoms remain outside the folded molecule.

The molecules were simulated also without the iodine interaction and the numbers in this case were approximately the same, indicating that even interacting with iodine, the molecule behaves as PAn and the iodine atoms do not affect significantly the molecular structure in this conformation.

The numbers have small variations compared with those of the monomers alone. The distance between the carbon

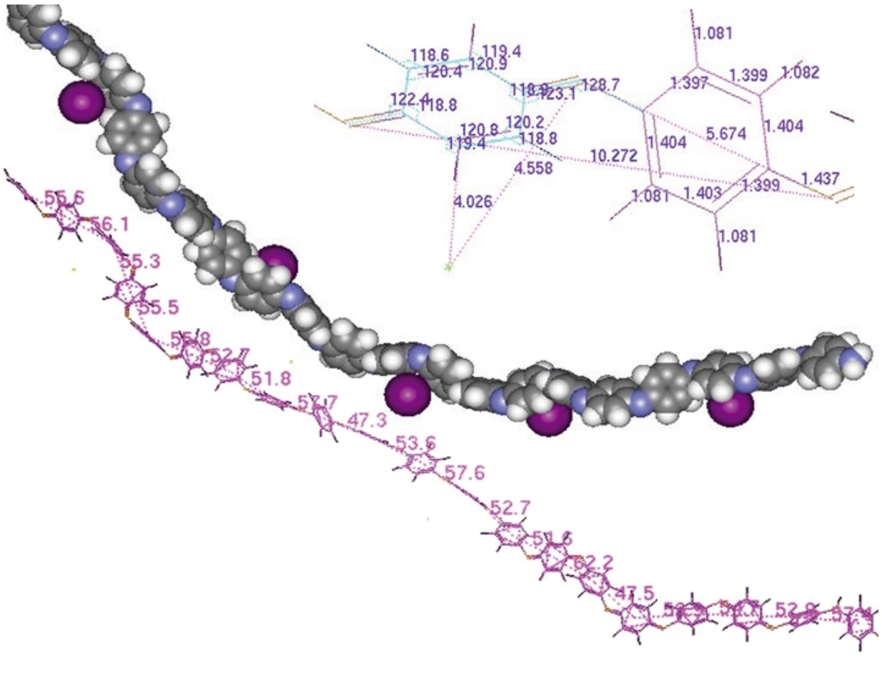

Fig. 6. Simulation of *para*-PAn in quinoidal structure with free iodine atoms.

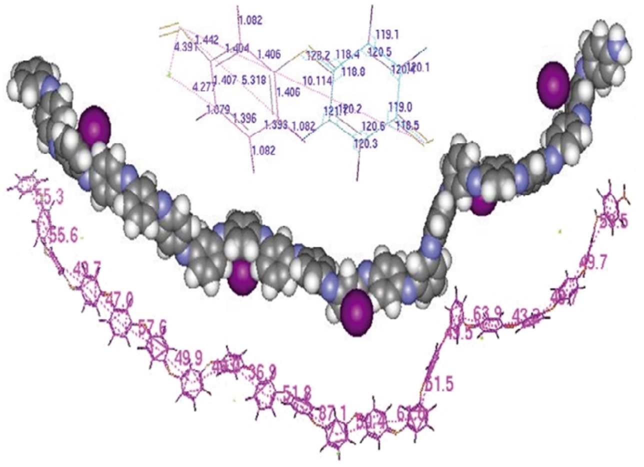

Fig. 7. Simulation of *meta*-PAn with quinoidal structure with free iodine atoms.

and iodine atoms varies from 4.26 to 4.58 Å. Although the molecule is very twisted and the iodine atoms cannot access the inner rings, the iodine atoms remain in a similar distance to the molecules as in the other polyanilines studied here.

3.4. para-Quinoid PAn with free iodine atoms

Fig. 6 shows a simulation of *para*-PAn with quinoidal structure (*p*-QPAn). The structure has alternated quinoid and benzoid monomers with C=N– bonds. This is the highest oxidation state and one of the most electrically conductive structures of polyanilines. This arrangement is simulated to interact with free iodine. The structure has a similar behavior as the previous arrangement set. The nitrogen atoms are used as rotation points to accommodate consecutive monomers searching one of the minimum energy states. In this configuration the iodine atoms are also located very near to the molecule.

The average angle between planes is 54.2°. The greatest angle in this arrangement is 62.2° and the smallest one is 14.9°. The C–N=C angle is 128.7°. The N–I and C–I distances are 4.55 and 4 Å, respectively.

