

# Plasma Polymerization of Random Polyaniline–Polypyrrole–Iodine Copolymers

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**ABSTRACT:** This work presents the synthesis by plasma and the characterization of polypyrrole–polyaniline–iodine copolymer thin films. The objective was to study the conditions to randomly copolymerize different and noncombinable monomers to create new copolymers with enhanced selective properties. The study was focused on the influence of the monomer mass ratio  $r$  on the structure of the copolymers. The monomer ratio  $r$  is important since it represents the contribution of each monomer to the structure and to the properties of the copolymer. The mainstream techniques used to characterize the plasma polymers were infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The electric conductivity was studied as a function of the relative humidity. The results indicated that the copolymers with iodine have better conductive properties at lower relative humidity and that the copolymers without iodine are more stable at moderately high temperatures. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 263–270, 2002

**Key words:** plasma polymerization; dielectric properties; thin films; polypyrroles

## INTRODUCTION

Tremendous advances have been made during the last decade in our understanding of the chemistry, structure, electrical and optical phenomena, processing, and applications of organic semiconductor thin films such as polythiophene, polyaniline (PAn), polypyrrole (PPy), and their derivatives. The very great interest in these polymers is due largely to their ease of synthesis by chemical or electrochemical oxidative and plasma polymer-

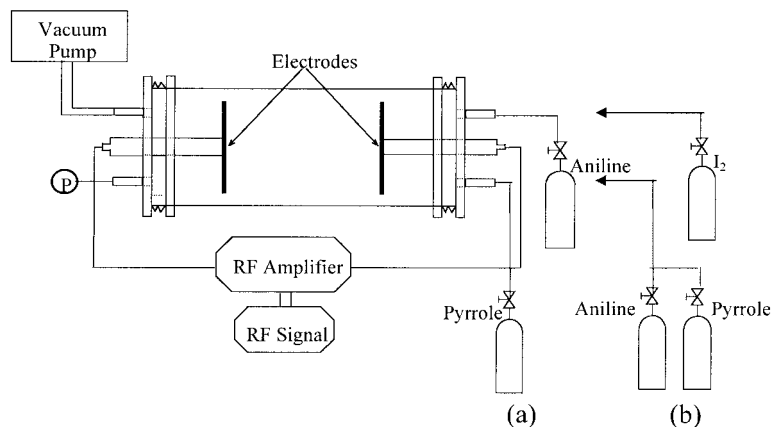
ization techniques and to their very considerable electrical potential.<sup>1–3</sup> Thus, to increase the electric properties, these two polymers were copolymerized with other polymers, in some cases with the result that the conductivity's magnitude is reduced instead of increased. For example, PAn was combined with polyester with a final reduction in the conductivity, and with poly(methyl methacrylate) and poly(vinyl chloride), with an increase in the conductivity, especially at low temperature.<sup>4</sup> PPy was copolymerized with polyamide, increasing also its conductivity.<sup>5</sup> PAn and PPy were combined with several anions, such as iodine, or with metals, with the same purpose of increasing the conductivity.<sup>6–8</sup>

Thin films of PAn<sup>6,9,10</sup> and PPy<sup>11</sup> can be formed by plasma polymerization. This technique is

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**Figure 1** Experimental device; synthesis of (a) PAY and (b) PAY/I.

widely used to produce components for microelectronics, photosensitive surfaces, and semiconductor organic thin films.<sup>12–14</sup> Within a plasma, it is possible to form thin films of material free of external agents to the reaction. In these conditions, two or more monomers can be mixed to form ions and radical particles, with possibilities for reaction among them, building more complex molecules. These molecules can react again to form heavier products, producing new random copolymers. Other components can be added to this gas mixture, such as iodine, which can be incorporated into the copolymer structure with the purpose to increase the electrical or other properties in the material. In this way, the formation of random plasma copolymers is possible in a simpler way than the traditional synthesis of those polymers.

Therefore, the objective of this work was to explore the potential of the plasma polymerization technique to synthesize multicomponent copolymers. Aniline and pyrrole were chosen to be combined, forming new copolymers, because of the interesting electric properties of each of these homopolymers. The work included the synthesis by plasma and the characterization of those aniline–pyrrole copolymers (PAY), as thin films, and the same copolymers with iodine added (PAY/I). The copolymers were characterized using scanning electron microscopy (SEM), infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The electric properties of the copolymers were evaluated at different humidity conditions.

