Synthesis and in situ FTIRS characterization of conducting polymers obtained from aminobenzoic acid isomers at platinum electrodes

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Abstract

The electrochemical homo-polymerization of o-, m- and p-aminobenzoic acids has been performed on Pt electrodes in perchloric acid aqueous medium by cyclic scanning of the potential. Different limit potentials were employed to obtain thin polymeric films. When the switching potential was extended beyond the respective monomer oxidation peak, a rather degraded material was obtained. In situ FTIR spectroscopy has been used to characterize the redox response of films synthesized at the lower potential limits. Characteristic absorption features related with benzenoid and quinoid rings and different types of C-N bonds suggest the presence of redox processes similar to those undergone by the parent compound polyaniline. In addition, the existence of a chemical interaction between -COOH and -NH- groups in the reduced state of the three homopolymers studied can be suggested. Carbon dioxide has been detected at potentials higher than 1.0 V (RHE) irrespective of the polymeric material, thus indicating its degradation.

Keywords: Aminobenzoic acid; Electropolymerization; Cyclic voltammetry; in situ FTIR spectroscopy

1. Introduction

Organic conducting polymers can be switched reversibly between their conducting and insulating redox states through electrochemical oxidation/reduction processes [1]. Such reactions induce the exchange of counter-ions with the electrolytic medium in order to preserve the electroneutrality of the organic film. In particular, it is known that the electrochemical oxidation of polyaniline (Pani) from the leucoemeraldine insulating form to the emeraldine conducting form is associated with the penetration of electrolyte anions within the polymer matrix [2]. It is expected that a number of future applications of Pani take advantage of this exchange ability. However, the commercial use of this material is limited by its poor processability and low operation pH range inherent to the pristine polymer [1–3].

In order to obtain a more processable material that can be dissolved in common solvents, or even in aqueous medium, the modification of the Pani chemical structure is necessary by, for instance, the introduction of some...
hydrophilic groups [1,3]. There exist two synthesis routes to achieve the chemical modification. On the one hand, a pristine Pani can be prepared through the chemical polymerization of the aniline monomer and, subsequently, the desired chemical modification of the polymer can be performed, see for example [4,5]. A second possibility is the direct synthesis of the material by chemical or electrochemical polymerization of the adequate substituted aniline monomer [6-8]. It has been reported that both procedures can yield more soluble materials, although the conductivity of the modified polymers decreases significantly, even by several orders of magnitude, compared with that of Pani [4,8-10].

The modification of the chemical structure of Pani has been also employed to widen the pH range within which the polymer is electrochemically active. It is known that, for the original polymer, the electroactivity is restricted to solutions of very low pH because a high protonation degree at the imine nitrogen atoms is needed [11]. In this way, the insertion of acidic groups in the polymer backbone could change the microenvironment of the imine centers, shifting the local pH to lower values. This hypothesis has deserved some critical comments [8], although it seems supported by the experimental result showing that Pani modified with either sulfonic or carboxylic substituents is able to keep partially its electroactivity in solutions of pH 7 and 10, respectively [4,8]. It is also worth mentioning that, additionally, the insertion of these kind of substituents results in the modification of the ion exchange properties of the film: sulfonated or carboxylated polyanilines are known to act as self-doped Pani derivatives [10]. In these materials, the anionic groups bonded to the hydrocarbon chain can compensate the positive charges generated along the polymer backbone during the oxidation processes. Consequently, the anions of the electrolyte do not penetrate the film and the excess of positive charge is eliminated by the expulsion of protons out of the organic matrix.

Despite the extensive literature dealing with the synthesis and characterization of sulfonated polyanilines, few papers pay attention to their parent carboxylated derivatives [12-21]. In addition, most of those reports are devoted to the study of the copolymers formed by either chemical or electrochemical polymerization of anilines and o-aminobenzoic acid (anthranilic acid) [12,13,15,17,21]. A comparison between the homopolymers synthesized electrochemically from o-, m- and p-aminobenzoic acids was reported for the first time by Thiemann and Brett [18,19]. The polymerization was carried out on glassy carbon and ITO electrodes and several ex situ characterization techniques were employed. They concluded that homopolymers derived from aminobenzoic acids are short-chain polymeric materials with a voltammetric behavior different from that displayed by polyaniline. Unfortunately, and probably due to the slow rate of electropolymerization, the IR characterization of the homopolymers was not done.