3.5. meta-Quinoid PAn with free iodine atoms

Fig. 7 shows a simulation of *meta*-PAn with quinoidal structure (*m*-QPAn) interacting with free iodine. This arrangement shows rotations of the nearest rings to the iodine atoms. The average angle is 52.6° and the rotation freedom is 40.9°, 63% greater than in the previous polyaniline. The C–N=C angle is 128.2°. The C–C bond is 1.81 Å and C=C is 1.397 Å. The N–I distance is 4.3 Å and the C–I is 4.2 Å.

3.6. ortho-Quinoid PAn with free iodine atoms

Fig. 8 contains a simulation of *ortho*-PAn in quinoidal structure (*o*-QPAn) with free iodine. The molecule does not present a lineal arrangement due to the small space for the rings to accommodate. The iodine atoms approximate to the chains as if it would be linked with the benzene rings.

The average angle is 50.7°, approximately 2° smaller than the previous *m*-QPAn. The rotation freedom is 23.3°, 24% greater than the arrangement without double bonds at nitrogen atoms. There are not big changes in the calculated bonds or angles in the polymer rings. The C–N=C angle is 128°. The N–I and C–I distances are 4.374 and 4.419 Å, respectively.

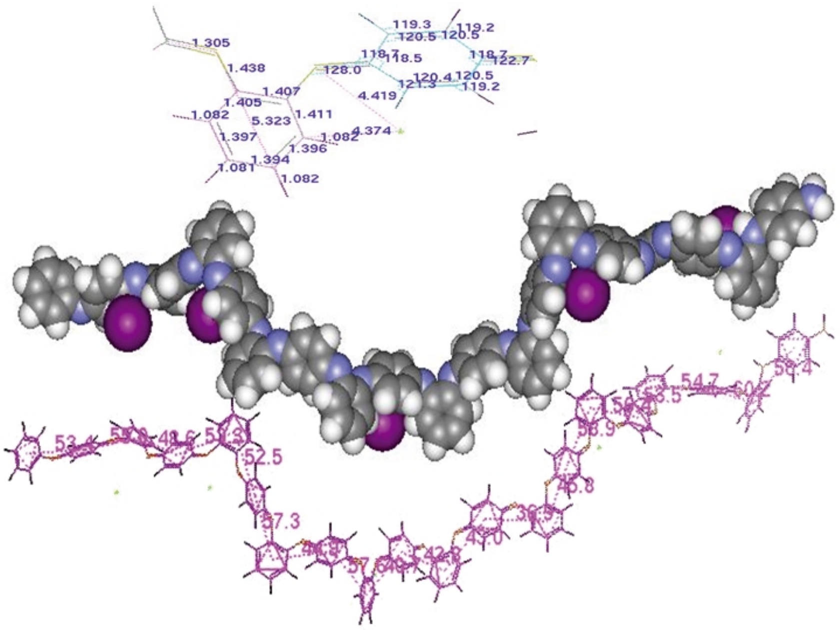

Fig. 8. Simulation of *ortho*-PAn with quinoidal structure with free iodine atoms.

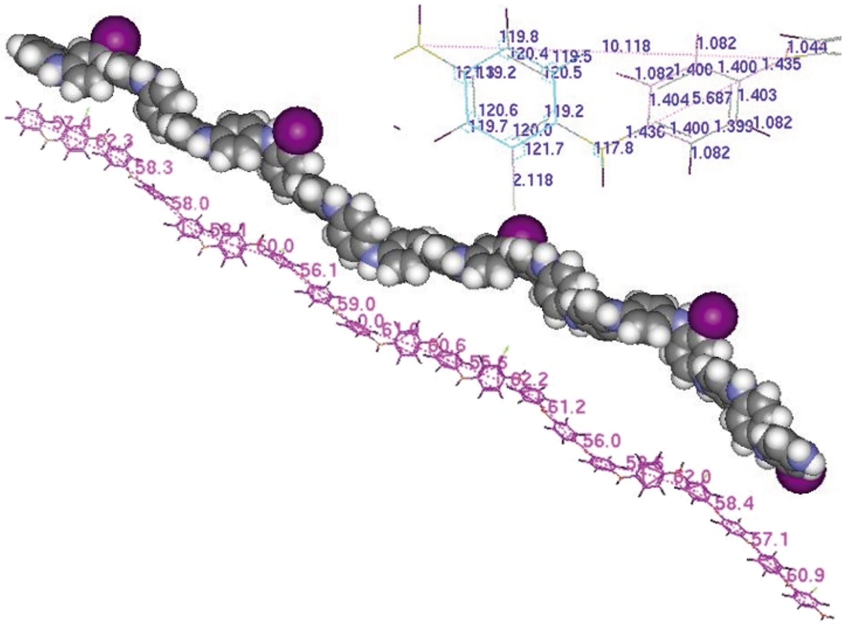

Fig. 9. Simulation of *para*-benzoid PAn/I with C–I bonds.

