Research & Reviews In

Electrochemistry

Voltammetric and *in-situ* FTIRS study of the electropolymerization of o-aminobenzoic acid at gold electrodes and graphite carbon electrodes; influence of pH on electrochemical behaviour of polymer films

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ABSTRACT

The electrochemical homo-polymerization of *o*-animobenzoic acid has been performed on gold and graphite carbon 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 graphite carbon electrodes. The polymers formed have been characterized Voltametrically, *in-situ* FT-IR spectroscopy and scanning electron microscopy were combined to study the redox behavior of the oxidation products. Characteristic absorption features related with benzenoid and quinoid rings and different types of C-N bonds point to the operation of redox processes similar to those undergone by the parent compound polyaniline. In addition, it has been suggested the existence of chemical interaction between -COOH and –NH groups in the reduced state of the homopolymer studied can be suggested. The electrochemical behaviour of the polymer films of *o*-aminobenzoic acid sample that, on the contrary that the polyaniline, is electroactive to values of pH over 3, this is due to the presence of the group -COOH in the structure of polymer. To pH superior to 5 the polymer films dissolve quickly.   © 2010 Trade Science Inc. - INDIA

INTRODUCTION

Polyaniline (PANI) has been known in a variety of forms for over a century[1,2], and as such must be considered as the oldest of the conducting polymers. It has always been at the forefront in the global search for commercially viable conducting polymers because of its unique reversible proton dopability, excellent redox recyclability, chemical stability variable electrical conductivity (which can be "tuned" by varying the pH at which it is prepared), low cost, and case of preparation.

In view of this, PANI can be used as an electrode material[3,4], in the fabrication of secondary batteries[5-7] in microelectronics[8,9], and as an electrochromic mate-

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rial[10-12]. Future high-technology applications in the area of recordable optical disks[13] and chemical sensors have also been suggested[14].

An important limitation to the application of PANI derives from the fact that on increasing the pH during electrosynthesis and during use there is a significant decrease in the conductivity of PANI films in the conducting state and the rate of polymerization is lower. These effects can be reduced to some extent by choice of appropriate counterions which enter the film (external doping), e.g.[15-19], in order to compensate the charge on the amino groups. As an alternative to the counterion strategy, co-polymerization with different monomers has been suggested.

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[20,21], sulphonic, e.g.[20,22,23] and phosphonic[24] acid substituents.

Despite the extensive literature dealing with the synthesis and characterization of sulfonated polyanilines, there are few papers paying attention to their parent carboxylated derivatives[25-33]. 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). A comparison between the homopolymers synthesized electrochemically from o-, m- and p-aminobenzoic acids was reported for the first time by Thiemann and Brett[31,32]. The polymerization was carried out on glassy carbon and ITO electrodes and several ex-situ characterization techniques were employed. It was 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 accomplished. The spectroscopic study was limited to the ex-situ IR inspection of the copolymers formed from o-, m- and p-aminoben-

zoic acids with aniline in feed ratios of 1:1.

In line with this background, the present contribution aims to characterize homopolymer of o-aminobenzoic acid 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 *in-situ* FTIRS could serve as an improved alternative to the copolymerization with aniline in order to obtain direct spectroscopic information from polyamino benzoic acids.

EXPERIMENTAL

The monomer 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 $HClO_4$, the aqueous buffer medium of the different pH was prepared from $HClO_4/NaClO_4$ solutions (Merck, p.a salts). All the solutions were made up with 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_2O (Aldrich) or 18.2 MΩ cm H_2O were used as the solvents.