## EXPERIMENTAL

The synthesis of PAY and PAY/I were carried out using a tubular glass reactor with an inner diam-

eter of 9 cm and a volume of 1500 cm<sup>3</sup> (ref. 10) as shown in Figure 1. The plasma was obtained using electric glow discharges with a resistive coupling mechanism with electrodes at a frequency of 13.56 MHz and power of 14–18 W. The discharges started at a pressure of  $4 \times 10^{-2}$  Torr. The electrodes, the rods, and the top of the reactor were made of stainless steel. The separation between the electrodes was approximately 9 cm. All the polymers were synthesized with approximately the same conditions in the reactor.

The synthesis time varied between 60 and 300 min. The injection of the dopant and the monomers to the reactor was made as the vapor phase. In the synthesis of PAY, each monomer was put into the reactor at a different port, as shown in Figure 1(a). In the synthesis of PAY/I, aniline and pyrrole were mixed before being put into the reactor and introduced into one of the ports; iodine was introduced into another access, as shown in Figure 1(b).

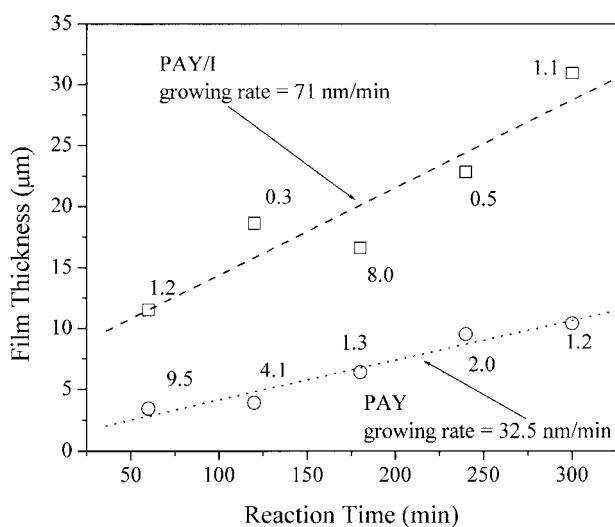
The monomer mass ratio,  $r = m_{\text{pyrrole}}/m_{\text{aniline}}$ , was calculated for each monomer mass used in the respective synthesis. The total quantities of both monomers in the reactor were not completely consumed in the copolymer because a small fraction of the monomers was removed by the vacuum system. The ratio was changed to determine the influence of each monomer in the properties of the final copolymer.

The copolymers studied in this work were formed on the glass section of the reactor. It is known that the structure and the properties of the polymers are strongly influenced by the electronic regions formed in the glow discharges with electrodes.<sup>15</sup> The structures of the polymers studied here are those formed in conditions belonging to the central section of the reactor.

The film thickness was measured with a Mitutoyo micrometer and is an average of the glass section in the reactor. The IR spectra were taken with an FTIR 2000 Perkin-Elmer spectrophotometer. TGA was done with a TA Instruments thermal analyzer. The heating ramp was 10°C/min in a nitrogen atmosphere, from 30 to 750°C. The electric resistance was measured with an OTTO MX620 digital multimeter in a capacitive arrangement with the film in the middle. The electric conductivity was calculated from the resistance data. A humidity chamber was used to induce a wide range of relative humidity (RH), between 15 and 92%, where the conductivity of the copolymer was studied. The micrographs were taken with a Philips XL 30 scanning electron microscope on the surface of the films.

## RESULTS AND DISCUSSION

PAY and PAY/I were synthesized by plasma polymerization at different reaction times of 60, 120, 180, 240, and 300 min. When the synthesis was concluded, PAY/I was kept in the reactor for 24 h in an iodine atmosphere to neutralize the last radicals that remained in the surface after the glow discharge. With this final treatment in the iodine atmosphere, the presence of oxygen diminished and the iodine content increased in the copolymers. Finally, the copolymers were washed with acetone to separate the remaining



**Figure 2** Growth of PAY and PAY/I films. The numbers in the plot indicate the mass ratio in the reactor:  $m_{\text{Pyrrole}}/m_{\text{Aniline}}$ .

