

Polymerization of Halogenated Anilines by Plasma

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ABSTRACT: This work presents an experimental study about the electric conductivity in polyanilines synthesized by plasma obtained from halogenated anilines in which chlorine or iodine atoms are bonded in meta position to the aniline rings. The objective is to study the enhancement of the electric conductivity of these structures due to the addition of electro-negative atoms to the polymeric chains. The results show that

the halogenated anilines produce polymers with an electric conductivity up to eight orders of magnitude higher than those of the undoped polyanilines, reaching $\sim 10^{-4}$ S/cm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4682–4689, 2006

Key words: plasma polymerization; polyaromatics; halogenated; polyaniline

INTRODUCTION

Polyaniline (PAn) presents great changes in its electronic configuration due to the oxidation degree and to the doping process used in its synthesis. These changes have resulted in conductivities with differences of many orders of magnitude. For this reason, PAn has been synthesized by different chemical, electrochemical, and plasma methods trying to control the oxidation degree and/or the doping level.^{1–9} Particularly, one important studied area has been the mechanisms of the electric charge motion along the polymers promoted by the halogenated dopants. Many doping strategies have been studied in this context, including experimental and theoretical works on polymers with halogens bonded to the aromatic rings.^{10–15}

The synthesis of PAn by plasma has also been studied by introducing iodine dopants with the result that the conductivity increases two or three orders of magnitude compared to the same polymer without dopants.^{16–19} Another alternative, barely experimented by the use of plasma before, is to polymerize anilines with halogens bonded to the monomer rings. The plasma polymers in those conditions are not doped strictly speaking, although the final electronic configuration could improve the transport of electric charges along the chains, given the additional electronegativity provided by the halogens. Nevertheless, depending on the position of the halogens in the aniline rings, the chains

can grow in other substitutions different from the usual para position in most polyanilines.

In this work, we present a report on the synthesis by plasma of polyanilines with iodine or chlorine atoms bonded to the meta position in the aniline rings. Considering that plasma synthesized polyanilines grow predominantly in para position respect to the aniline rings, meta and ortho halogenated anilines could generate equivalent structures in the polymerization, because, when the polymer is forming, the monomers accommodate with the halogens randomly located in one or in the other side of the chains. Consequently, in both cases, the structure in the final polymers is similar. Hence, studying the formation of polyanilines starting from meta halogenated anilines, the polymerization of the ortho case is also included. Polyanilines formed from para halogenated aniline are different, because the halogen atoms do interfere in the growing of polyanilines that uses this position, making polymers with different growing tendency.

Therefore, the objective of this work is to study the structure and conductivity of the polymers formed from *m*-Cl-Aniline and *m*-I-Aniline, named *m*-PAnCl and *m*-PAnI, respectively. The names were assigned following the position of the halogen atoms in the starting monomers and not as a consequence of the position where the polymers grow. The structure and properties are compared with those obtained from polyaniline doped with iodine (PAn/I) and polyaniline without dopants (PAn), all of them synthesized by plasma.

EXPERIMENTAL

The polymers were synthesized within a 1500 cm³ cylindrical glass reactor, 9 cm in diameter and 25 cm

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long, containing two flat stainless steel electrodes with a 7 cm diameter, placed 10 cm apart. The electrodes were connected to a 13.5 MHz RF generator in a resistive arrangement. In this configuration, the monomers and the oligomers in formation constitute the gas that is excited and ionized to the point of plasma. The energy transferred from the electric field to the gas can be related to the resistance of the current flowing from one electrode to the other.

The reactor presents six access ports, which provide connection to the vacuum system, electrodes, diagnostic instruments and to the monomer and dopant reservoirs. The system includes a condenser cooled with liquid nitrogen intended to trap the gases and particles leaving the reactor. The starting monomers (Aldrich) were aniline, *m*-I-Aniline, and *m*-Cl-Aniline, according to the synthesis.

Each monomer polymerizes at a particular range of thermodynamic and electric conditions, however, all the syntheses were made at $\sim 10^{-2}$ mBar and a 50–60°C temperature range, measured on the external wall of the reactor. Two fans located at the sides of the reactor maintained this temperature range. The synthesis of *m*-PANi was developed with a power supply between 152 and 163 W, during a reaction time in the 60–180 min interval. The synthesis of *m*-PANCl was completed in the 60–300 min range between 14 and 16 W. PAn and PAn/I were synthesized at, approximately, 12 W at the same pressure, temperature and geometric arrangement.⁵

The power needed to synthesize *m*-PANi is approximately 10 times greater than that demanded by the other polymers presented in this work. Yet, the former was a "minimum" value enough to produce *m*-PANi in the reactor with the same geometric configuration. The reaction rate is not a linear function of the power. At lower values, the reaction was so slow that almost no polymer was formed during the time interval established in this work. The high power applied to this polymer, however, can have collateral consequences as it can increase the fragmentation of the chemical species participating in the polymerization. This effect will be discussed further on.