The working electrode for the voltammetric study was a spherical polycrystalline gold electrode with an area of about 3 mm^2 and graphite carbon disc electrode (GC) diameter 0.5cm. For the *in-situ* spectroscopic characterization, the polymers were grown up on a mirror-polished gold 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 Au working electrode was thermally cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water and the graphite carbon electrode was polished with diamond lapping compound (Kemet International Ltd.) down to 1μm particle size on a polishing cloth. Then, it was transferred to the working solution which was previously deaerated by bubbling N_2. Cyclic voltammograms were recorded at 50 mV s^{-1} and at room temperature. After polymerization, the working
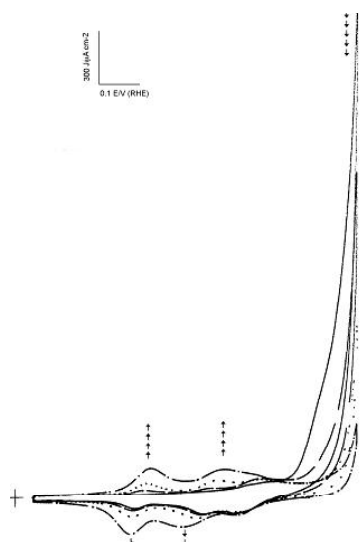
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Figure 1: Cyclic voltammograms recorded for a gold electrode in 0.1M HClO₄ during the electrochemical oxidation of o-aminobenzoic acid. Scan rate 50 mV s⁻¹
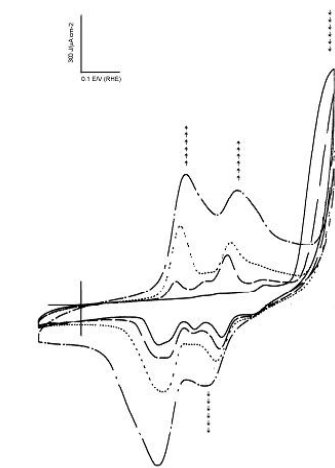

Figure 2: Cyclic voltammograms recorded for a graphite carbon electrode in 0.1M HClO₄ during the electrochemical oxidation of o-aminobenzoic acid. Scan rate 50 mV s⁻¹

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 0.1M 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 spectro electrochemical cell was provided with a prismatic CaF_2 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 $\Delta R/R$, 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.

Scanning electron microscopy (SEM) was performed on films deposited on gold electrodes with a HITACHI S-3000 N microscopy.

RESULTS AND DISCUSSION

Electrochemical study

Figures 1 and 2 show the cyclic voltammograms (CVs) recorded during the synthesis of o-aminobenzoic acid films in aqueous solutions of 0.1M HClO₄ as electrolyte at room temperature. The overall observations and results according to obtained CVs are listed below: when the applied potential is cycled to positive potential maximal, the anodic current to increase, showing that the monomer dissolved in the solution, oxidized at the surface of the electrode. The electrochemical polymerization characteristics of the monomer on the different electrodes (gold. graphite carbon) are almost the same during the first positive cycle. At higher potentials (1.20V) little oxidation takes place and there fore high anodic current flows.

Form the synthesis in the electrochemical depicted in figure 1 with, at least, two distinct redox processes. The redox potentials and current densities corresponding to these peaks for different electrode of the o-aminobenzoic acid isomer.

The cyclic voltammograms curves grow with the number of cycles for all electrodes used, in decanting the formation of conducting polymer films in cash case. Additionally, the difference between of the current density maximal during the first cycle of the oxidation of monomer and current density at the redox peaks after 25 potential cycles small in all results of the synthesis electrochemical of films on the graphite electrodes. This voltammetrie behavior contrasts with recorded, under the same experimental conditions, during the synthesis electrochemically on gold. From this it can be inferred that the electrochemical polymerization of the o-aminobenzoic acid isomer on graphite carbon to synthesis larger amounts of material.
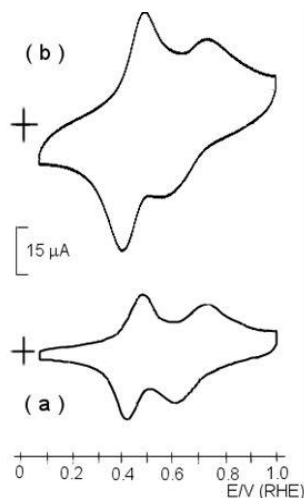
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Figure 3: Voltammetric response of poly(o-aminobenzoic acid) film in 0.1M perchloric acid background solutions. Films deposited on a: (a) gold electrode and (b) graphite carbon electrode, after 25 potential cycles in 0.1M HClO$_4$ containing 10 mM o-aminobenzoic acid at the following anodic potential limit 1.20V. Scan rate 50 mV s^{-1}

