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Molecular Simulation of the interaction Polyaniline-Iodine by plasma

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Introduction

A molecular simulation study of plasma polymerized polyaniline-iodine compounds is presented. The simulation of the structure with a minimal energy state in the polymers is supported in IR spectroscopy data of the polymers which suggest that the 1,4, 1,3, and 1,2 substitutions of the benzene rings are synthesized at the same time in the reactor. This simulation gives the possibility of visualizing the arrangements of the atoms of polyanilines interacting with iodine atoms.

The calculation was carried out using the molecular simulation program Cerius 2 [9]. This program has different calculation modules, however, only the molecular mechanics section was used in this work. In this module, the molecules can be formed using the atomic dimensions. Once the molecule is constructed, extreme conditions are applied in order to obtain one of the minimum energy states. The polymers were represented with segments of 20 monomers.

Aniline

The aniline molecule is formed by a benzene ring linked with an amine group. In Fig. 1, a molecular simulation of aniline is shown as a representation of the volumetric conformation with the calculated atomic bonds and the angles among atoms. Carbons are the grey spheres forming hexagons. Aniline is a ring with 6 carbons and 1 nitrogen atom linked to the ring. The whole structure forms a flat plane. The white semicircles surrounded the structure are the hydrogen atoms.

The angles between the atoms have small differences due to the convergence in the calculation. The C-C and C=C distances are approximately 1.4 Å. These distances are 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.

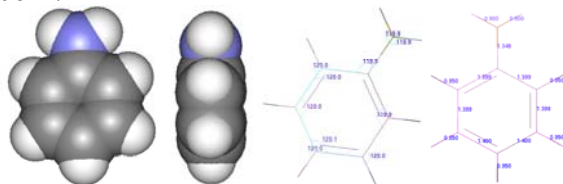


Fig. 1 – Molecular simulation of the aniline molecule.

Polyaniline

Polyaniline chains can grow in 3 directions respect to

the nitrogen position in the monomer. These are the ortho (1,2), meta (1,3), and para (1,4) substitutions shown in Fig. 2. Combinations of this substitution in polyaniline ordinarily appear when the polymer is synthesised by plasmas.

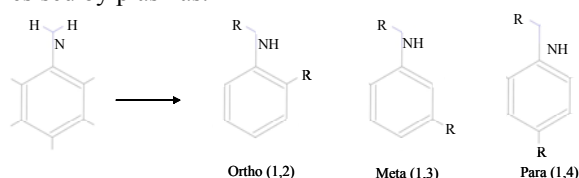


Fig. 2 – Substitutions in aniline where the polymer can grow.

When the polymers are synthesized and doped simultaneously in plasma, the position of the dopant in the polyaniline chains is not easy to define because of the very energetic conditions developed in the reactor. One possibility is that the iodine atoms remain free but trapped in the polymer chains without chemical bonds. The simulation presented here considers this alternative with the three substitutions in the benzene rings.

1,4 PAn with free iodine

Fig. 3 shows a simulation of the 1,4 PAn interacting with free iodine. The big and dark atoms in the next figures correspond to the iodine atoms. 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. The interatomic 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 1.4 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 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 biggest one is 59.8°. The differences between the angles can be seen as an approximation to a freedom of rotation between consecutive benzene planes. 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 volume image 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 4.69 Å and the nitrogen to the same iodine atoms is 3.9 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 4.77 Å, and the largest carbon-iodine distance is 6.66 Å.

According with 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 and polymer can be found in doping processes.

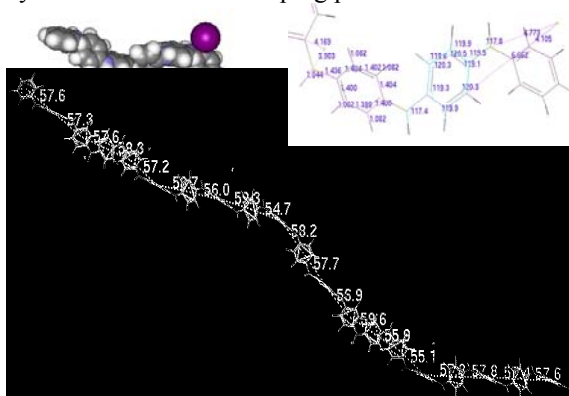


Fig. 3 - Simulation of 1,4 PAn with free iodine.