3.7. para-Benzoid PAn/I with C–I bonds

PAn/I with C–I bonds in *para* position in the benzene rings (*p*-BPAn/I) is simulated in Fig. 9. The molecule presents a linear tendency with small variations in the rings bonded with iodine. In this arrangement, the average angle between planes with iodine is 61.4° and the angle of the planes without it is 58.3°. The freedom rotation in the rings with iodine is 2.2° and without it is 4.9°. The C–I bond is 2.118 Å and the I–C–C angle is 121.7°. The H–C–N angle is 117.9°. The average angle in the chain is 59.08°, that is 1.7° greater than in the *p*-BPAn chain with free iodine. The rotation freedom is 6.8°, also greater than that in the arrangement in Fig. 3.

3.8. meta-Benzoid PAn/I with C–I bonds

Fig. 10 shows the simulation of *meta*-benzoid PAn/I (*m*-BPAn/I) with C–I bonds in *ortho* and *para* positions of the benzene rings. In this arrangement, the benzene rings adopt different angles as a result of the iodine interaction, which produces an almost helicoidal structure.

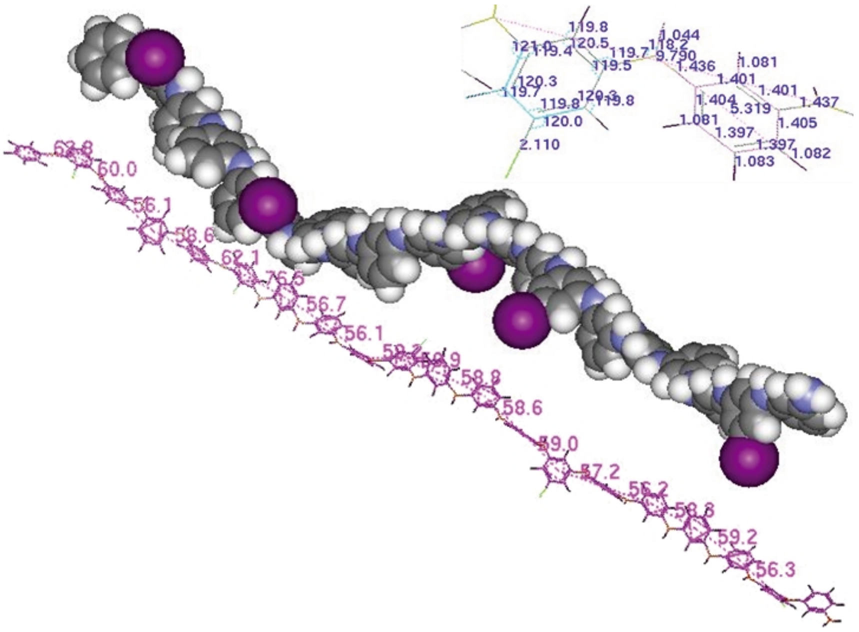

Fig. 10. Simulation of *meta*-benzoid PAn/I with C–I bonds.