TABLE 1: Potentials for the onset of polymer oxidation, voltammetric charge measured for the oxidation of *o*-aminobenzoic acids. Calculated from 0.3 to 0.9V

Electrodes	$Q_{poly(2-ABA)}/\mu C$
Gold (Au)	95
Graphite carbon (GC)	835

The highest current densities corresponding to the anodic peaks are observed for the polymerization of graphite carbon electrode by gold electrode.

Fallowing the synthesis process, the electrodes coated with the polymeric films were rinsed with water and then immersed in the background electrolyte free of monomer. The electrochemical behavior of the films was tested in the 0.06 -1.0V potential range. Figure 3-a shows the CV recorded for a modified electrode of gold and figure 3-b the corresponding profile for o-aminobnzoic acid polymer created for graphite carbon electrode in 0.1M HClO$_4$. The CV presented in figure 3-a, it can be observed that the voltammetric response of poly(2-ABA) synthesized after 25 potential cycles

up to 1.20V[34] generates an electroactive film with, at least, two distinct redox processes. i.e, in CV of poly(2-ABA) the first one appears at 0.48/0.42V, which results in a peak separation, ΔE_p, close to 60mV; the second process is observed at 0.73/0.61V and gives a $\Delta E_p = 120$mV.

Figure 3-b shows the CVs recorded for poly(2-ABA) for a similar experiment to that shown in figure 3-a, in all cases the same voltammetric behaviour of the 2-ABA polymer was obtained on gold electrode. In addition, in figure 3-b, the charge associated with this redox couple is more important than that obtained under quiescent conditions. Consequently, a thick film is obtained after the oxidation of 2-ABA in 0.1M HClO$_4$. The reactivity of the graphite carbon electrode is probably mist important for the formation of a polymer. Therefore, the growth rate of the poly(2-ABA) on Au electrode should be slower than the on GC electrode, as observed here. The TABLE 1 shown these films prepared on different electrodes in the same condition, the polymers obtained on GC from the *o*-aminobenzoic acid isomer oxidation could reach higher thickness at identical polymerization. The resulted confirmed this observation of CVs of the oxidation during the synthesis of the 2-ABA isomer. The formation of polymer 2-ABA has also been confirmed by values of voltammetric charge.

The initiation process of the electrochemical polymerization was thought to be the formation and reactions of the cation radicals[35] and dimeric species[36]. The mechanism of the electrochemical polymerization of monomer is believed to proceed via a radical cation which reacts further with the radical cation of the monomer to build up the polymer chain. The possible reaction mechanisms for homo-polymerization have been given in Scheme 1.

