

## Electrochemical Synthesis of Poly(*o*-aminobenzoic Acid) and Poly(*o*-aminobenzoic Acid-*co*-aniline): Electrochemical and *In-situ* FTIRS Characterization

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**Abstract:** The electrochemical of *o*-aminobenzoic acid and of mixtures of aniline and *o*-aminobenzoic acid in various ratios has been performed on platinum electrodes in perchloric acid aqueous medium by cyclic scanning of the potential. Polymers are formed in all cases and the rate of polymerization is increased by the addition of aniline. The electrochemical oxidation and the polymers formed have been characterized voltammetrically, the overall observation and results indicate as the CV curves grow with the number of cycles for all electropolymerization and the structures of copolymers in block. The results of *in-situ* FTIR spectroscopy reveals the existence of chemical interaction between the –COOH and –NH groups in the reduced state of the all films studied can be suggested. A possible scheme of reaction mechanism for homo- and copolymer of 2-ABA and ANI has been suggested.

**Key words:** Aminobenzoic acid • Electropolymerization • Cyclic voltammetry • *in-situ* FTIR spectroscopy • Scanning electron microscopy.

### INTRODUCTION

Electrically conducting polymers have attracted a great deal of attention in the last few decades because of their unusual intrinsic properties. The possibility of synthesizing materials having combined properties of organic polymers and of semiconductors becomes the main interest for both the academician and industrial researchers [1-4]. Among conducting polymers, polyaniline (PANI) is the most frequently used one for commercial applications, probably due to its thermal and environmental stability [5-7]. The multi various applications for conducting polymer demand different properties and good processability. As far as PANI is concerned, its insolubility in common organic solvents and infusibility restricts processability.

Another way of reducing the pH dependence is through substituted (self doped) polyanilines, achieved by introduction of the substituent into the pre-formed polymer or by polymerization of substituted anilines.

The introduction of acidic groups as ring substituents influences the acidity constants of the amine groups and appears to offer advantages at less acidic pH values, since conductivity does not fall off dramatically with increase in pH as happens with PANI. This has been done with carboxylic [8, 9], sulphonic, e.g. [8, 10, 11] and phosphonic [12] acid substituents.

Copolymerization of aniline with some of its derivatives, which bear various functional groups leads to modified copolymers, having some remaining functionalities and possessing interesting properties. The primary advantage of copolymerization is that it leads to a homogenous material, the properties of which can be regulated by adjusting the ratio of the concentration of monomers in the feed. In this present study, aminobenzoic acids and aniline have been selected as monomers for performing electrochemical copolymerization in 0.1M HClO<sub>4</sub> medium. Cyclic voltammetry was used to deposit polymeric films on platinum working electrode and subsequent characterization. Copolymers

were synthesized and the composition of the two monomers in the copolymer and reactivity ratios of ABA and ANI were determined. Since this characterization tool allows to obtain vibrational information from very small amounts of material, it is believed that *in-situ* FTIRS could serve as an improved alternative to the copolymerization with aniline in order to obtain direct spectroscopic information from polyaminobenzoic acids.

**Experimental:** The monomer 2-ABA employed for the polymerization reaction were of reagent grade supplied by Merck. The electrolytic medium employed for the synthesis and the electrochemical characterization of the polymeric materials was 0.1M HClO<sub>4</sub> in ultrapure water (18.2 MΩ cm). The *in-situ* FTIR experiments were also carried out in perchloric acid aqueous solutions but either 99.9%-D D<sub>2</sub>O (Aldrich) or 18.2 MΩ cm H<sub>2</sub>O were used as the solvents.