**Table I** Growth Rate of Different Polymers Synthesized by Plasma

Polymer	Growth (nm/min)
PAn <sup>10</sup>	35.5
PAn/I <sup>10</sup>	63.8
PPy <sup>11</sup>	48.2
PPy/I <sup>11</sup>	64.4
PAY	32.5
PAY/I	71.0

iodine and oligomers of aniline and pyrrole. To compare the electric conductivity of the copolymers with the individual homopolymers, thin films of PAn/I and PPy/I were synthesized at 180 min of reaction with the same conditions.

### Growth of Film

Figure 2 shows film growth as a function of the reaction time. The numbers in Figure 2 indicate the monomer mass ratio in the reactor.  $R$  was varied to make the properties of the copolymer closer to PAn or PPy. If the copolymer is synthesized using similar mass for each monomer,  $r$  should be equal to 1;  $r < 1$  indicates a high proportion of aniline in the copolymer. On the other hand,  $r > 1$  means that pyrrole has made a major contribution to the copolymer structure.

Figure 2 shows that the growth of all the copolymer films is linear and that the mass ratio is not important for the thickness of both polymers, because  $r$  varied from 1.2 to 9.5 in PAY and from 0.3 to 8 in PAY/I, with approximately the same growing rate for each polymer. However, the significant variable in the film thickness is the reaction time.

The growing of PAY/I is sensitive to more variables, the reaction time, and the contribution of the iodine atoms to the reaction. The PAY film thickness was between 3.5 and 10.5 µm with a growing rate of 32.5 nm/min. PAY/I films had growth between 12 and 33 µm, with a growth rate of 71 nm/min. PAY/I had a growth rate approximately twice that of PAY. The notable increase in the thickness of PAY/I films can be due to the great size of the iodine atoms.

Table I shows the growth rate of PAn, PAn/I, PPy, PPy/I, PAY, and PAY/I. Table I shows that the growth of PAY films is smaller than that of PAn and PPy, indicating that PAY follows its own tendency in the conformation of the structure.

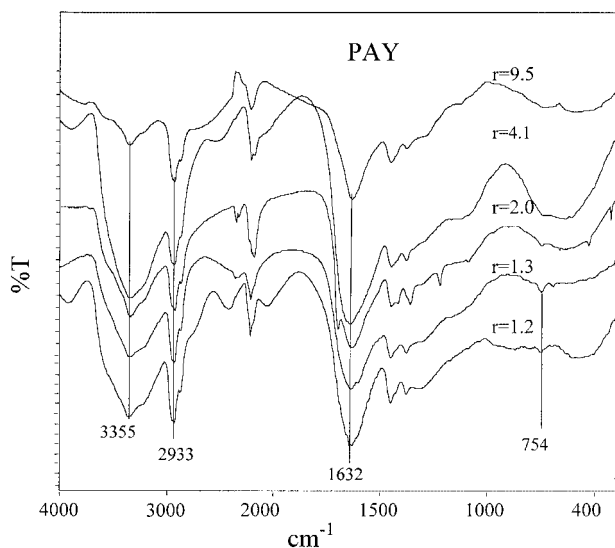
However, the growth rate of PAY/I is higher than that of the others. This result suggests that the copolymer has the ability to include more iodine atoms than can the respective homopolymers. As the electric conductivity in PAN and PPy is enhanced with the presence of iodine atoms, this kind of ability can be used to increase the electric properties.

### IR Analysis

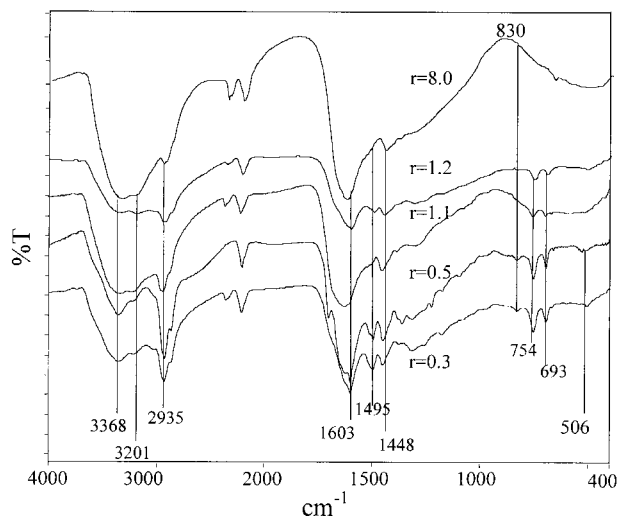
The infrared spectra of PAY are presented in Figure 3. Several peaks belonging to PPy and PAN appeared, indicating that both monomers were combined to form new copolymers, maintaining some of the individual characteristics of the initial monomers.