In-situ FTIR spectroscopic study

The previous voltammetric study suggests that only
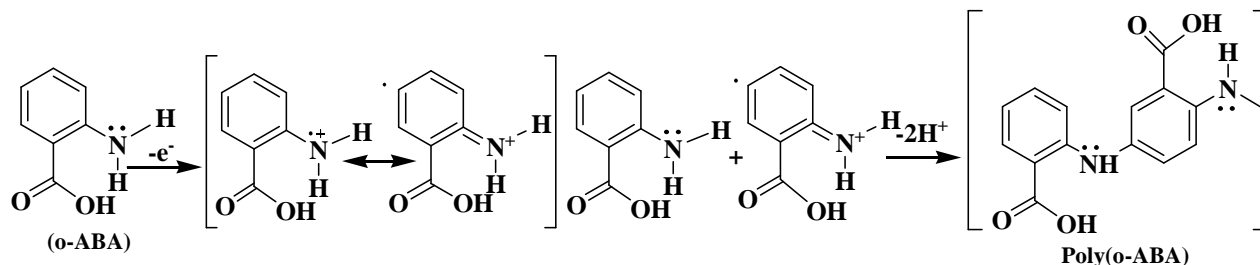
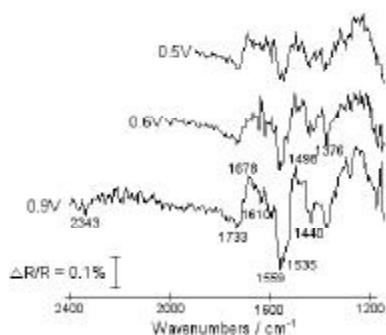**Scheme 1 : Homo-polymerization of *o*-aminobnzoic acid**

Figure 4: In situ FTIR spectra collected during the oxidation on a gold electrode of a poly(o-aminobenzoic acid) film in 0.1M HClO₄ solution. Reference potential 0.2V. Sample potentials indicated for each spectrum. 1000 interferograms were recorded at each potential. 8 cm⁻¹ resolution

Figure 5: In situ FTIR spectra collected during the oxidation on a gold electrode of a poly(o-aminobenzoic acid) film in 0.1M HClO₄ / D₂O solution. Reference potential 0.2V. Sample potentials indicated for each spectrum. 100 interferograms were recorded at each potential. 8 cm⁻¹ resolution
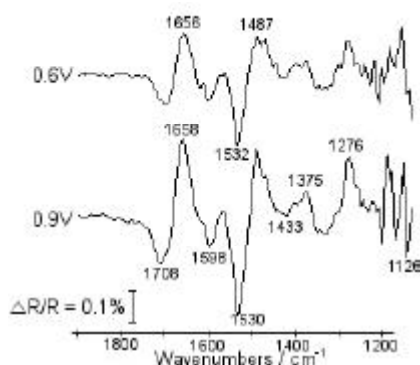
TABLE 2: Assignments of the vibrational bands for the reduced and oxidized forms of poly (o-aminobenzoic acid) in acidic H₂O and D₂O solvents[27,29,30,37-39]

	Frequency/cm⁻¹		Assignments
	H₂O	D₂O	
	1676	1660	Carboxylic acid (C=O) str.
Reduced state	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.
Oxidized state	1560-30	1532	Quinoid ring (C=C) str
	1480-40	1435	Quinoid (>C–N=) str
	1378	1336	Intermediate order (C···N) str.
	1124	1121	ClO₄⁻

small amounts of polymerization products can be isolated on the surface of the gold working electrodes from the oxidation of *o*-aminobenzoic acid isomer. In spite of this fact, the high sensitivity of the *in-situ* FTIR spec-

troscopy technique allows to obtain vibrational spectra of poly(*o*-ABA) with quite good S/N ratio. Figure 4 shows the spectra, obtained for a Au electrode covered with poly(2-ABA) in H₂O + 0.1M HClO₄ solution, taking the reference spectrum at 0.2V and stepping the sample potential to higher values. The reference spectrum contains vibrational information on the reduced polymer form and then the potential to which the sample is taken was increased to include vibrational information associated with the oxidized form of poly(2-ABA). The spectra of figure 4 display several absorption bands whose intensities increase as the potential is shifted to more positive value, thus showing the progress of the oxidation processes with the applied potential. Characteristic positive-going bands are observed at 1676, 1502, 1300 and 1257 cm⁻¹ which are indeed related with vibrational modes concerning to the reduced form of the polymer. Moreover, downward bands which appear at 1733, 1620, 1563, 1536, 1443 and 1371cm⁻¹ are related to vibrations coming from the oxidized state of the polymer. It should be noted the formation of carbon dioxide at 1.0V(band at 2344 cm⁻¹), which is revealing the overoxidation (and degradation) of the polymeric material at such a 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 interpreted in terms of the existence of chemical interaction between the carboxylic and the amino groups in the reduced state of poly(2-ABA). It is well known that this kind of interaction lowers considerably the C = O stretching frequency of aryl carboxylic acids with amino or hydroxyl groups in the *ortho* position[37]. Thus, when the polymer is oxidized, amine nitrogens transform into protonated imines and the C = O stretching frequency re-