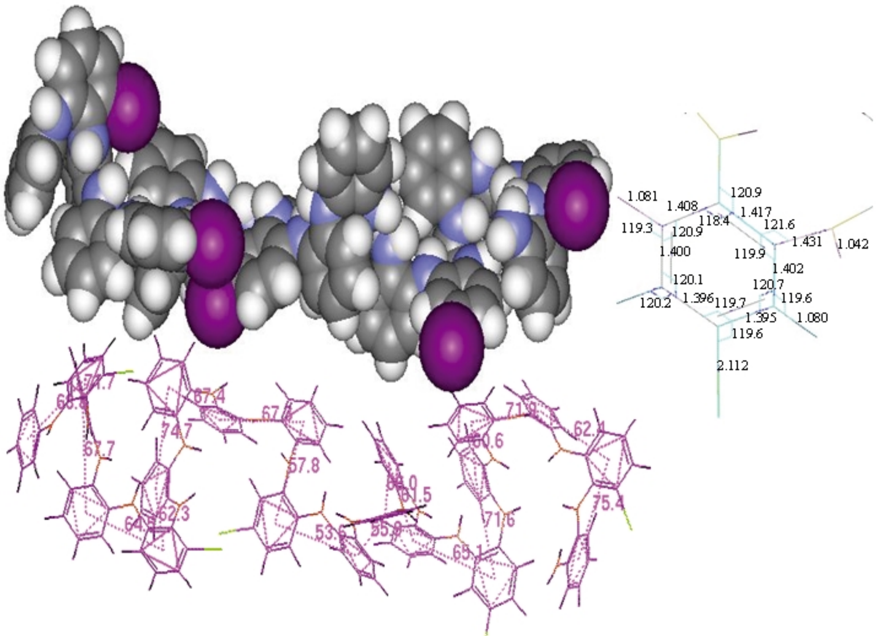

Fig. 11. Simulation of *ortho*-benzoid PAn/I with C–I bonds.

The average angle between the rings with iodine is 62.9°, slightly greater than that of *p*-BPAn/I. In the case of the rings without iodine, the average angle between planes is 57.8°. The freedom of rotation in the rings with iodine is 17.5° and without it is 3.9°. The C–I bonds are 2.1 Å long.

The average angle in the chain is 56.05° and the rotation freedom in the rings is 20.4° which is 56% greater than the equivalent *m*-BPAn case presented before. This can be due to the different equilibrium position of the C–I bond. Such arrangement can originate not very compact films given the relatively high volume occupied by the twisted chains.

3.9. ortho-Benzoid PAn/I with C–I bonds

ortho-BPAn/I with C–I bonds is simulated in Fig. 11. The molecule shows a very disordered arrangement without important differences compared with the BPAn structure interacting with free iodine atoms. The average angle between planes with iodine is 68.2° and, without it is 63.7°.

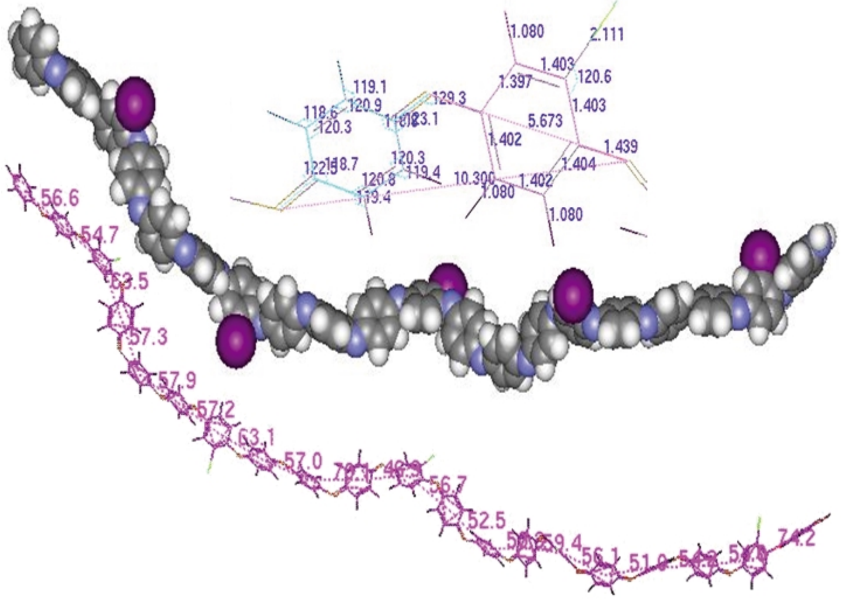

Fig. 12. Simulation of *para*-PAn/I with quinoidal structure.