The absorption at 3355 and 1632  $\text{cm}^{-1}$  corresponds to the amine and/or imine N—H stretch in the PAY structure. This absorption has a wide interval wavelength since both monomers contain amine groups. The peak at 2933  $\text{cm}^{-1}$ , corresponding to the asymmetric aliphatic C—H stretching of  $sp^3$   $\text{CH}_3$  and  $sp^3$   $\text{CH}_2$  groups,<sup>12</sup> indicates the existence of alkyl groups, which may have originated from some broken aniline or pyrrole rings. The N—H bending in amines is observed at 1632  $\text{cm}^{-1}$ . This peak is broad, because it also includes the contribution of the C=N imine stretch and the C=C alkene stretching.

In the region between 400 and 1000  $\text{cm}^{-1}$ , two different absorptions are shown in the spectra.



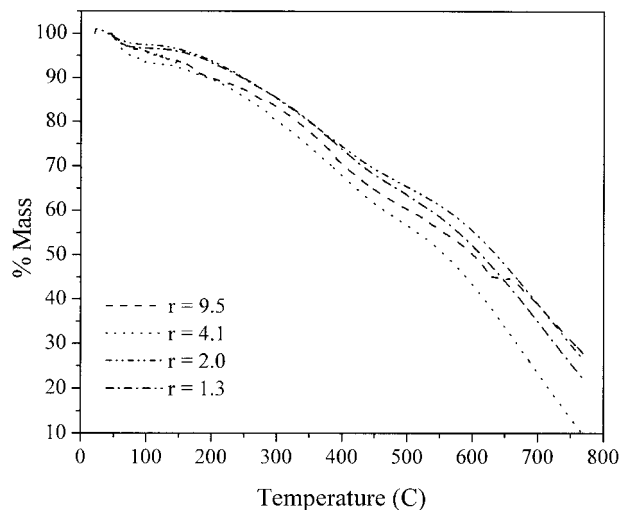
**Figure 3** IR spectra of PAY at different mass ratio compositions.



**Figure 4** IR spectra of PAY/I at different mass ratio compositions.

The copolymers with  $r > 1.5$  present one wide characteristic band of PPy polymerized by plasma,<sup>11</sup> an indication that pyrrole is dominant in the structure of these copolymers. This band is less intense in the films with  $r$  between 1.2 and 1.3, because the proportion of pyrrole decreases, increasing the influence of aniline. However, the width of the band covering 400–1000  $\text{cm}^{-1}$  indicates a complex absorption because this peak is wider depending on the mass relation, that is, wider when  $r > 1.5$ . The films with an approximately equal quantity of both monomers ( $r \approx 1$ ) have little absorption defined at 754  $\text{cm}^{-1}$  and a wider absorption band around 3368  $\text{cm}^{-1}$ .

IR spectra of the PAY/I films are shown in Figure 4. The samples with a large amount of aniline,  $r < 1$ , present three peaks at 693, 754, and 830  $\text{cm}^{-1}$ . Those peaks are characteristic of PAN/I polymerized by plasma<sup>10</sup> and can be assigned to the disubstitutions in the benzene rings. Only the two first peaks are present in the films with  $r > 1$ . However, PAY/I with  $r = 8.0$  does not present these absorptions, indicating the greater contribution of PPy. The spectra show, with the exception of this last sample, that the structures of the copolymers have the contribution of both monomers. Figures 3 and 4 also show that the FTIR spectra of PAY and PAY/I have differences in absorption at 506  $\text{cm}^{-1}$ , which belongs to the iodine bonds, and at 1495  $\text{cm}^{-1}$ , an indication that their respective molecular structures are different depending on the mass ratio composition and on the contribution of the iodine atoms.