FORMATION OF THE FILMS

During the polymerization, the molecules increase in size within the gas-phase forming oligomers. Later on, the molecules go to the surface of the reactor where the process continues until they reach their final size. Thus, the polymers are obtained as thin films adhered to the internal walls of the reactor. The films have had to be swelled with acetone to detach them from the walls. Once separated, the thickness of the layers was measured by means of a Mitutoyo micrometer. Figure 1 shows the average thickness of

polyanilines as a function of the reaction time; it contains also the growing rate of poly(*ortho*-chloroaniline) (*o*-PANCl) to compare with that of the *m*-PANCl.

After the first minutes of reaction, the polymers exhibit linear growing tendencies; *o*-PANCl and *m*-PANCl grow at 25 nm/min, *m*-PANi at 217 nm/min, PAn at 32 nm/min, and PAn/I at 63 nm/min.⁵ Both, *o*-PANCl and *m*-PANCl, have approximately the same growing rate although the monomers are different, provided that the structure of both polymers are equivalent.

PAn/I and *m*-PANi grow faster than the other polymers, most probably because of the large size of the iodine atoms. In a spherical approach, the atomic radius of I and Cl would be 1.33 and 0.99 Å respectively. This difference would make the iodo-polyaniline much thicker than the chloro-polyaniline films. However, another factor that influences also in the thickness of the films is the halogen content in the polymers, which vary depending on the energy and the duration of the discharges. In this sense, *m*-PANi exhibited the greatest energy during the synthesis and this condition also contributed to maximize its growing rate among the other polymers.

MORPHOLOGY OF HALOGENATED POLYANILINES

From a global point of view, the plasma polyanilines, halogenated or not, grow into layer structures, most of the times due to small pressure variations during the synthesis. The morphology was studied by comparing the conformation of polymers synthesized for the reaction time: 180 min. The morphologic and elemental analysis was performed using a Philips XL30 scanning electron microscope coupled with an energy dispersive spectroscopy (EDS) probe. The thickness of the films, measured from the SEM pic-

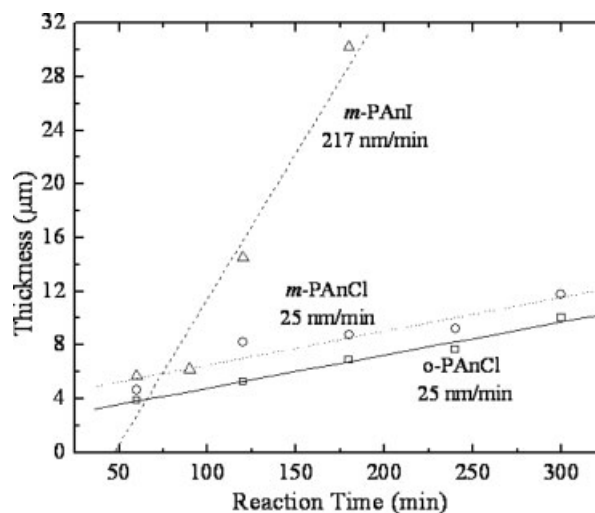


Figure 1 Halogenated PAN thickness as a function of the reaction time.

tures, varied from 4 to 20 μm with respect to those measured with the micrometer.

Figure 2 shows the morphology of the polymers. The micrograph 2(a) corresponds to PAN. It exhibits a granular surface and compact stacked layers with approximately the same thickness. In Figure 2(b), PAN/I appears to be formed by thick compact layers with many small hollow sections between them that produce a spongy texture. The iodine trapped between the layers during the doping can originate such spongy materials. The layers have solid sections with different thickness; from 5 to 12 μm .

Figure 2(c) corresponds to *m*-PANI showing a smooth surface built by compact layers and with small holes in the middle and thickness in the range of 15–20 μm . The high power needed to synthesize this polymer does not affect the roughness of the surface or the layer by layer deposition showed by the other polymers.