The spectroscopic study was limited to ex situ IR measurements of the copolymers formed from o-, m- and p-aminobenzoic acids with aniline for reactant ratios of 1:1.

The present contribution aims to characterize homopolymers of aminobenzoic acids at the molecular level and in the electrochemical environment by means of a powerful technique such as the in situ FTIR spectroscopy. Since this characterization tool allows to obtain vibrational information from very small amounts of material, it is believed that it could serve as an improved alternative to obtain direct spectroscopic information from polyaminobenzoic acids. In this way, the in situ FTIRS method could allow the problems associated to the copolymerization of polyaminobenzoic acids with aniline to overcome.

2. Experimental

The monomers employed for the polymerization reaction were of reagent grade supplied by Merck. The electrolytic medium used for the synthesis and the electrochemical characterization of the polymeric materials was a 0.1 M HClO₄ in ultrapure water (18.2 MΩ cm). The in situ FTIR experiments were also carried out in perchloric acid aqueous solutions but using either 99.99% D₂O (Aldrich) or 18.2 MΩ cm H₂O as solvents.

The working electrode for the voltammetric study was a spherical polycrystalline platinum electrode with an area of about 4 mm². For the in situ spectroscopic characterization, the polymers were grown up on a mirror-polished platinum disk electrode. The counter electrode was a platinum wire in all cases. All potentials were measured against a reversible hydrogen electrode (RHE) immersed in the working solutions through a Luggin capillary. The bare Pt working electrode was thermally cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water. Then, it was transferred to the working solution which was previously deaerated by bubbling N₂. Cyclic voltammograms were recorded at 50 mV s⁻¹ and at room temperature. After polymerization, the working electrode was extracted from the electrochemical cell, thoroughly rinsed with water to remove any attached monomer species and transferred to a clean background solution containing 0.1 M HClO₄ (free of any monomer) to be characterized by voltammetric or spectroscopic techniques.

A Nicolet Magna 850 spectrometer was employed for the in situ FTIR experiments. The spectroelectrochemical cell was provided with a prismatic CaF₂ window beveled at 60°. The interferograms were acquired with the working electrode surface pressed against this window.
and were collected at 8 cm⁻¹ resolution. The final spectra are presented in the usual form ΔRR/R, for which, positive-going (upward) bands are related with vibrational modes that disappear (or become inactive) at the sample potential. On the contrary, negative-going (downward) bands are displayed when the related vibration mode develops (or becomes active) at the sample potential.

3. Results and discussion

3.1. Electrochemical study

The electrochemical polymerization of the three aminobenzoic acid isomers was carried out in 0.1 M HClO₄ solutions containing, respectively, 10 mM of the corresponding monomer. The platinum working electrode was immersed in the polymerization media at a controlled potential of 0.06 V in order to avoid the initial oxidation of the monomeric species. Fig. 1(a) shows a single potential excursion performed between 0.06 V and 1.6 V in solutions containing o-aminobenzoic acid. The onset of its oxidation occurs at around 1.05 V and, after displaying a shoulder, the current reaches a maximum at 1.24 V. After this peak has been surpassed, an overlapped voltammetric wave of lower intensity is also recorded. Finally, the current falls continuously until the upper potential limit is reached. This voltammetric behavior contrasts with that recorded, under the same experimental conditions, during the oxidation of m-aminobenzoic acid, Fig. 1(b), and p-aminobenzoic acid, Fig. 1(c). Firstly, the initial stages of the electrochemical oxidation of the two latter species are shifted 80 mV to more positive potentials with respect to the o-aminobenzoic isomer. Furthermore, the main anodic feature for these monomers peaks at around 1.3 V in both cases. This value represents a close to 50 mV positive shift in the absence of current shoulders. Finally, the existence of a second anodic maximum (similar to that recorded for the ortho isomer) peaked at 1.48 V for the m-aminobenzoic and at 1.38 V for the p-aminobenzoic acid isomer can also be observed in their respective voltammetric curves.