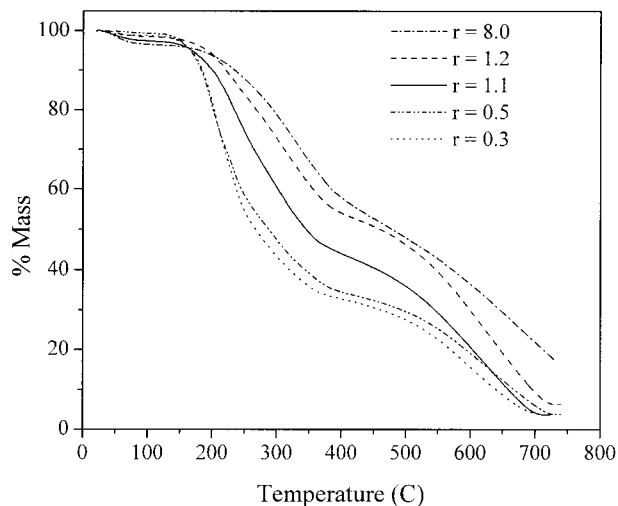


**Figure 5** Thermal decomposition of PAY films.

### TGA

The thermal decomposition of PAY is shown in Figure 5. PAY loses between 3 and 7% of its initial mass between approximately 30 and 100°C, due to evaporation of the humidity and solvents trapped in the films. After that, there are two important decreases of mass: The first one begins at 150°C, finishing around 450°C, and could be assigned to the thermal degradation of the crosslinked chains. In this temperature interval, PAY loses 30–40% of its initial mass. At 450°C, the second mass loss begins and continues to 770°C. This loss could be associated with the decomposition of the lineal part of the chains. After 770°C, the residual mass is around 35–10% of the initial mass. From the TGA of PAN and PPy, it can be seen that, at this temperature, both still retain approximately 40% of the mass.<sup>10,11</sup> The thermal decomposition is approximately the same for all the samples. There are no significant differences as  $r$  increases.

The thermal decomposition of PAY/I is shown in Figure 6. PAY/I loses 0–4% of the initial mass between 25 and 100°C due to humidity and solvents trapped in the samples. All the PAY/I samples show two important mass losses: The first one begins about 150°C, ending approximately at 350°C. This percentage of mass loss is not present in PAY and could be due to the evaporation of iodine atoms not strongly bonded to the structure. Iodine atoms have a high weight, tending toward a drastic decrease in the copolymer mass. The next decrease of mass is between 450 and 750°C with 50 to 3% of the initial mass. This indicates

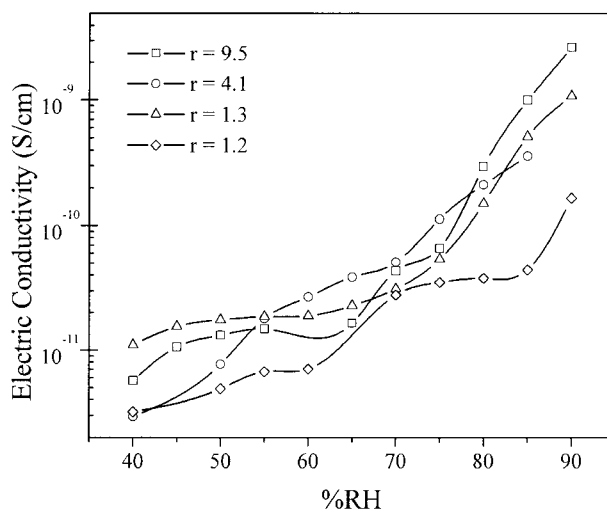


**Figure 6** Thermal decomposition of PAY/I.

that the complex structure of the samples, except the one with  $r = 8.0$ , has completely degraded. At 750°C, the fragments remaining, with a great percentage of pyrrole, continues the decomposing tendency. This copolymer has higher stability in the entire temperature interval, compared with the other curves, having approximately the same degradation as that of PPy/I<sup>11</sup> synthesized by plasma in the first 400°C.

### Electric Properties

Figure 7 presents the electric conductivity versus the relative humidity (RH) of PAY films. It shows