#### **Electrochemical Synthesis of Homo/Copolymers:**

The electrochemical copolymerization was performed in a single compartment reaction cell fitted with platinum disk (area 4 mm<sup>2</sup>) as working electrode, a platinum wire and reversible hydrogen electrode (RHE) as auxiliary electrode and reference electrode, respectively by using (EG&G mdel), potentiostat/Galvanostat (HQ instruments mod 101). The copolymer films were deposited electrochemically on the Pt electrode surface from aqueous 0.1M HClO<sub>4</sub> solution of mixture of *o*-aminobenzoic acid and aniline by reversible cycling the potential between 0.06V and 1.20V at a constant scan rate of 50 mV/s. The cyclic voltammograms (CVs) of the growing film of copolymer were recorded continuously and coincidentally with synthesis.

Electrochemical homopolymerization of *o*-aminobenzoic acid and aniline were also performed by cyclic voltammetry in the same potential range.

**In-Situ Spectroelectrochemical Studies:** A Nicolet Magna 850 spectrometer was employed for the *in-situ* FTIR experiments. The spectroelectrochemical cell was provided with a prismatic CaF<sub>2</sub> window beveled at 60°. The interferograms were acquired with the working electrode surface pressed against this window and were collected at 8 cm<sup>-1</sup> resolution. The final spectra are presented in the usual form  $\Delta R/R$ , 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.

## **RESULTS AND DISCUSSION**

#### **Electrochemical Homopolymerization of 2-ABA:**

A solution consisting of 0.01M *o*-aminobenzoic acid and 0.1M HClO<sub>4</sub> was used for the synthesis of poly(2-ABA). The electrochemical polymerization of 2-ABA was carried out by using repeated potential cycling between 0.06V and 1.20V Fig 1. An anodic peak appears at 1.20V on the cyclic voltammogram for the first cycle and then its peak current decreases quickly with time.

During the first cathodic scan of potential less positive on polymerization an three reduction peak was observed beyond 0.80V, 0.65V and 0.51V that it shows its corresponding tips of oxidation in the second positive cycle. The peak of oxidation in the second scan positive at 0.45V, 0.65V and 0.84V. In the subsequent CVs of the three redox characteristics of the polymerization which represents the growth of poly(2-ABA).

#### **Electrochemical Copolymerization of 2-ABA and ANI:**

Fig. 2 shows the cyclic voltammograms for the electrolysis of a solution consisting of 0.01M *o*-aminobenzoic acid, 0.3mM aniline and 0.1M HClO<sub>4</sub>. An anodic peak appears a more positive potential at 1.20V for the first cycle. This peak is caused by the oxidation of 2-ABA and aniline at the platinum electrode, since the oxidation peak of 2-ABA is at 1.24V in 0.1M HClO<sub>4</sub> solution [13] and the oxidation peak of aniline in the acidic solution is near 1V for the first cycle [14]. The simultaneous oxidation of 2.ABA and ANI results in their copolymerization. There are two anodic peaks at 0.47V and 0.77V respectively, with corresponding reduction counter parts at 0.75V, 0.66V and 0.37V on each curve in Fig 2. However, three pairs of redox peaks appear on the cyclic voltammograms for the electrochemical polymerization of aniline in the acidic solution [14]. Also, the CVs of the synthesis of 2-ABA films Fig. 1, shows two pairs of redox. Thus, the charge associated with the second pair of redox peaks in the electrochemical polymerization of copolymer Fig. 2 is more important than that obtained in the synthesis of homopolymer 2-ABA the current of all peaks, increase as the number of potential cycles increases. This indicates that the copolymer film grows with time.

