

## SYNTHESIS AND CHARACTERIZATION OF POLY(m-IODINE-ANILINE) BY PLASMA

<sup>1</sup>M.A. Enríquez, <sup>1,2</sup>M.G. Olayo\*, <sup>2</sup>G.J. Cruz, <sup>3</sup>J. Morales, <sup>3</sup>R. Olayo

<sup>1</sup>Facultad de Química, UAEM, Paseo Tollocan y Colón, Toluca, Mex., 50000, México

<sup>2</sup>Departamento de Síntesis y Caracterización, ININ, Apdo. Postal 18-1027, D.F., 11801, México,

<sup>3</sup>Departamento de Física, UAM-I, Apdo. Postal 55-534, D.F., 09340, México.

\*[gog@nuclear.inin.mx](mailto:gog@nuclear.inin.mx)

### Introduction

Aniline is a classical monomer to obtain semiconductor polymers, copolymers or complex doped polymers<sup>1-3</sup>. The synthesis by plasma of polyanilines has been studied using different dopants to increase the electric conductivity. Although the increment in the conductivity by adding dopants has been important, one of the main problems in the stability of the material lie in the fact that the dopant does not bond with the polymer, thus, sooner or later it is lost with the consequent decay in the conductivity.

In this work, the synthesis by plasma of poly(m-iodine-aniline) (m-PAnI), starting from m-iodine-aniline monomers is presented. The polymers were characterized by infrared spectroscopy, scanning electronic microscopy and X-ray diffraction. The results are compared with similar iodine doped polyanilines (PAn/I) with the purpose to study the behavior of the iodine dopant in both kinds of polymers.

### Results

The atomic N/I relationship of polyanilines shows the content of iodine in the material, see Fig. 1. Each N atom represents one aniline ring in the polymer, therefore, the N/I relationship indicates the number of aniline rings per iodine atom that remains in the material after the synthesis by plasma. One interesting point to remark is the same tendency of iodine loss in both polymers.

The N/I relationship in the monomer is 1. So, the ideal N/I in the polymer should be 1. However, this relation has values from 3 to 20 in the polymers indicating a high loss of iodine in both

syntheses. When iodine is chemically bonded to the monomer, the m-PAnI curve indicates a loss of iodine from 3 to 12 times. Nevertheless, in PAn/I the evolution of the relationship goes up and down losing iodine from 2 to 22 times. At the same synthesis time, 60 min, the difference between both polymers is around 5 aniline rings per iodine atom. This difference looks approximately the same in the interval of 50-100 min of synthesis time.

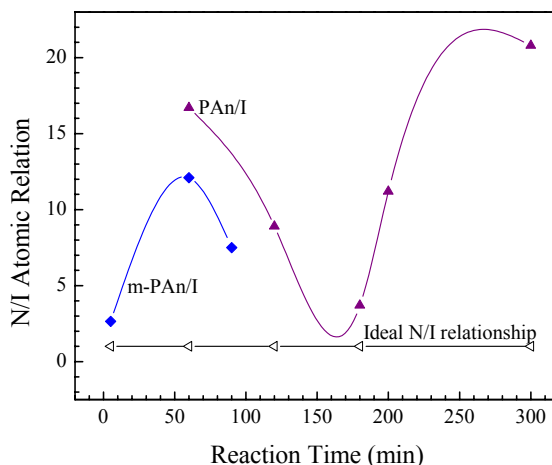


Fig. 1 - N/I Atomic relation at different synthesis time.

The infrared spectra of 3-PAnI synthesized at 5 and 90 min and PAn/I at 180 min appear in Fig 2. The spectra of 3-PAn/I present absorption bands in  $3390\text{ cm}^{-1}$  corresponding to the aromatic amines, the band centered at  $2396\text{ cm}^{-1}$  indicates  $=\text{C}-\text{H}$  groups, in the  $2362\text{ cm}^{-1}$  the presence of  $\text{C}=\text{N}-\text{H}^+$  is found, in  $1650\text{ cm}^{-1}$  are indicated the vibrations of  $\text{C}=\text{C}$ , the absorption

in  $1450\text{ cm}^{-1}$  indicates C-H vibrations inside of the plane, in  $699\text{ cm}^{-1}$  is found the meta substitution in the aniline ring and in  $520\text{ cm}^{-1}$  the C-I interaction. These two last bands at  $699$  and  $520\text{ cm}^{-1}$  are found in the three spectra.