Figure 2(d) corresponds to *m*-PANCl. It is also composed by solid layers with small agglomerates distributed on the surface. This kind of agglomerates does not appear in the plasma iodine polymers or in the polyanilines without doping. Some of the agglomer-

ates have rectangular and triangular faces with sides of $\sim 10 \mu\text{m}$. It is important to notice the regular sides and faces of the agglomerates. The weight percentage of chlorine in the flat surface is approximately 10%, and reaches up to 30% in the agglomerates, with an approximated N/Cl atomic ratio of 0.2. This high concentration of chlorine in the polymers is probably the promoter of the agglomerates. Each individual layer is thinner than those of *m*-PANI, 2–3 μm . As it will be discussed in the following sections, this polymer presents the highest crystallinity among the polyanilines studied in this work. The halogens bonded to the polyanilines produce films with more compact layers.

ELEMENTAL ANALYSIS

Figure 3 shows the atomic N/X ratio in the halogenated polyanilines, where $X = (\text{I or Cl})$, as a function of the reaction time. This ratio represents the number of aniline rings per halogen atoms that survive in the polymer. Thus, as one benzene ring is bonded to one nitrogen atom in the monomer, their N/I and N/Cl ratios are 1, and the ideal atomic N/X ratio in the poly-

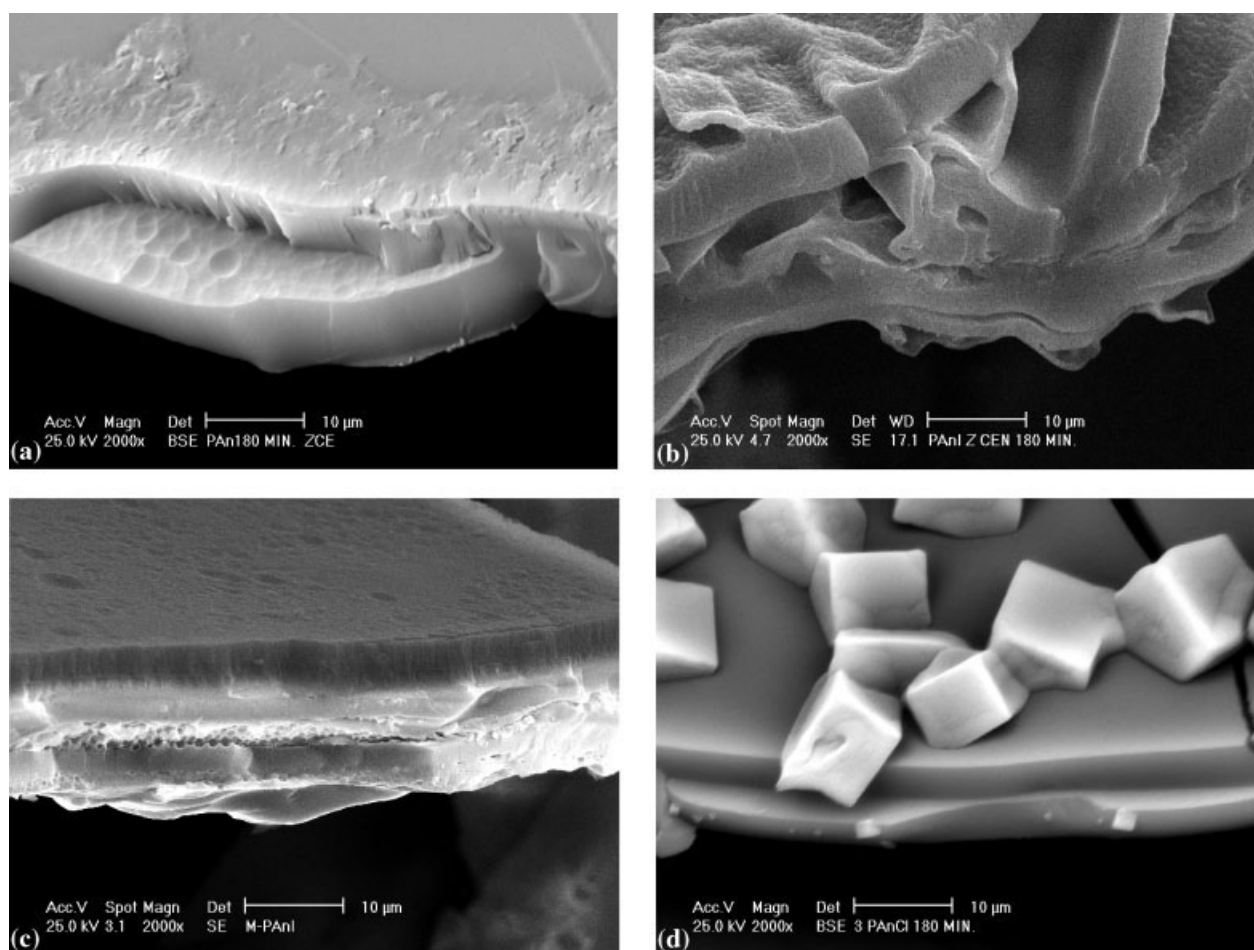


Figure 2 Morphology of plasma halogenated polyanilines. (a) PAN; (b) PAN/I; (c) *m*-PANI; (d) *m*-PANCl.