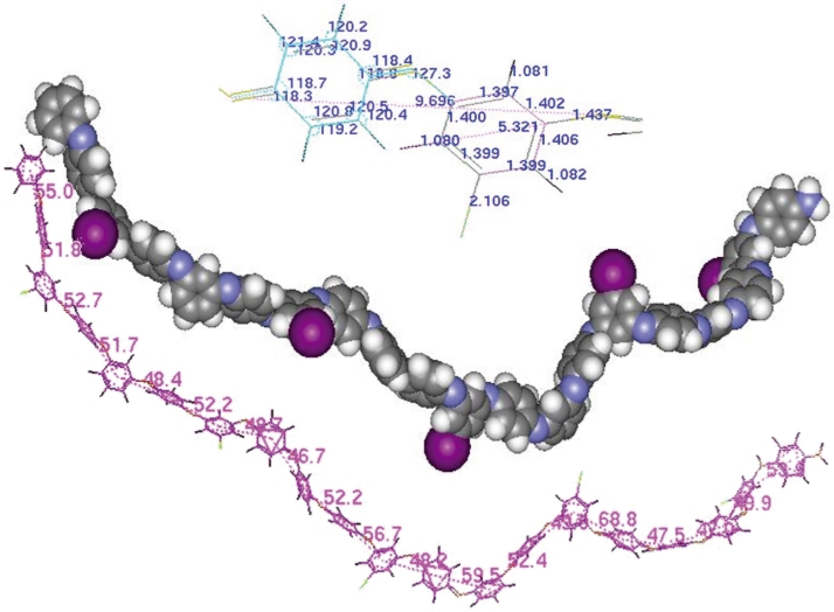

Fig. 13. Simulation of *m*-PAn/I with quinoidal structure.

The rotation freedom in the rings with iodine is 8.1° and without it is 18°, that is 55% greater than the rings with iodine. If the entire molecule is considered, the rotation freedom is 20.8°, i.e. 3.1° greater than in the *o*-BPAn molecule with free iodine arrangement. The C–I bond length is 2.11 Å, which is not very different from the length of this bond in the preceding structures.

3.10. para-Quinoid PAn/I with C–I bonds

Fig. 12 shows the simulation of *para*-quinoid PAn/I (*p*-QPAn/I) with C–I bonds. In this structure, iodine promotes the tilt of the rings, since the angles between the planes with iodine are greater than the angles between the rings without it. As iodine atoms are bigger than hydrogen ones, the molecule results in a wider opening between rings in the zone where iodine is bonded.

The average angle between planes with iodine is 60.6° and without it is 55.4°. The difference is approximately 5.2°. The freedom of rotation in the rings with iodine is 7.4° and without it is 23.2°. The iodine atoms limit the freedom of movement in the monomers in approximately 68%. The larger volume of the iodine atoms also limits the rotation angle in the rings where it bonds. Nevertheless, the interesting point in this chain lies in the C–I bond that measures 2.1 Å. The angle between rings is 129.3°.

3.11. meta-Quinoid PAn/I with C–I bonds

A simulation of *meta*-PAn/I with quinoidal structure (*m*-QPAn/I) is shown in Fig. 13. The molecule has the tendency to grow more disorderly than the *p*-QPAn/I molecules. In this case, iodine atoms do not present a strong influence on the molecule conformation.

In this arrangement, great angles between the rings with iodine are observed. The average angle between rings with iodine is 58.3° and, without it is 50°. This is 14% smaller than the angles with iodine. The rotation freedom of the rings with iodine is 16.1° and without it is 5.7°.

The C–I bond is 2.1 Å long, the same as in the previous simulation. The angle between rings is 127.3°: 2° smaller than in the *para* arrangement. The distance between rings is 9.7 Å and the transversal longitude of the ring is 5.3 Å. These distances present differences of ± 0.06 Å with respect to the *p*-QPAn/I structure showed in Fig. 12.

All in all, the difference in the angles between planes with and without iodine in this and the previous simulation is 3.1° where the average angle among planes in all the structure is

Table 1
Average angles and freedom of rotation of benzene rings for the different substitutions

Polymer	Substitution	Freedom of rotation	Average angle (°)
BPAn with free I	*para*	4.9	57.38
BPAn with free I	*meta*	11.6	56.09
BPAn with free I	*ortho*	17.7	64.6
QPAn with free I	*para*	14.9	54.2
QPAn with free I	*meta*	40.9	52.6
QPAn with free I	*ortho*	23.3	50.7
BPAn/I with C–I	*para*	6.8	59.08
BPAn/I with C–I	*meta*	20.4	56.05
BPAn/I with C–I	*ortho*	20.8	64.8
QPAn/I with C–I	*para*	23.2	56.5
QPAn/I with C–I	*meta*	22.1	51.9
QPAn/I with C–I	*ortho*	36.1	52.4