The fact that the ortho-substituted monomer is oxidized at lower potentials seems to reflect a higher stability of the meta and para substituted anilines compared to the former isomer. This seems to be supported by the results shown in Table 1, for which, the oxidation charge recorded under the voltammetric curves decreases in the order ortho > para > meta, thus pointing that the electrochemical reactivity increases oppositely, i.e. from the meta to the ortho isomer. It should be noted that, due to the slow rate of polymerization, the voltammetric charge measured for each curve corresponds essentially to the oxidation of the respective monomeric species, with negligible contribution of the polymeric products. Thus, it would be expected that the polymer obtained from the o-aminobenzoic acid oxidation could reach higher thickness at identical polymerization times and lower potential.

Poly(aminobenzoic acid) films have been synthesized by cyclic scanning of the potential between 0.06 V and three different switching potentials. This experimental strategy has been followed in order to assess the role

| Table 1 |
| Potentials for the onset of monomer oxidation, potentials of the anodic main peaks and voltammetric charge measured for the oxidation of o-, m- and p-aminobenzoic acids |
| $E_{\text{onset}}$ (V) | $E_{\text{peak}}$ (V) | $Q_{\text{oxidation}}$ (μC) |
| o-Aminobenzoic acid | 1.05 | 1.24 | 1680 |
| m-Aminobenzoic acid | 1.13 | 1.28 | 1230 |
| p-Aminobenzoic acid | 1.13 | 1.29 | 1540 |

* Calculated from 1.0 to 1.6 V and without double layer capacity correction.
played by the upper potential limit reached during the synthesis in the electrochemical properties of the deposited polymers. A higher potential limit in the CVs makes it possible to synthesize larger amounts of material keeping constant the number of sweeps done. However, the use of very high potentials could affect the quality (electroactivity, degradation level, etc.) of the obtained polymer. Accordingly, it would be desirable to reach a compromise between the polymerization rate and the required film quality. The switching potentials we selected are marked with arrows in Fig. 1 for each monomeric species. The first upper potential limit was located just before the respective first anodic peaks. The second limit was set at around 1.4 V, that is after the main anodic peak and, finally, the polymers were also synthesized by scanning of the potential up to 1.6 V. The voltammetric response of poly(o-aminobenzoic acid) synthesized after 25 potential cycles up to 1.2 V (a), 1.37 V (b) and 1.6 V (c) are shown in Fig. 2. Following the synthesis process, the electrodes coated with the polymeric films were rinsed with water and then immersed in the background electrolyte free of monomer at 0.06 V. The electrochemical behavior of the films was tested in the 0.06–1.0 V potential range. From the voltammetric responses depicted in Fig. 2 it can be observed that the potential limit of 1.2 V generates an electroactive film with, at least, two distinct redox processes. The first one appears at 0.48/0.42 V, which results in a peak separation, $\Delta E_p$ close to 60 mV; the second process is observed at 0.73/0.57 V and gives a $\Delta E_p = 160$ mV. This voltammetric profile contrasts with those recorded for the polymers grown up to 1.37 V and 1.6 V, for which no redox response can be observed in Fig. 2(b) and (c). From this result it can be inferred that the potential cycling beyond the limit corresponding to the main anodic peak at 1.24 V in Fig. 1(a) results in the generation of non-electroactive poly(o-aminobenzoic acid) films, probably as a consequence of their degradation.