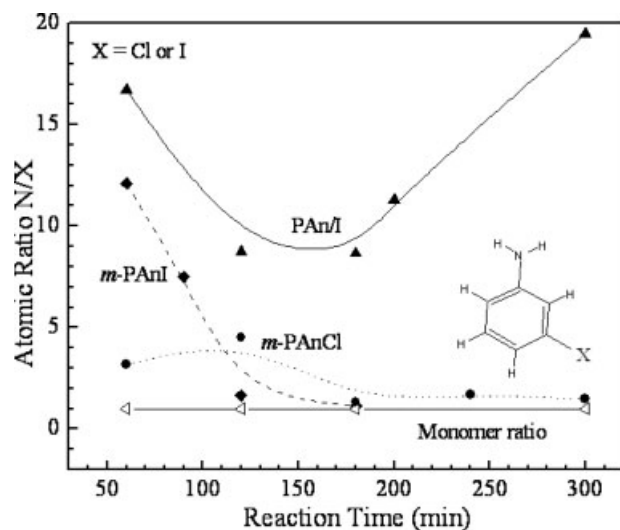


Figure 3 Nitrogen/halogen atomic ratio in polyanilines as a function of the reaction time.

mers should also be 1. However, it is important to remember that, if the plasma particle energy is sufficiently high, the collisions can break an important proportion of the molecules in the polymerization and could change the N/X ratio in the final polymers.

After a 60 min reaction time, *m*-PAnI has 12 aniline rings per iodine atom indicating that the polymers lose most of the halogens during the synthesis due to the high discharge energy. At this time, the polymers could not have enough thickness to keep the released halogens inside the layers. At longer reaction times, the thickness of the layers increases rapidly and the iodine loss is reduced. At 120 min, the N/I ratio approximates to one iodine atom per one aromatic ring, and this relationship is maintained at further reaction times.

In PAn/I there is a competitive process of bonding and releasing halogens during the reactions. The atomic N/I ratio indicates 8–20 rings per iodine atom during the studied reaction time. In *m*-PAnCl, the atomic N/Cl ratio indicates that there are 1–5 aniline rings per chlorine atom along the synthesis. At 60 min N/Cl = 3; after that, this ratio increases slightly to 5 and decrease to 1 at 180 min. This ratio is maintained up to 300 min at one or two aniline rings per chlorine atom.

The N/X ratio suggests that at short reaction times, the polymers lose iodine more easily than the chlorine atoms. This could be a consequence of the high power needed to polymerize *m*-PAnI.

Table I contains the wt % of each element in the polymers. PAn/I presents a iodine content of 3–15%, *m*-PAnI oscillates between 10% and 47% of iodine and the content of chlorine in *m*-PAnCl varies in the 8–26% interval. Note the difference between the highest iodine content in PAn/I and *m*-PAnI, which

TABLE I
Halogen Content (wt %) in Polyanilines

| Polymer | Reaction time (min) | | | | |
|-----------------|---------------------|------|------|------|------|
| | 60 | 120 | 180 | 240 | 300 |
| PAn/I | 8 | 8.6 | 14.8 | 4.9 | 3.7 |
| <i>m</i> -PAnI | 10.5 | 35.9 | 47.6 | 42.0 | – |
| <i>m</i> -PAnCl | 11.4 | 7.8 | 25.8 | 12.2 | 16.7 |

reached almost three times. This difference reflects in the atomic ratios in Figure 3.

STRUCTURE OF POLYANILINES

The IR analysis of the polymers was carried out on a FTIR 2000 PerkinElmer spectrophotometer. Figure 4 shows the IR spectra of the polyaniline films. The IR data was taken directly from the films, without substrates, using 32 scans. The absorption at 3032 and 2941 cm^{-1} belongs to the aromatic and aliphatic C–H bonds, respectively. Both absorptions have approximately the same intensity in the case of polymers with the halogens chemically bonded: *m*-PAnI and *m*-PAnCl. The polymers without halogens in the monomers present a much higher absorption of the C–H aliphatic bonds.