Reduced form of poly(o-aminobenzoic acid)　　**Oxidized form of poly(o-aminobenzoic acid)**
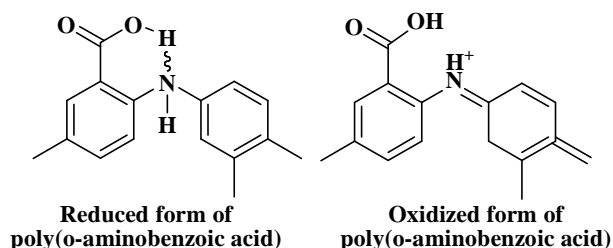
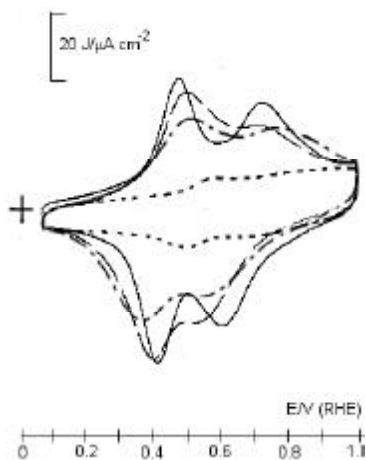**Scheme 2**

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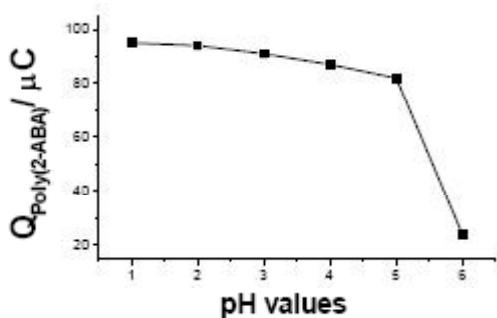**Figure 6: pH 1, 3, 5 and 6**

Figure 7: pH and potential (Q)

turns 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 figure 4 was reproduced in 0.1M HClO$_4$/D$_2$O. Working with D$_2$O solvent allows the "mobile" acid H atoms of poly(2-ABA) to be replaced by D atoms (H/D ratio is about 0.001 in the electrolytic medium). 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 figure 5, for which 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, for instance, 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. Besides, the broad positive-going absorption

peaked at 1372 cm^{-1} in figure 5 which could be tentatively associated with the C–H bending mode at benzenoid rings, cannot be paired easily with any feature of the spectra collected in H$_2$O. A feasible explanation to this result may be found in the fact that the 1400 to 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. With regard to the oxidized form of poly(2-ABA), 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. 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.

Effect of pH value on the cyclic voltammograms of poly(2-ABA)

The cyclic voltammograms of poly(o-aminobenzoic acid) at different pH values are also presented here. After the electropolymerization process the filmed electrode was extracted from the electrochemical cell and rinsed with water to remove any attached monomer species and transferred to the second cell containing HClO$_4$/NaClO$_4$ solution with pH 1.0, 3.0, 5.0 and 6.0, respectively. The behavior of polymer in different values from pH is in figure 6, it is observed that the current of both typical processes redox of poly(2-ABA) diminishes when increasing pH. It has been possible to verify that this diminution must to the partial dissolution of the film by effect of the presence of the group –COOH, that it increases the electrostatic interactions with the dissolvent as pH becomes alkaline (pK$_a$ of the carboxylic is approximately 2 and, therefore, is mainly like carboxylate anion to pH > 3). This phenomenon of dissolution is as much more important whichever greater is pH of electrolytic means figure 7. If the electrode