Fig. 3 shows the cyclic voltammograms recorded for poly(m-aminobenzoic acid) for a similar experiment to that shown in Fig. 2. The synthesis of the polymeric film was concluded after 25 potential cycles up to 1.25 V (a), 1.4 V (b) and 1.6 V (c). Contrary to what is observed for

![Fig. 2. Voltammetric response of poly(o-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO₄ containing 10 mM o-aminobenzoic acid at the following potential limits: (a) 1.2 V; (b) 1.37 V; (c) 1.6 V. Scan rate 50 mV s⁻¹.](image1)

![Fig. 3. Voltammetric response of poly(m-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO₄ containing 10 mM m-aminobenzoic acid at the following potential limits: (a) 1.25 V; (b) 1.4 V; (c) 1.6 V. Scan rate 50 mV s⁻¹.](image2)
the poly(o-aminobenzoic acid), the voltammetric curves displayed a unique redox process at 0.64/0.53 V. Both the peak separation, $\Delta E_p = 110$ mV, and the middle potential, $E = 0.59$ V, are similar in the three cases. Additionally, the intensity of the redox peaks in Fig. 3 indicates that those poly(m-aminobenzoic acid) films whose synthesis has been restricted at potentials lower than that of the main anodic peak in Fig. 1(b) are more electroactive. This is in agreement with the behavior of the parent poly(o-aminobenzoic acid). The middle potential value of the redox process of poly(m-aminobenzoic acid) is shifted around 140 mV to higher potentials in relation to the first process recorded for the parent polymer in Fig. 2. Such a result seems to indicate that the polymer generated from the meta isomer is considerably more difficult to oxidize than that derived from the ortho species. This could be interpreted as a consequence of the existence of different degradation and branching levels, but also to the presence of polymer chains with shorter length in poly(m-aminobenzoic acid). In fact, assuming a head-to-tail coupling as the main path to grow the polymeric chains, both the ortho and meta isomers should produce polymers with quite similar chemical structure: the ortho position with respect to one carboxylate group at a given monomeric unit (which is occupied by a nitrogen atom) would be located in meta with respect to the carboxylate group of the neighboring unit. This picture is the same for both "ideally grown" polymeric chains, as can be clearly observed in Scheme 1.

Finally, we have examined the redox behavior of those films generated from the electrochemical polymerization of p-aminobenzoic acid at 1.25 V, 1.37 V and 1.6 V. Since the para position is occupied in this monomeric species, the polymerization process should proceed either through the ortho or meta position, or by a combination of both. Consequently, the chemical structure of the film formed is expected to be quite different from that of poly(om-aminobenzoic acids). Fig. 4 shows the voltammetric behavior recorded between 0.06 V and 1.0 V for the films obtained according to Fig. 1(c). Again, only the polymeric material synthesized by cyclic scanning of the potential up to 1.25 V displays a clear redox process. In particular, the voltammetric profile shows that the anodic part of the redox process seems to be split into two overlapping peaks centered at 0.63 V and 0.73 V. On the contrary, the cathodic branch of the cyclic voltammogram displays only a single peak, which is centered at 0.57 V and involves an electrical charge corresponding to, approximately, the sum of the two anodic peaks (69.5 $\mu$C for the oxidation and 69.3 $\mu$C for the reduction cycle in the 0.5–0.9 V potential range).

### 3.2. In situ FTIR spectroscopic study

The previous voltammetric study suggests that only small amounts of polymerization products can be isolated on the surface of the Pt working electrodes from the oxidation of aminobenzoic acid isomers. In spite of this fact, the high sensitivity of the in situ FTIR spec-

### Scheme 1.

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[Chemical structures of o-aminobenzoic acid, poly(o-aminobenzoic acid), m-aminobenzoic acid, and poly(m-aminobenzoic acid) are shown here.]
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The voltammetric response of poly(p-aminobenzoic acid) films in 0.1 M perchloric acid background solutions. Films deposited on a Pt electrode after 25 potential cycles in 0.1 M HClO₄ containing 10 mM p-aminobenzoic acid at the following potential limits: (a) 1.25 V; (b) 1.37 V; (c) 1.6 V. Scan rate 50 mV s⁻¹.