To discuss the effects of this absorption in the plasma polyanilines, let us use a ratio that expresses the aromaticity degree (*A*) in the polymers as the ratio of the IR absorption intensity of the aromatic C–H groups divided by the sum of both, the aliphatic and the aromatic C–H absorption ($A = I_{\text{Aromatic}} / (I_{\text{Aromatic}} + I_{\text{Aliphatic}})$). This ratio is important as the plasma particle energy can easily go beyond the atomic bonding energy of the compounds participating in the chemical

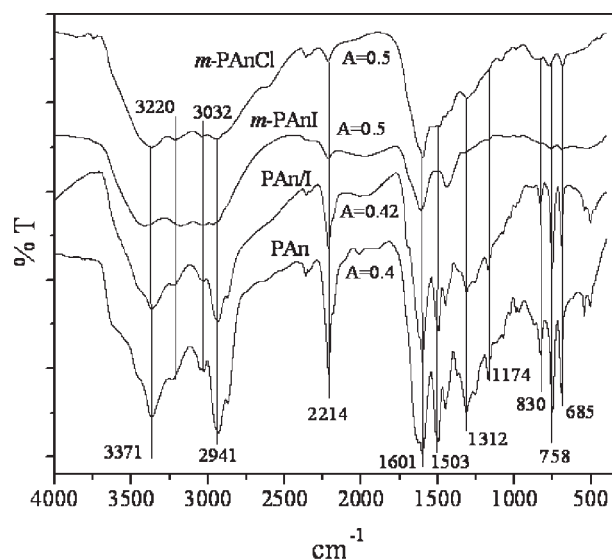


Figure 4 IR spectra of polyanilines *A* is the aromaticity ratio in the polymers.

reactions, breaking the molecules. Thus, this ratio represents, indirectly, the fraction of the aromatic rings in the polymers.

The aromaticity ratio in nonplasma Aniline, taken from the Aldrich standards,²⁰ can be calculated from 0.95 to 0.83 depending on the aggregation state of the monomer and on the measuring conditions. It is difficult to obtain $A = 1$ because of the impurities in the synthesis and the interaction among molecules in the condensed phase. *N*-methylaniline measures $A = 0.55$ while aniline with two methyl groups in the benzene rings, 2,4 dimethylaniline, yields $A = 0.44$. These two nonplasma compounds are used only to compare their A ratio with those of the plasma polymers synthesized in this work.

The recorded average A ratio in the plasma polymers was as follows: PAn had 0.4, PAn/I had 0.42, both, *m*-PAnI and *m*-PAnCl had approximately the same 0.5. These values indicate that the rings of the halogenated polymers show more stability with respect to the energy of the plasma discharges.

Ramification is more or less usual in polymers synthesized by high energy plasmas because the monomer fragments that participate in the polymers, bonded with them as lateral small chains or between two consecutive aniline rings, could break the "conductive" electronic clouds in the polymer. Crosslinking can be considered somehow different, because, if the monomers are joined consecutively using different substitutions in the benzene rings, the aromaticity of the whole network can be maintained. The intensity of these phenomena is different in the polymers, depending on the chemical nature of the monomers and on the energy involved in the polymerization.

A similar discussion can arise from the absorption peak at 2214 cm^{-1} , associated to the $\text{C}\equiv\text{N}$ bonds, appearing because of the strong oxidation of the monomers in the plasma. The absorption of these bonds in the polymers could be proportional to the broken aniline rings. This effect on the halogenated polymers is reduced, compared with that of nonhalogenated polyanilines.

The absorption bands centered at 3371 and 3220 cm^{-1} correspond to the $\text{N}-\text{H}$ groups. The $\text{N}-\text{H}$ peaks suggest the presence of benzoid rings in the polymers, which could be predominant in PAn and PAn/I. From a theoretical point of view, the best electronic configuration of PAn for the movement of electric charges would be that with the highest oxidation state, which can be obtained alternating quinoid and benzoid rings along the chains.

The absorptions centered at approximately 1600 and 1500 cm^{-1} are characteristic of the amine aromatic compounds, as in the case of the polymers synthesized in this work. The 1601 cm^{-1} peak can be assigned to the $\text{C}=\text{C}$ combined with the $\text{C}=\text{N}$ groups in quinoid structures. On the other hand,

near 1503 cm^{-1} the absorption of $\text{C}=\text{C}$ can be found combined with the $\text{C}-\text{N}$ groups in benzoid polyanilines. The combination of these bands represents the oxidation degree in the polymers.¹² PAn and PAn/I display a strong presence of benzoid polyanilines, but the small intensity of the 1503 cm^{-1} peak suggests that *m*-PAnCl and *m*-PAnI tend to develop comparatively more quinoid structures. This means that the electric charges are more probable to move inside these last halogenated polymers. The substitutions in the benzene rings from the initial monomers could promote the formation of such structures in the final polymers.