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Figure 8: Scanning electron micrographs of interface of poly-meric films formed on gold electrode in 0.1M HClO$_4$ solution form o-aminobenzoic acid

again takes pH = 1 it observes CV similar of the target of the gold electrode. We can say that the polymer film dissolves totally in the electrolyte has supported pH = 6. The voltammetric characteristics of the film of poly(2-ABA) stay until pH = 5 invariable, i.e. poly(2-ABA) it continues being electroactive to greater values of pH > 3, the electrochemical behavior of the polymer films of *o*-aminobenzoic acid sample that, on the contrary that the polyaniline, is electroactive to values of pH over 3 (where the polyaniline without modifying basically does not present some electroactivity).

Morphology

Figure 8 shows an scanning electron microscopy of interface of a typical area of the deposit of the three aminobenzoic acid polymers on the right was carried out on electrode of gold on the left. All thin films sur-faces of poly(2-ABA) coating are covered by uniform coverage. The film coating clearly indicate a smooth morphology. Nevertheless, the layers of polymer film do not reach a very great thickness. This small thick-ness must be responsible for the high permeability shown by all polymers species like protons and anions that were observed in the cyclic voltammograms experi-ences.

CONCLUSIONS

Following conclusions have been drawn from the present study:

i   The cyclic voltammetric investigation clearly indi-cated the formation of electroactive poly(2-ABA) films on two electrodes of gold and of graphite car-bon.

ii   It is observed that the anodic current densities of polymerization of polymers films are graphite carbon.

iii The rate of polymer film growth resulting from electropolymerization of aminobenzoic acids is much lower for the polymerization on electrode of gold than on graphite carbon.

iv   In overall results, 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 is "set free" and the C = O stretching frequency returns to the characteristic value for a carboxylic acid.

v   The scanning electron microscopy results also show tat cyclic voltammetric suggests that only small amounts of polymerization products can be isolated on the surface of the Au and graphite carbon electrodes from the oxidation of 2-ABA isomer.

vi   The electrochemical behavior of the polymer films of *o*-aminobenzoic acid sample that, on the contrary that the polyaniline, is electroactive to values of pH over 3, this is due to the presence of the group – COOH in the structure of polymer. To pH superior to 5 the polymer films dissolve quickly.

REFERENCES

[1] H.Letheby; J.Chem.Soc., **15**, 161 **(1962)**.
[2] A.G.Green, A.E.Woodhead; J.Chem.Soc., **97**, 2388 **(1910)**.
[3] N.Oyama, T.Ohsaka; Synth.Met., **18**, 191 **(1987)**.
[4] R.Noufi, A.J.Nozik, J.White, L.F.Warren; J. Electrochem.Soc., **129**, 2261 **(1982)**.
[5] K.Okabayashi, F.Goto, K.Abe, T.Yoshida; Synth. Met., **15**, 365 **(1987)**.
[6] E.M.Genies, M.Lapkowski, C.Santier, E.Vieil; Synth.Met., **18**, 631 **(1987)**.

Full Paper

[7] N.L.D.Somasiri, A.G.Macdiarmid; J.Appl. Electrochem., **18**, 92 **(1988)**.

[8] E.W.Paul, A.J.Ricco, M.S.Wright; J.Phys.Chem., **89**, 1441 **(1985)**.

[9] S.Chao, M.S.Wrighton; J.Am.Chem.Soc., **109**, 6227 **(1987)**.

[10] A.Katani, J.Yano, K.J.Sasaki; J.Electroanal.Chem. Interfacial Electrochem., **209**, 227 **(1986)**.

[11] A.Watanabe, K.Mori, Y.Iwasaki, Y.Nakamura; J. Macromolecules., **30**, 1793 **(1987)**.

[12] B.Aurian Blajeni, S.C.Holleck, B.H.Jackman; J. Appl.Electrochem., **19**, 331 **(1988)**.