The spectroscopy technique allows to obtain vibrational spectra of poly(o-aminobenzoic acid) with quite good S/N ratio. Fig. 5 shows a set of in situ FTIR spectra obtained for a Pt electrode covered with poly(o-aminobenzoic acid) in 0.1 M HClO₄ medium. Following the electropolymerization process the filmed electrode was transferred to the spectroelectrochemical cell which was free of any monomeric species. The electrode was then carefully pressed against the prismatic CaF₂ window and a reference spectrum was acquired at 0.2 V. After that, the potential was stepped sequentially to higher values (which are indicated in Fig. 5) and a sample spectrum was acquired at each potential. By referring each of the sample spectra to the reference collected previously it is possible to follow spectroscopically the redox transition undergone by poly(o-aminobenzoic acid). The spectra of Fig. 5 display several absorption bands whose intensities increase as the potential is shifted to more positive values, thus showing the progress of the oxidation processes with the applied potential. Characteristic positive-going bands are observed at 1676, 1505, 1310 and 1242 cm⁻¹ which are indeed related with vibrational modes concerning to the reduced form of the polymer. Moreover, downward bands which appear at 1720, 1600, 1560, 1536, 1443 and 1378 cm⁻¹ are related to vibrations coming from the oxidized state of the polymer. It should be noted the formation of carbon dioxide at 1.0 V (band at 2344 cm⁻¹), which reveals the overoxidation (and degradation) of the polymeric material at that potential. The preservation of the carboxylic group in the chemical structure of the polymer is evidenced by the presence of the 1676 cm⁻¹ (reduced form) and 1720 cm⁻¹ (oxidized form) absorption bands. The significant shift in the peak frequency for this band upon oxidation (more than 40 cm⁻¹ to higher energies) can be due to the existence of chemical interaction between the carboxylic and the amino groups in the reduced state of poly(o-aminobenzoic acid). It is well known that this kind of interaction decreases considerably the C=O stretching frequency of aryl carboxylic acids with amino or hydroxyl groups in the ortho position [22]. Thus, when the polymer is oxidized, amine nitrogens transform into protonated imines and the C=O stretching frequency returns to its characteristic value, which is higher than 1700 cm⁻¹. This situation is illustrated in Scheme 2.

In order to facilitate the band assignments, the experiment of Fig. 5 was reproduced in 0.1 M HClO₄/D₂O. The use of D₂O solvent allows the "mobile" acid H atoms of poly(o-aminobenzoic acid) to be replaced by D atoms (H/D ratio is about 0.001 in the electrolytic...
As a result, the amino and carboxyl groups of the polymer will be deuterated whereas ring hydrogens will remain unchanged. The spectra obtained in deuterated water are displayed in Fig. 6. Here it is observed the shift of several absorption features to lower energies. Table 2 summarizes the peak frequencies observed for both the reduced and oxidized states of the polymer and includes the proposed band assignments in both solvents. Some remarkable features of the reduced state are that both the carboxylic C=O and the aromatic C–C stretching vibrations are slightly red shifted upon deuteration, whereas the effect of deuteration on the benzenoid ring deformation and amine C–N stretching seems more significant. Also, the broad positive-going absorption peaked at 1372 cm\(^{-1}\) in Fig. 6 which could be tentatively associated with the C–H bending mode in benzenoid rings, cannot be paired easily with any feature of the spectra collected in H\(_2\)O. An explanation of this result can be that the 1400–1350 cm\(^{-1}\) spectral region has several contributions in H\(_2\)O medium (from both the oxidized and reduced state of the polymer). In this way, the disappearance of the 1372 cm\(^{-1}\) mode is visible only in D\(_2\)O solvent, for which this frequency range is quite free of perturbations. Regarding the oxidized form of poly(o-aminobenzoic acid), the negative-going bands observed in H\(_2\)O and D\(_2\)O can be easily paralleled. Thus, imine (1600 cm\(^{-1}\)) and quinoid ring C=C (doublet at 1536–1560 cm\(^{-1}\)) stretching vibrations remain almost unaltered upon deuteration. On the contrary, C–N bonds with quinoid character which appear at around 1400 cm\(^{-1}\) in H\(_2\)O seem to be downshifted in D\(_2\)O.