The bands centered at 1312 and 1174 cm^{-1} belong to anilines linked with alkyl groups, and represent, in some way, the fragments of the broken rings attached to the polymers. Both absorptions are weak on *m*-PAnCl and *m*-PAnI suggesting that they have a lower proportion of alkyl groups in their chains in comparison with PAn and PAnI. The halogenated aniline rings are apparently more stable with respect to the energy of the discharges than the simple rings. It is convenient to emphasize that the high power needed to synthesize *m*-PAnI does not produce more broken rings than those found in *m*-PAnCl, which was synthesized at much lower power.

The absorption near 830 , 758 , and 685 cm^{-1} represent different substitutions in the benzene rings of polyanilines. Most of these substitutions are originated by the growing of the polymers in the different positions of the aniline rings. Particularly, the substitution 1,4 in the polymers, which is associated with the 830 cm^{-1} peak, is reduced in *m*-PAnCl and *m*-PAnI because the initial monomer molecules have one halogen atom occupying the near 1,3 substitution (meta). Therefore, the atomic volume of the halogen atoms in such position reduces the possibilities of the polymers to grow using the 1,4 substitution.

THERMAL STABILITY

Plasma doping usually involves particles with high energy and this characteristic promotes chemical reactions between the polymers and the dopants. From this point of view, plasma doping can be considered as a physical-chemical process different from the traditional nonplasma doping. The latter is essentially a physical process where the dopants are released from the polymers in aging processes or under strong energetic conditions.

The thermal decomposition of the plasma polyanilines, as a function of the temperature, is shown in Figure 5(a). Figure 5(b) presents the derivative of the thermal decomposition with the purpose of differentiating each decomposition stage in the polymers. The thermal data were recorded using a Dupont 2000 ther-

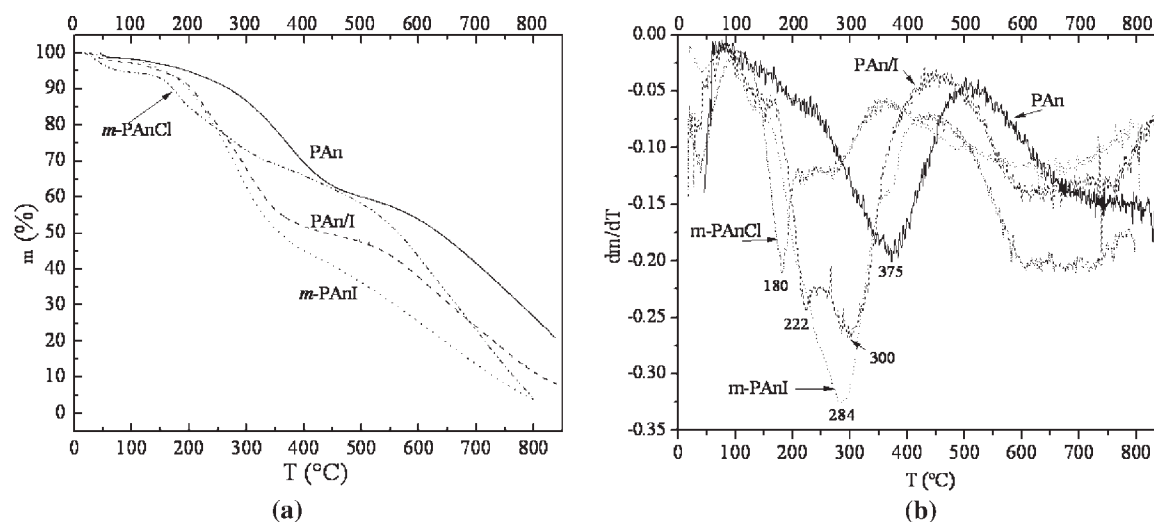


Figure 5 Thermal decomposition of halogenated polyanilines. (a) Thermal decomposition. (b) Derivative of thermal decomposition.

mogravimetric analyzer in a nitrogen atmosphere with a 10°C/min ramp in the 20–800°C interval.

The first loss in all polymers is found in the 20–100°C interval and can be associated to the water and solvent molecules trapped in the structure. After this region, the true decomposition of the material begins. Table II contains the percentage in mass and the temperature intervals of each decomposition stage for all polymers studied in this work.

The first decomposition in PAn, located from 100 to 230°C, can be originated from the escape of the short chains, which is ~ 5% of the total mass. The second decomposition is centered at 375°C and ends at ~ 500°C. This region contains 33% of the total mass and represents the medium-size chains. The last decomposition starts after 500°C and comprehends the greater polymer chains, which are ~ 60% of the total mass. The three decomposition stages can be seen in Figure 5(b).