To study the effect of the ratio of the monomer concentration on the copolymerization rate, the concentrations of 2-ABA and HClO<sub>4</sub> were hold constant and the ANI concentration was varied. The CVs of copolymerization of the three copolymers are very similar in shape to those in Fig 2. However, the currents of all peaks in the synthesis of films increase quickly with the number of cycles and their peak currents are higher

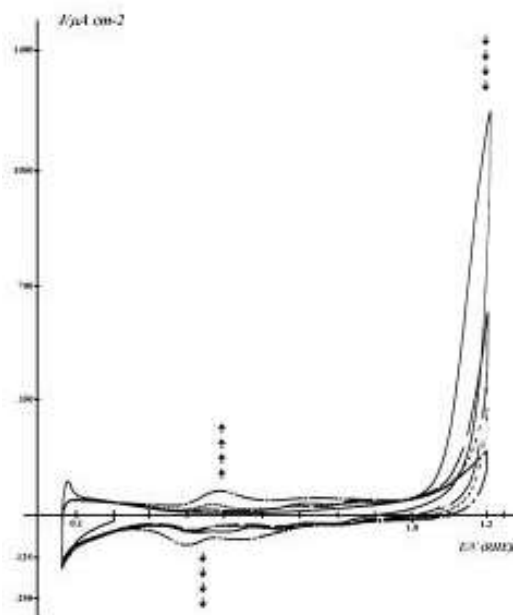


Fig. 1: Cyclic voltammograms recorded for a platinum electrode in 0.1M HClO<sub>4</sub> during the electrochemical oxidation of 10 mM *o*-aminobenzoic acid. First potential cycle (---), 2° (- - -), 5° (• • •) and 25° (-•-•-). Scan rate 50 mV s<sup>-1</sup>.

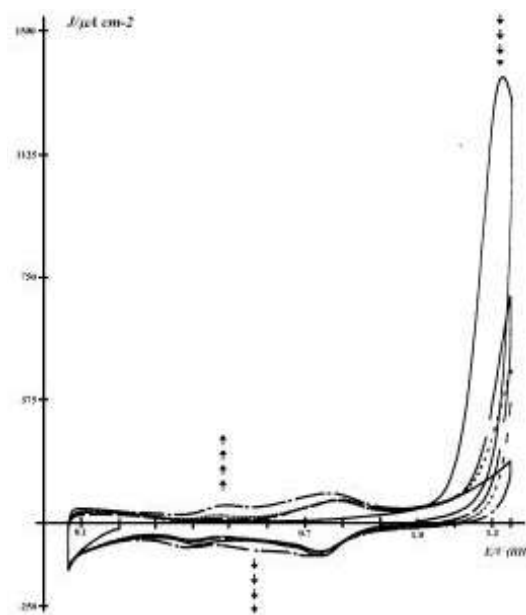


Fig. 2: Cyclic voltammograms recorded for a platinum electrode in 0.1M HClO<sub>4</sub> during the electrochemical oxidation of 10 mM *o*-aminobenzoic acid and 0.3 mM aniline. First potential cycle (---), 2° (- - -), 5° (• • •) and 25° (-•-•-). Scan rate 50 mV s<sup>-1</sup>.

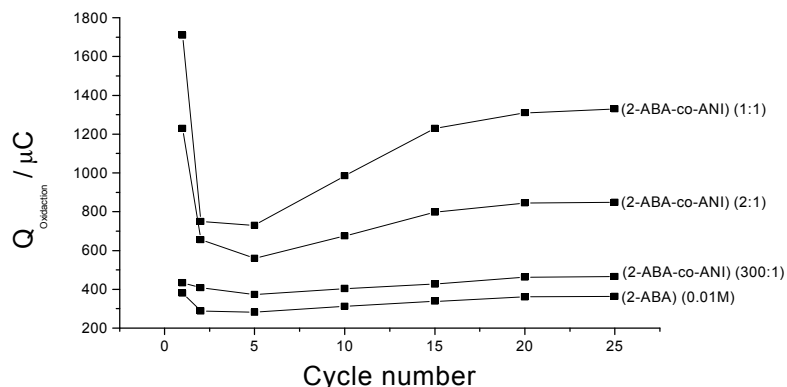


Fig. 3: Dependence of the cathodic charge on the cycle number of (2-ABA-co-ANI) films.

than those of the corresponding peaks in Fig. 2 at the same cycle. Also, the currents of all peaks on curves 1-25 in each CV recorded during the electrochemical copolymerization of 2-ABA with ANI for different feed ratios of ANI increases with increase in the amount of ANI in the feed. This indicates that the copolymerization rate in the solution containing greater amounts of ANI, the rate of film growth is much lower for the homopolymerization of 2-ABA than for copolymerization because 2-ABA inhibits film growth.