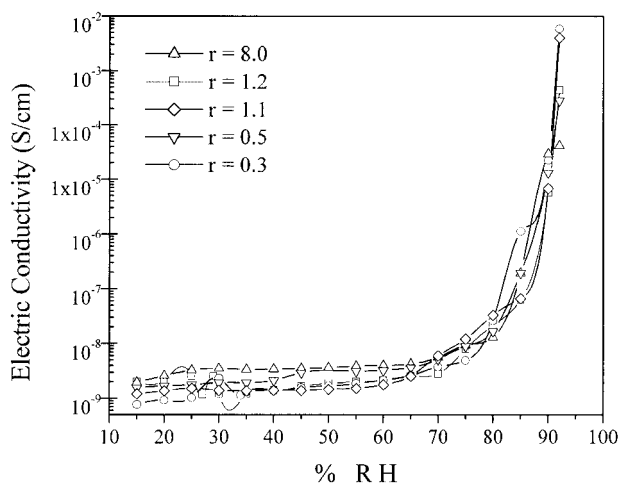


**Figure 7** Evolution of electric conductivity of PAY with RH.

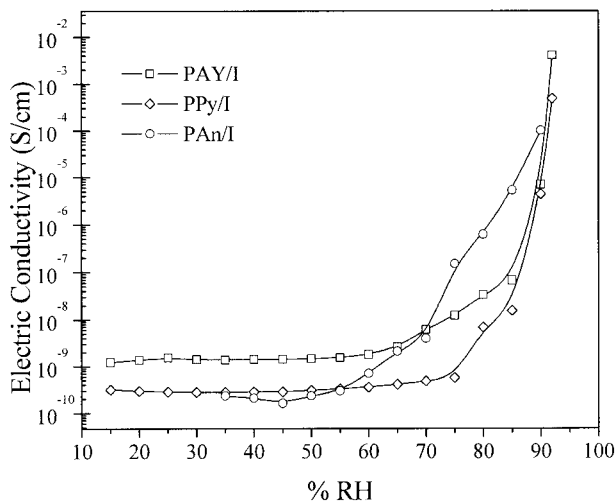
that the conductivity of PAY varies between  $10^{-12}$  and  $10^{-9}$  S/cm. The behavior of the conductivity in PAY is approximately linear with the RH. This figure shows that the mass ratio is not very important for the electric conductivity of PAY. However, the presence of water in the structure of the copolymer significantly increases the electric conductivity. This effect is not due to the intrinsic conductivity of the copolymer, but to the contribution of the water molecules in the transport of charges.

The electric conductivity of PAY/I is shown in Figure 8. The electric conductivity varied between  $10^{-9}$  and  $10^{-3}$  S/cm for RH between 15 and 92%. As with PAY, the mass ratio does not influence significantly the electric conductivity. However, two main regions of conductivity can be appreciated in the behavior of PAY/I: The first region is located at  $10^{-9}$  S/cm for RH below 70%. In this region, the conductivity is approximately constant, indicating that humidity is not important to the mechanisms of conduction. The second region has conductivity between  $10^{-9}$  and  $10^{-3}$  S/cm for RH between 70 and 92%. In this region, an important increase of six orders of magnitude in the conductivity can be appreciated. It should be noted that the increase of conductivity occurs at a greater concentration of water. This behavior was also shown by PAn/I and PPy/I and originates from the interaction of the water molecules with the copolymer structure.

Figure 9 shows a comparison of the electric conductivity of PAn/I, PPy/I, and PAY/I. The conductivity of PAY/I at 92% RH is  $10^{-3}$  S/cm. The



**Figure 8** Evolution of electric conductivity of PAY/I as a function of RH.



**Figure 9** Electric conductivity of PAY/I, PPy/I, and PAn/I.

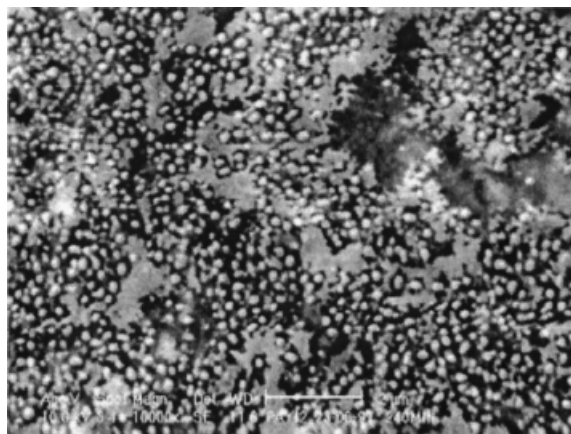
conductivity of PPy/I and PAn/I, at the same conditions of synthesis, has approximately the same order of magnitude. The plot shows that PAY/I has better conductivity than that of PAn/I or PPy/I at low RH. The random combination of both monomers in the structure of the copolymer results in better conditions for the intrinsic movement of the electrons in the networks. However, the same characteristic at high RH results in conductivity between that of the two monomers. This behavior suggests that the properties of both polymers have combined to form a new material with its own characteristics. The influence of iodine in this material is significant and places this copolymer in the region of semiconductors.