The halogenated polymers have the first decomposition in the 100–160°C interval. However, considering that some of these chains have an additional mass due to the halogen atoms linked physically or chemically to them, these polymers have a more pronounced mass loss than PAn in this temperature interval.

The thermograms show that the iodine polymers, PAn/I and *m*-PAnI, follow very similar main decomposition trend in the 160–430°C interval, albeit *m*-PAnI loses more mass than PAn/I, at the same temperature. Nevertheless, the fact that PAn/I has the iodine atoms linked in a plasma doping process and *m*-PAnI has the iodine atoms chemically bonded from the monomer molecules, gives PAn/I a bimodal decomposition centered at 222°C and 300°C, respectively. The first decomposition of PAn/I in this region could be associated more predominantly with the iodine content, 18%, and the second decomposition with the halogenated medium-size chains, 26%. In turn, *m*-PAnI decomposes in only one trend, centered at approximately 284°C, which includes small free iodine content and the medium chains having a 52% loss mass. The one-modal decomposition in *m*-PAnI also indicates that their molecules are more stable than those of PAn/I. The high power used in the synthesis of *m*-PAnI does not induce a multimodal decomposition, which could arise from the release of halogens and/or from many fragments of polymer. The last decomposition associated with the greater polymer chains begins after 430°C following an almost linear decomposition tendency in both iodine polymers.

TABLE II
Mass Loss (wt %) in Halogenated Polymers

| Polymer | Water and solvents | Chains | | | Halogen |
|-----------------|--------------------|-------------|--------------|-----------|--------------|
| | | Short | Medium | Long | |
| PAn | 2 (20–100) | 5 (100–230) | 33 (230–500) | 60 (500–) | – |
| PAn/I | 3 (20–100) | 3 (100–165) | 26 (165–450) | 50 (450–) | 18 (165–265) |
| <i>m</i> -PAnI | 2 (20–100) | 3 (100–155) | 52 (155–420) | 43 (420–) | * |
| <i>m</i> -PAnCl | 5 (20–100) | 2 (100–145) | 15 (210–360) | 68 (360–) | 10 (145–210) |

Values inside parentheses indicate the temperature interval in °C.

* Included in the medium chains loss.

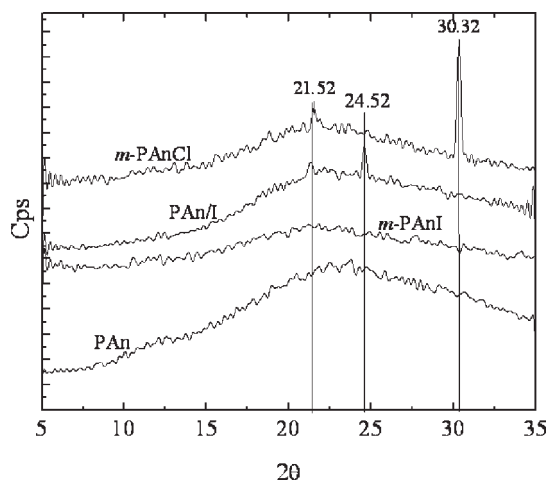


Figure 6 X-ray diffraction of halogenated polyanilines.

m-PAnCl presents a slightly different decomposition profile having a faster decay than the other polymers with respect to temperature. Between 20 and 100°C it loses 5% of humidity. In the 145–360°C interval, the free halogen fraction and most medium polymer molecules are lost.¹⁷ There are two decomposition trends in this region; the first one ends at 210 and is centered at 180°C, which can be associated with the release of free chlorine atoms representing ~10% of the total mass. The second one, which is wider, is located from 210 to 360°C and can be related with the loss of the medium chains of polymer, 15% of mass. After that point, the decomposition is faster up to 800°C, where about 96% of the mass is lost.

The free halogen fraction found in *m*-PAnI and *m*-PAnCl can be seen as a physical doping element in the polymers that starts from the release of halogen atoms because of the collisions with the particles in the plasma. Part of these atoms is trapped in the chains and another fraction leaves the reactor through the vacuum system.

CRYSTALLINITY

Plasma polyanilines are considered mainly amorphous polymers with small crystallinity when iodine or chlorine participates in its structure (Fig. 6). In this work, the crystalline percentage of the polymers has been calculated from the comparison between the amorphous and crystalline area signals taken from X-ray diffraction scans produced by means of a Siemens D-500 diffractometer. The polymers used in this analysis were synthesized during a 180 min reaction time.