The growths of the polymers films were monitored as a function of potential cycle number by measurement of the charge under the cathodic portion of the CVs. The cathodic charge of the polymer is proportional to the thickness of the film. Fig 3. shows the cathodic charge as a function of cycle number of poly(2-ABA) and of poly(2-ABA-co-ANI).

The voltammetric response of poly(2-ABA) and the three poly(2-ABA-co-ANI) for different feed ratios of aniline as 300:1, 2:1 and 1:1 synthesized after 25 potential

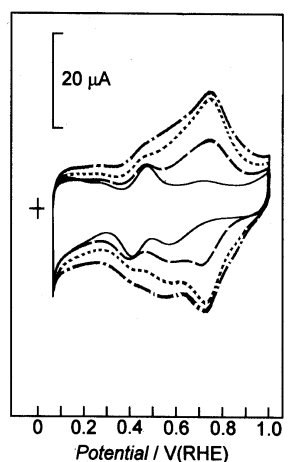


Fig. 4: Voltammetric response of polymer films formed by electropolymerization of 10 mM 2-ABA (---) and mixture of 2-ABA and ANI: 300:1 (-.-), 2:1 (•••) and 1:1 (-••-) in 0.1M perchloric acid background solutions. Films deposited on a platinum electrode after 25 potential cycles in 0.1M HClO<sub>4</sub> at the following anodic potential limit 1.2V. Scan rate 50 mV s<sup>-1</sup>.

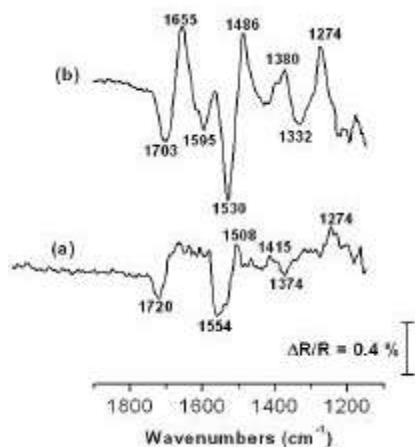


Fig. 5: *In-situ* FTIR spectra collected during the oxidation of a poly(*o*-aminobenzoic acid) film in 0.1M HClO<sub>4</sub>: (a) H<sub>2</sub>O solution and (b) D<sub>2</sub>O solution. Reference potential 0.2V. Sample potentials 0.9V. 1000 interferograms were recorded at each potential. 8 cm<sup>-1</sup> resolution.

cycles up 1.20V are shown in Fig. 4. 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 0.06V. The electrochemical behavior of the films was tested in the 0.06-1.0V potential range. From the voltammetric responses depicted in Fig. 2 it can be observed that all

electroactive films with, at least, two distinct redox processes.

In CVs recorded for poly(2-ABA) observed two processes redox at 0.48/0.42V and 0.73/0.57V. However, the currents of second pair of redox peaks are lower than those of the corresponding peaks in first redox process. Also, the two redox characteristics of homopolymer appear on each curve of copolymer clearly in Fig 4. Thus, this behavior is in contrast to the CV for poly(2-ABA), i.e. The currents of second redox process are higher of the first redox peaks. Like appear one cathodic peaks at 0.70V. However, it is clear that the currents of the anodic peak at 0.73V and the two cathodic peaks at 0.57V and 0.70V increase quickly with the higher feed ratios of ANI in the copolymer. And thus, the rate of film growth is much lower for the polymerization of 2-ABA than for the mixture of the monomers 2-ABA/ANI. On the other hand, it is interesting to note that the broad voltammetric charge increase by the increase of the amount of ANI for mixture of the monomers. In addition, appearance of redox processes for poly(2-ABA) in all CVs of poly(2ABA-co-ANI) and as appearance of all pair redox for PANI in all CVs of copolymers, this indicates as the copolymer it shows a structures "in block". That is to say, the copolymer seems formed by certain dominions in which the fraction of polyaniline is majority and others in which it is poly(2-ABA) the main component. This would explain the maintenance of voltammetric characteristics of both components in the copolymer.