The PAn/I spectra present very similar absorptions between  $3800$  and  $1650\text{ cm}^{-1}$ . However, below  $1650\text{ cm}^{-1}$  a great number of absorptions between  $830$  and  $745\text{ cm}^{-1}$  corresponding to para and ortho disubstitutions of the benzenic rings appear in the spectra.

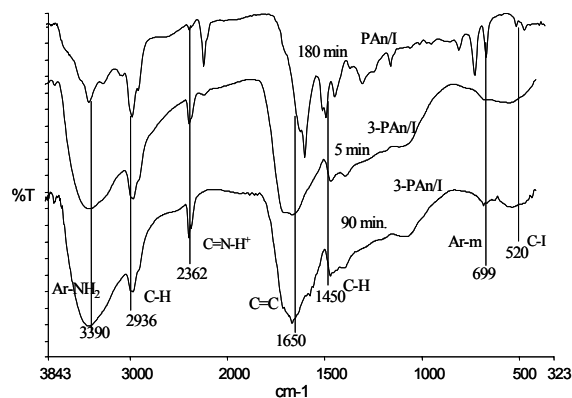


Fig. 2 - IR spectra of 3-PAnI and PAn/I.

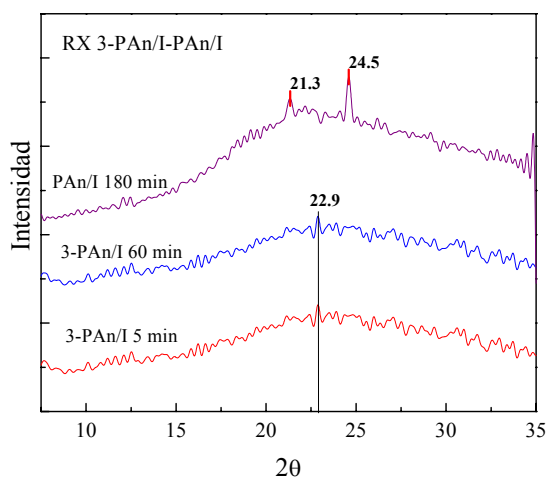


Fig. 3 - X-ray diffraction of 3-PAn/I.

Although it is common that polyaniline presents an amorphous phase, this amorphism can change when iodine participates in the structure as an aggregate. In Fig. 3 a diffractogram of both polymers is presented. The diffractogram of PAn/I presents small diffraction peaks at  $21.3^\circ$  and  $24.5^\circ$ . These peaks coincide with those reported for polyanilines. The crystallinity

percentage is 6%. The m-PAnI spectra practically show an amorphous structure with a small peak in  $22.9^\circ$ . This corresponds to an approximately 2% of crystallinity. The amorphism of m-PAnI can be due to the iodine atoms that reduce the possibility of forming ordered structures in the solid phase.

The PAn/I doped electric conductivity was calculated between  $10^{-10}$  and  $10^{-4}\text{ S/cm}$ , while the 3-PAnI was between  $10^{-13}$  and  $10^{-12}\text{ S/cm}$ . The doped polymers exhibited better conductivity than the polymers with the iodine atoms chemically bonded.

## Conclusions

The energy of the particles in the plasma reached the rupture energy of the C-I bonds, but many C-I bonds survive the energy of the discharges. This fact has to be analyzed with the energy zones imposed in the reactor. Thus, when the iodine atoms are bonded to the benzene rings, the content of iodine in the polymer was higher than that in the doped polymers. However, neither the ortho and para disubstitutions of the aniline rings nor the agglomerates found in the morphology of the doped polyanilines appeared in the 3-PAnI. The crystallinity was lower in m-PAnI than in PAn/I, the free iodine atoms from the dopant can be arranged among the polymer chains better than the chains with the atoms chemically bonded of the m-PAnI.

## Acknowledgements

The authors want to thank to CONACyT for the partial support of this work.

## References

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