### Morphology

Figures 10–12 show  $10,000\times$  micrographs of PAY/I with  $r = 0.5, 1.1,$  and  $8.0,$  respectively. The micrographs suggest that the growth of the films occurs due to agglomerates with diameters between  $0.2$  and  $0.4 \mu\text{m}$ . These agglomerates are less concentrated in the surfaces as  $r$  increases, suggesting that they can be originated from the presence of the PAn/I monomeric units. SEM micrographs of PAn, PAn/I, PPy, and PPy/I can be found in refs. 10 and 11.

### CONCLUSIONS

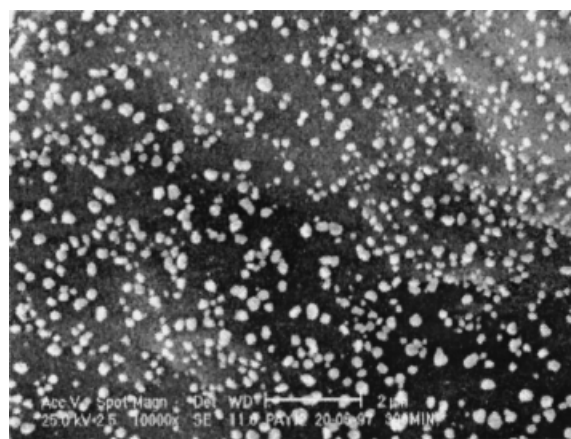
The random PPy–PAn–iodine copolymers were obtained by plasma as thin films. This opens up



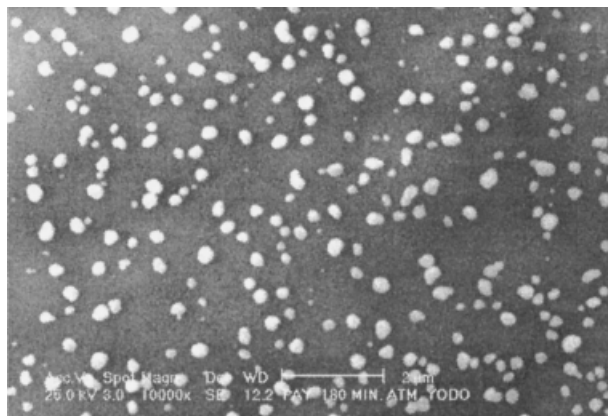
**Figure 10** Micrograph of PAY/I at  $r = 0.5$  and a magnification of  $10,000\times$ .

many perspectives in the copolymerization of different organic monomers, free of external chemical reagents, with a wide variety of physical and chemical properties. The copolymers have the presence of two aromatic rings in the structure: aniline and pyrrole. The mass ratio of the monomers is important because it influences the structural evolution and the physical characteristics of the final copolymer. However, this ratio has little influence on the electric conductivity of the copolymer. PAY has a conductivity between  $10^{-12}$  and  $10^{-9}$  S/cm and PAY/I presents a conductivity of  $10^{-9}$  and  $10^{-3}$  S/cm with two overlapped conduction mechanisms. The first one is active at less than 70% RH and the second one is active at more than 70% RH.

The increase in conductivity was less than one order of magnitude for PAY/I compared with that



**Figure 11** Micrograph of PAY/I at  $r = 1.1$  and a magnification of  $10,000\times$ .



**Figure 12** Micrograph of PAY/I at  $r = 8.0$  and a  $10,000\times$  magnification.

of PAN/I and PPy/I. This increase was shown at less than 70% RH and can be due to the greater quantity of iodine that the copolymer can react with. This effect can be seen in the growth rate of the copolymer, which is higher than that of PAN/I and PPy/I and was calculated as 32.5 nm/min for PAY and 71 nm/min for PAY/I.

PAY showed different thermal stability from that of PAN and PPy. PAY/I has less thermal stability than has PAY at relatively low temperature, possibly due to the iodine atoms that are more easily evaporated. The micrographs of PAY/I showed that the microscopic morphology is due to agglomerates randomly distributed all over the film. The concentration of the agglomerates is reduced as the presence of the monomeric units of PAN/I is reduced.

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