**In-Situ FTIR Spectroscopic Study:** To gain further knowledge on the structure of the films formed during the electrochemical oxidation of 2-ABA and of 2-ABA with ANI at pH 1, *in-situ* FTIR spectroscopy was employed.

Figure 5 shows a set of *in-situ* FTIR spectra obtained for a Pt electrode covered with poly(2-ABA) in 0.1M HClO<sub>4</sub> medium. Following the electropolymerization process the filmed electrode was transferred to the spectroelectrochemical cell which was free of on monomeric species. The electrode was then carefully pressed against the prismatic CaF<sub>2</sub> window and a reference spectrum was acquired at 0.20V. Figs 5-a and 5-b shows the spectra of a poly(2-ABA) in 0.1M HClO<sub>4</sub> solution, in absence of 2-ABA, in water and deuterated water respectively.

The reference spectrum was acquired at 0.20V (1000 interferograms), so it contains the vibrational information corresponding to the reduced form of the film. The electrode is then polarized to 1.0V and the sample spectrum was collected. Similar bands are observed in both spectra.

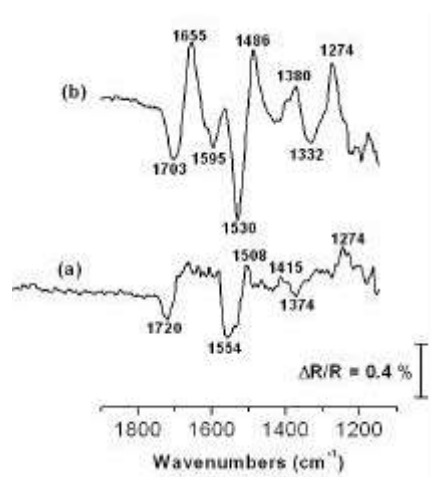


Fig. 6: *In-situ* FTIR spectra recorded during the oxidation of a poly(2-ABA-co-ANI) film, mixture (300:1) in 0.1M HClO<sub>4</sub> solution. Reference potential 0.2V. Sample potentials indicated for each spectrum. 1000 scans at each potential. 8 cm<sup>-1</sup> resolution

Figure 5-a displays several absorption bands, the bands is also present in the spectra in D<sub>2</sub>O Fig 5-b here it is observed the shift of several absorption features to lower energies. Some remarkable features of the reduced state are that both the carboxylic C=O at 1660 cm<sup>-1</sup> and the aromatic C-C stretching vibrations are slightly red shifted upon deuteration at 1489 cm<sup>-1</sup> whereas the effect of deuteration on the benzenoid ring deformation and amine C-N stretching seems more significant at 1277 cm<sup>-1</sup>. Also, the broad positive-going absorption peaked at 1372 cm<sup>-1</sup> in Fig 5-b 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<sub>2</sub>O. An explanation of this result can be that the 1400-1350 cm<sup>-1</sup> spectral region has several contributions in H<sub>2</sub>O medium (from both the oxidized and reduced state of the polymer). In this way, the disappearance of the 1372 cm<sup>-1</sup> mode is visible only in D<sub>2</sub>O solvent, for which this frequency range is quite free of perturbations. Regarding the oxidized form of poly(2-ABA), the negative-going bands observed in H<sub>2</sub>O and D<sub>2</sub>O can be easily paralleled. Thus, imine 1600 cm<sup>-1</sup> and quinoid ring C=C (doublet at 1536-1560 cm<sup>-1</sup>) stretching vibrations remain almost unaltered upon deuteration. On the contrary, C-N bonds with quinoid character which appear at around 1400 cm<sup>-1</sup> in H<sub>2</sub>O seem to be downshifted in D<sub>2</sub>O. The negative-going band at 1120 cm<sup>-1</sup> which overlaps the quinoid C-H in-plane bending is clearly assigned to perchlorate anions, which penetrate the