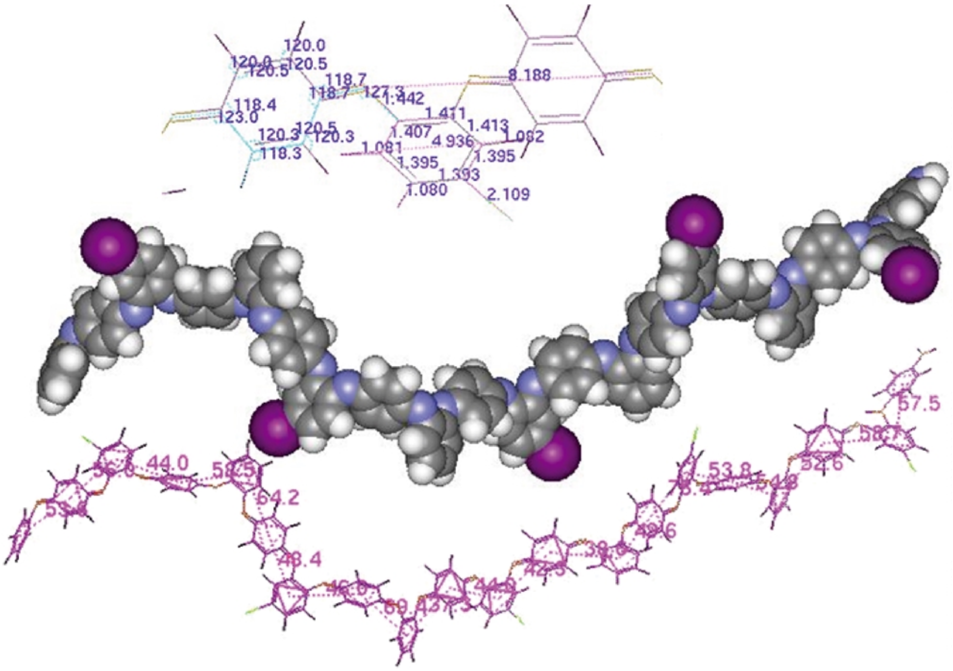

Fig. 14. Simulation of *ortho*-PAn/I with quinoidal structure.

51.9° with a freedom rotation of 22.1°. This difference can generate more compact polymer films in the *m*-QPAn/I.

3.12. ortho-Quinoid PAn/I with C–I bonds

ortho-PAn/I with quinoidal structure (*o*-QPAn/I) is simulated in Fig. 14. The molecule is non-linear as a result of the proximity between the benzoid rings and iodine, which results in very different angles between planes. The molecule grows with a tendency to follow a different direction in each segment. It is probable that the polymers formed in this way have spongy appearance. This conformation is similar to that of *o*-PAn with free iodine.

The angles between planes with iodine in this arrangement are 56.1° in average and are approximately 9% greater than the angles without iodine. The average angle between planes in the whole chain is 52.4° and the average rotation freedom is 36.1°. The C–I bonds are 2.1 Å, that is approximately the same than in the other polyanilines and the angle between the rings is 127.3°, approximately the same as in the *m*-QPAn/I. The distance between two consecutive rings is 8.1 Å and the width of the rings is around 4.9 Å. These distances are smaller than those in the preceding polyanilines with the same arrangement.

The average angles and the freedom of rotation are concentrated in Table 1 for all cases. In PAn with free iodine and PAn/I with C–I bonds, the average angles and the freedom of rotation are greater in the *ortho* substitution. In PAn quinoidal with free iodine, the greatest freedom of rotation belongs to the *meta* substitution and the largest average angle is found in the *para* substitution. PAn/I quinoidal with C–I bonds displays the greatest freedom of rotation and the average angle in the *ortho* substitution.

4. Conclusions

The results obtained from our simulation of plasma generated polymers show a probable conformation of the molecules which evolves from the initial conditions imposed on the program. These analyses constitute a considerable help in understanding the possible structures formed in the polymers. Because of their tendency to twist the chains, a higher content of *ortho* and *meta* polyanilines can lead to the production of spongy materials. On the other hand, a smaller content of these polyanilines makes more compact films. The freedom of rotation in the rings indicates that, in the *para* and *meta* QPAn/I, the polymers tend to form more uniform and compact structures, and that the *ortho* polyanilines originate arrays with a greater disorder.

Considering the two simulations where iodine participates, the C–I distances are similar in all the polyanilines. However, in the arrangements where iodine is not bonded with the polymer, the distance between the iodine atoms and the nearest carbon is approximately two times the length of the C–I bonds. Although in both cases, iodine has a great influence in the angles between planes and in the freedom rotation of the molecule.

The different substitutions in the aniline rings, where the polymers can grow, are observed at a distinct ratio in the synthesis by plasma, according to the energetic regions in the reactors. However, the polymers can grow with one substitution in the benzene rings in one step and another substitution in the next. Thus, the real polymers can combine the three kinds of substitutions in each chain, resulting in very complex polymers. Thus, the present kind of simulation proves to advance our understanding of the polyanilines synthesized by plasma.

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