![Scheme 2.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignments</th>
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</thead>
<tbody>
<tr>
<td>Reduced state</td>
<td></td>
</tr>
<tr>
<td>1676</td>
<td>Carboxylic acid (C=O) stretching</td>
</tr>
<tr>
<td>1505</td>
<td>Aromatic (C–C) stretching</td>
</tr>
<tr>
<td>1372</td>
<td>(C−H) bending</td>
</tr>
<tr>
<td>1310</td>
<td>Benzenoid ring deformation</td>
</tr>
<tr>
<td>1242</td>
<td>Benzenoid (C–N) stretching</td>
</tr>
<tr>
<td>Oxidized state</td>
<td></td>
</tr>
<tr>
<td>1720</td>
<td>Carboxylic acid (C=O) stretching</td>
</tr>
<tr>
<td>1600</td>
<td>Imine (C=N) stretching</td>
</tr>
<tr>
<td>1560-30</td>
<td>Quinoid ring (C=C) stretching</td>
</tr>
<tr>
<td>1480-40</td>
<td>Quinoid (&gt;C=N=) stretching</td>
</tr>
<tr>
<td>1378</td>
<td>Intermediate order (C–N) stretching</td>
</tr>
<tr>
<td>1124</td>
<td>Cl(_4)</td>
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</table>

Fig. 6. In situ FTIR spectra collected during the oxidation of a poly(o-aminobenzoic acid) film in 0.1 M HClO\(_4\)/D\(_2\)O solution. Reference potential 0.2 V. Sample potentials indicated for each spectrum. 100 interferograms were recorded at each potential. 8 cm\(^{-1}\) resolution.
The negative-going band at 1120 cm\(^{-1}\) which overlaps the quinoid C-H in-plane bending is clearly assigned to perchlorate anions, which penetrate the film to compensate the positive charges generated during the oxidation process. It should be noted that, in strongly acidic medium, the protonated carboxylic group is not able to balance the charge by itself.

The assignment of the characteristic vibrational bands for poly(o-aminobenzoic acid) facilitates the identification of the absorption features in the spectra collected for poly(m-aminobenzoic acid). Fig. 7 shows a set of in situ FTIR spectra obtained in the 1100-2500 cm\(^{-1}\) spectral region for the latter material in a parallel experiment to that shown in Fig. 5. Similarly to poly(o-aminobenzoic acid), the presence of two different absorptions for the carboxylic C=O stretching vibration at 1700 cm\(^{-1}\) (reduced) and 1729 cm\(^{-1}\) (oxidized form) reveals the existence of chemical interaction between the –COOH and –NH groups in the reduced state of the polymer. Negative-going absorption bands in the vicinities of 1550 cm\(^{-1}\), which are ascribed to the formation of C=C structures, in addition to the disappearance of the C-C stretching mode at ca. 1500 cm\(^{-1}\) reveal the loss of aromatic character at the benzenoid rings and their transformation into quinoid centers as the potential is made more positive. Moreover, different C=N vibrational features related with amine, imine or intermediate order bonds can be also observed in this spectra. From the similarities found between the spectra shown in Fig. 7 and those in Fig. 5, it can be concluded that, from an spectroscopic standpoint, the redox process of poly(m-aminobenzoic acid) is rather similar to that occurring in the parent poly(o-aminobenzoic acid).

Finally, Fig. 8 shows the in situ FTIR spectra collected during the anodic polarization of a Pt electrode covered with a poly(p-aminobenzoic acid) film. Characteristic infrared absorptions in the 1200-1500 cm\(^{-1}\) and in the 1650-2500 cm\(^{-1}\) spectral ranges are similar to those displayed by both poly(o-aminobenzoic acid) and poly(m-aminobenzoic acid). In particular, it is clear that the three polymeric films undergo a degradation reaction yielding CO\(_2\) (band at 2344 cm\(^{-1}\)) at potentials higher than 1.0 V. Moreover, the chemical interaction between adjacent amino and carboxylic groups seems to be supported by the bipolar character of the absorption centered at around 1700 cm\(^{-1}\) which is due to the C=O stretching mode. However, an interesting difference appears between the spectra of Fig. 8 and those of Figs. 5 and 7. Contrary to its parent polymers, the spectra obtained during the oxidation of a poly(p-aminobenzoic acid) film are dominated by the vanishing of a vibrational mode at 1609 cm\(^{-1}\). Both the frequency and the positive character of this clear-cut band agree with the disappearance of either an N-H deformation vibrational mode of a primary aromatic amine or a C=C stretching of aromatic rings. The first possibility implies, necessarily, the presence of significant amounts of free amino groups in the chemical structure of this polymeric film.
This would mean that poly(p-aminobenzoic acid) is composed of large numbers of short-chain oligomeric species (probably no longer than trimers or tetramers) each one having a primary amino group at the end.