Table 1: Assignments of the vibrational bands for the reduced and oxidized forms of poly (*o*-aminobenzoic acid) in acidic H<sub>2</sub>O and D<sub>2</sub>O solvents [15-20]

| Frequency / cm <sup>-1</sup> |                  | Assignments                   |
|------------------------------|------------------|-------------------------------|
| H <sub>2</sub> O             | D <sub>2</sub> O |                               |
| 1676                         | 1660             | Carboxylic acid (C=O) str.    |
| 1505                         | 1489             | Aromatic (C-C) str.           |
|                              | 1372             | (C-H) bending                 |
| 1310                         | 1277             | Benzenoid ring def.           |
| 1242                         |                  | Benzenoid (C-N) str.          |
| 1720                         | 1702             | Carboxylic acid (C=O) str.    |
| 1600                         | 1599             | Imine (C=N) str.              |
| 1560-30                      | 1532             | Quinoid ring (C=C) str        |
| 1480-40                      | 1435             | Quinoid (>C=N=) str           |
| 1378                         | 1336             | Intermediate order (CLN) str. |
| 1124                         | 1121             | ClO <sub>4</sub> <sup>-</sup> |

film to compensate the positive charges generated during the oxidation process. Table 1 summarizes the peak frequencies observed for both the reduced and oxidized states of the polymer and includes the proposed band assignments in both solvents.

The spectra of Fig 6 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. To that shown in Fig. 5. Similarly to poly(2-ABA), the presence of two differ Fig 6 shows the *in-situ* FTIR spectra collected during the anodic polarization of a Pt electrode covered with a poly(2-ABA-co-ANI) film obtained in the 1100-2000 cm<sup>-1</sup> spectral region for the latter material in a parallel experiment to that shown in Fig 4. Similarly to poly(2-ABA), the presence of two different absorptions for the carboxylic C=O stretching vibration at 1656 cm<sup>-1</sup> (reduced) and 1707 cm<sup>-1</sup> (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 1532 cm<sup>-1</sup>, which are ascribed to the formation of C=C structures, in addition to the disappearance of the C-C stretching mode at ca. 1490 cm<sup>-1</sup> reveal the loss of aromatic character at the benzenoid rings and their transformation into quinoid centers as the potential is mode 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 6 and those in Fig 5, it can be concluded that, from a spectroscopic standpoint, the redox process of poly(2-ABA-co-ANI) is rather similar to that occurring in the parent poly(2-ABA).



**Comparative Reaction Mechanism:** The comparative mechanism of *o*-aminobenzoic acid oxidation and/or polymerization is described in scheme 1. The mechanism of the electrochemical polymerization of monomer is believed to proceed via a radical cation which reacts with a second radical cation to give a dimer. This reacts further with the radical cation of monomer to build up the polymer chain. In case of copolymerization, a chain might be built up by formation through conjugation of radicals of two different monomers followed by propagation (the voltammetric characteristics of copolymer films indicate as structures in block and the mechanism proposition in this case it is structures parfait). The possible reaction mechanisms for homo- and copolymerization have been given in scheme 1 and scheme 2, respectively.

### CONCLUSIONS

The cyclic voltammetric investigation clearly indicated the formation of electroactive poly(2-ABA) and poly(2-ABA) films in perchloric acid aqueous medium. In addition, the all copolymer films have a structures in block.

*In-situ* FTIR spectroscopy has revealed that the polymeric materials 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 acid amino groups located in *ortho* position.

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