PAn/I yields small diffraction peaks at 21.5° and 24.5°, which coincide with those reported for polyanilines^{21–22} and presents, approximately, 6% of crystallinity. The *m*-PAnI spectrum shows a predominant

amorphous structure with an ~2% of crystallinity. In *m*-PAnCl, the amorphous structure includes an additional diffraction peak at 30.3° which increases the crystallinity up to 11%. In this case, the chlorine content promotes the additional crystallinity in the polymer and more ordered polymers should have higher electric conductivity.

ELECTRIC CONDUCTIVITY

The polymer electric conductivity was calculated on the basis of resistance measurements using a two-probe capacitive arrangement with two copper electrodes. The polymers were placed in the middle of the electrodes, powered at less than 10 V. The resistance can be affected by the hollow sections among the layers; however, no corrections were made to compensate this effect provided that we tried to evaluate the volumetric conductivity taking into consideration all the characteristics of the polymers.

Figure 7 shows the electric conductivity of polyanilines as a function of the reaction time. At a 60 min reaction, the conductivity of PAn reached 2.5×10^{-12} S/cm increasing slightly up to 3×10^{-11} at 300 min. PAn/I have a different evolution. At 60 min, the conductivity is 1.6×10^{-9} S/cm, which is three orders of magnitude greater than that of PAn at the same reaction time.

From a global point of view, at longer times the conductivity decreases approximately two orders of magnitude to 2.2×10^{-11} S/cm at 300 min. In this case, the dopant helps to increase the electric conductivity at low reaction times, but, at longer times, the potential fragmentation, ramification and crosslinking developed during the synthesis reduce the possibility of charge transport along the polymer. At 60 min of reaction, the *m*-PAnI conductivity is 10^{-4} S/cm and decreases to 10^{-6} S/cm at 180 min. The conductivity

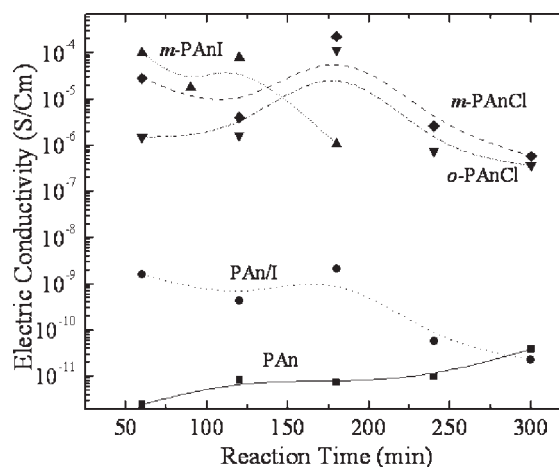


Figure 7 Electric conductivity of halogenated polyanilines as a function of the reaction time.

of *m*-PAnCl at 60 min is 1.5×10^{-5} S/cm and decreases slightly to 5.8×10^{-7} S/cm at 300 min.

It is important to observe the level of conductivity reached by the halogenated polymers. At low reaction times, their conductivity increases up to eight orders of magnitude with respect to PAn without doping. Such level of conductivity can be the result of the electronegativity induced by the halogens and the more "linear" polymer structure obtained. The latter can be better understood by considering that one of the possible positions (*meta*) of the aniline rings, where the chains can grow to form a networked polymer, is already occupied by the halogen atoms.

A second relevant consideration is that the conductivity of the halogenated polymers decreases slightly with the reaction time, conversely to the polymer behavior without doping. The ultimate crosslinking and ramification resulting from a long synthesis can be responsible for that reduction in conductivity.

CONCLUSIONS

Halogens can contribute to increase the electric conductivity in polymers synthesized by plasma. Some halogenated polymers acquire different properties according to the chemical nature of their starting monomer and to their doping mechanism. Thus, PAn doped by plasma with iodine exhibits a conductivity three orders of magnitude higher than that of PAn without doping. When the halogens are chemically bonded to the monomers, the conductivity improves up to eight orders of magnitude within the polymerization time studied, reaching 10^{-4} S/cm. This is one of the highest conductivity values achieved in polymers synthesized by radiofrequency plasmas.

The structure is mainly amorphous in all plasma polyanilines. However, *m*-PAnCl presents a small level of crystallinity that reaches up to 11%. It is possible that chlorine helps to form small crystalline arrangements. Yet, this effect does not take place when iodine participates in the polymers. The growing rate of the plasma polymers depends on the reaction time

and on the size of the dopant molecules. The halogens bonded to the initial monomers produce films with more compact layers, which can be associated to structures with less fragmentation and ramification than those found in the polymers developed from nonsubstituted monomers. Iodine dopants make fast growing polymers. PAn, *m*-PAnI, and *m*-PAnCl display compact layers stacked with small spaces in between.

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