The second hypothesis means the existence of diverse vibrational modes for the aromatic ring C–C stretching because the transformation of benzenoid rings into quinoid ones is indeed testified by the existence of a positive-going band at 1520 cm\(^{-1}\) and its coupled negative-going band near 1560 cm\(^{-1}\). It is very difficult to ascertain which hypothesis reflects the real situation but experiments performed using D\(_2\)O as solvent have revealed the presence of a positive-going feature with lower intensity centered at 1605 cm\(^{-1}\) (figure not shown).

Since the amine hydrogen atoms could be exchanged with electrolyte deuterons, the result suggests that the electroactive. 1609 cm\(^{-1}\) vibrational mode should be better ascribed to a C–C stretching of benzenoid rings.

Regarding the possible structure of poly(p-aminobenzoic acid), the following points should be considered: (i) carboxylic groups are electron withdrawing substituents and deactivate the aromatic ring directing the substitution to the position meta to them (this would yield an ortho-substituted polymer with respect to the amino group); (ii) it seems rather difficult for the p-aminobenzoic acid monomer to undergo a para coupling reaction similar to that found for polyaniline because IR spectroscopy indicates that most of the carboxylic groups are kept in the polymer structure after the polymerization. Then, the existence of significant amounts of para-substituted chains has to be discarded; (iii) on the other hand, the chemical interaction between –COOH and –NH groups observed by in situ FTIR spectroscopy would be only possible if both functionalities were in ortho position. As the latter hypothesis seems supported by an experimental result, we propose that the preferential growth of poly(p-aminobenzoic acid) could take place via the incorporation of p-aminobenzoic monomers at the ortho position to the carboxylic group, as shown in Scheme 3, although contribution of meta-substituted rings to the real polymer structure cannot be discarded.

### 4. Conclusions

The electrochemical homo-polymerization of ortho, meta and para aminobenzoic acid isomers has been performed in strongly acidic medium on platinum electrodes under similar experimental conditions. It has been observed a strong effect of the switching potential on the film quality (degradation level) for the three polymers investigated. Those films generated at moderate potentials (below the first anodic maximum) are more electroactive.

In situ FTIR spectroscopy has revealed that the three polymeric materials degrade yielding CO\(_2\) when submitted at potentials higher than 1.0 V (RHE), at least if a substrate of platinum is employed. This means that the electrochemical synthesis is a process in which polymerization and degradation reactions are coupled because the lower potential limit required to produce the oxidation of the monomeric species is around 1.1 V. The unexpected low frequency observed for the C=O stretching mode of –COOH in the reduced state of the polymers strongly suggests that there exists a chemical interaction (hydrogen bonding) between the carboxylic and amino groups located in ortho position. When the polymers are oxidized, the carboxylic group does not interact and the C=O stretching frequency recovers the characteristic value for a carboxylic acid.

Despite the different voltammetric response shown by poly(o-aminobenzoic acid) and poly(m-aminobenzoic acid), the spectroscopic results point that both polymeric materials undergo very similar redox processes. This suggests that the chemical structure of both polymers could be similar, being the different voltammetric behavior due to the existence of different chain lengths, branching degree and degradation level. The comparison between the in situ FTIR spectra obtained for poly(p-aminobenzoic acid) and poly(o/m-aminobenzoic acids) suggests that the oxidation process of the former material involves a slightly different chemical transformation. This could be interpreted by the occurrence of coupling of monomers at the ortho position to the amino group, which would yield a polymeric structure somewhat different to that proposed for poly(o/m-aminobenzoic acids).

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