[13] E.Edelson; Pop.Sci., **6**, 90 **(1990)**.

[14] A.Boyle, E.M.Genies, M.Lapkowski; Synth.Met., **28**, 769 **(1989)**.

[15] L.Duic, Z.Mandic; J.Electroanal.Chem., **335**, 207 **(1992)**.

[16] R.Saraswathi, S.Kuwabata, H.Yoneyama; J.Electroanal.Chem., **335**, 223 **(1992)**.

[17] C.M.A.Brett, A.M.Oliveira Brett, J.L.C.Pereira, C. Rebelo; J.Appl.Electrochem., **23**, 332 **(1993)**.

[18] R.Cordova, M.A.del Valle, A.Arratia, H.Gomez, R.Schrebler; J.Electroanal.Chem., **377**, 75 **(1994)**.

[19] Z.Mandic, L.Duic, F.Kovacicek; Electrochim.Acta, **42**, 1389 **(1997)**.

[20] A.A.Karyakin, A.K.Strakhova, A.K.Yatsimirsky; J.Electroanal., **371**, 259 **(1994)**.

[21] N.Toshima, H.Yan, Y.Gotoh; M.Ishiwatari; Chem. Lett., **37**, 2229 **(1994)**.

[22] A.A.Karyakin, I.A.Maltsev, L.V.Lukachova; J. Electroanal.Chem., **402**, 217 **(1996)**.

[23] H.Tang, T.Yamashita, A.Kitani, S.Ito; Electrochem. Acta, **43**, 2237 **(1998)**.

[24] S.C.Ng, H.S.O.Chan, H.H.Huang, P.K.H.Ho; J. Chem.Soc.Chem.Commun., 1327 **(1995)**.

[25] H.S.O.Chan, S.C.Ng, W.S.Sim, K.L.Tan, B.T.G. Tan; Macromolecules, **25**, 6029 **(1992)**.

[26] H.S.O.Chan, S.C.Ng, S.H.Seow, W.S.Sim, T.S.A. Hor; J.Thermal Anal, **39**, 177 **(1993)**.

[27] P.S.Rao, D.N.Sathyanarayana; Polymer., **43**, 5051 **(2002)**.

[28] M.S.Wu, T.C.Wen, A.Gopalan; Mater.Chem.Phys., **74**, 58 **(2002)**.

[29] B.L.Rivas, C.O.Sanchez; J.Appl.Pol.Sci., **89**, 2641 **(2003)**.

[30] H.Yan, H.J.Wang, S.Adisasmito, N.Toshima; Bull. Chem.Soc.Jpn., **69**, 2395 **(1996)**.

[31] C.Thiemann, M.A.Brett; Synth.Met., **123**, 1 **(2001)**.

[32] M.A.Brett, C.Thiemann; J.Electroanal.Chem., **538**, 215 **(2002)**.

[33] H.J.Salavagione, D.F.Acevedo, M.C.Miras, A.J. Motheo, C.Barbero; J.Polym.Sci.Part A.Polym. Chem. (In press).

[34] A.Benyoucef, F.Huerta, J.L.Vazquez, E.Morallon; Euro.Poly.J., **41**, 843 **(2005)**.

[35] T.Inouc, T.Yamase; Bull.Chem.Soc.Jpn., **56**, 985 **(1983)**.

[36] Y.Wei, C.C.Chan, J.Tian, G.W.Jang, K.F.Hsuch; Chem.Mater., **3**, 888 **(1991)**.

[37] G.Socrates; 'Infrared and Raman Characteristic Group Frequencies', Wiley, Chichester, **(2001)**.

[38] G.Louarn, M.Lapkowski, S.Quillard, A.Pron, J.P. Buisson, S.Lefrant; J.Phys.Chem., **100**, 6998 **(1996)**.

[39] Z.Ping, G.E.Nauer, H.Neugebauer, J.Theiner; J.Electroanal.Chem., **420**, 301 **(1997)**.