1,3 PAn with free iodine

The 1,3 PAn with free iodine simulation is shown in Fig. 4. This image presents the same rotation tendency in the rings, as the 1,4 PAn. There is not sufficient space for the hydrogen atoms around the rings, so the benzenic segments have to rotate, taking 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.

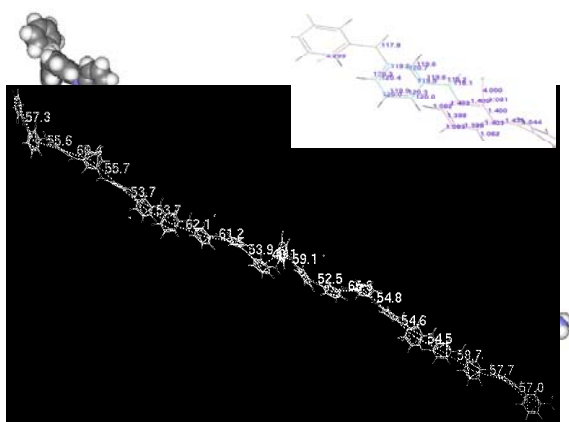


Fig. 4 –Simulation of 1,3 PAn with free iodine.

The average angle between planes is 56.09°. This indicates that the 1,3 PAn could be flatter than the similar 1,4 PAn. The rotation freedom in this arrangement is 11.6°, higher than the 1,4 PAn. An angle of 118.1° is

formed between the C-N and the N-H bonds, over which the benzene rings rotate. The distance C-I can be as short as 4 Å.

1,2 PAn with free iodine

In the same scheme, Fig. 5 presents a 1,2 PAn 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 about diverse axes to accommodate due to the proximity of the positions in the benzene rings where the chain grows.

This configuration has 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°. Something important to note in this arrangement is that the iodine atoms remain outside the cluster. In this way, the molecule behaves as PAn and iodine can not affect the molecular structure in this conformation.

The C-I distance varies from 4.26 to 4.58 Å. Although the molecule is very twisted and iodine can not access the inner rings, iodine remains in a similar distance to the cluster as in the other polyanilines studied here.

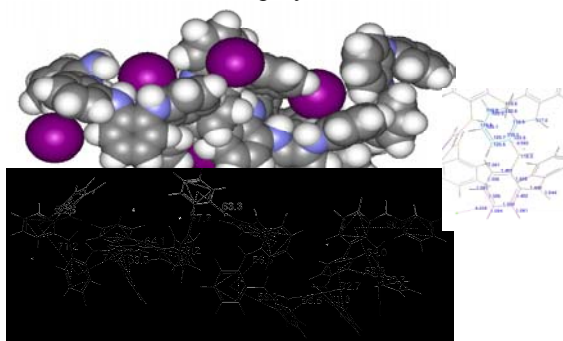


Fig. 5 – Simulation of 1,2 PAn with free iodine.

Conclusions

The results obtained in the simulated polymers show a probable conformation of the molecules. It is important to note that the benzene rings of anilines maintain their planar formation in all the structures. However, a difference of the aniline molecule without interactions, in the polymer, the benzenes rotate having the nitrogen atoms as points of rotation.

The 1,2 and 1,3 polyanilines can produce spongy materials. The smaller content of this polyanilines makes more compact films. 1,2 polyanilines originates structures with a great disorder. The distance between the iodine atoms and the nearest carbon is approximately two times the distance between the C-I bonds. Although iodine has a great influence in the angles between planes and in the freedom rotation of the molecule.

Acknowledgment

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