

# Electrochemical copolymerization of aniline and ortho-aminobenzylamine. Studies on its conductivity and chemical derivatization

Diego L. Raffa<sup>a</sup>, K.T. Leung<sup>b</sup>, Fernando Battaglini<sup>a,\*</sup>

<sup>a</sup> *INQUIMAE, Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 2, C1428EHA Buenos Aires, Argentina*

<sup>b</sup> *Department of Chemistry, University of Waterloo, 200 University Avenue W, Waterloo, Ont., Canada N2L 3G1*

Received 5 May 2005; received in revised form 25 July 2005; accepted 17 October 2005

Available online 29 November 2005

## Abstract

The electrochemical copolymerization of aniline and *o*-aminobenzylamine (ABA) leads to a polymer with aliphatic amino groups able to be derivatized. The synthesized material has a stoichiometry ABA:aniline ca. 1:1 when their ratio in the precursor solution range between 90:10 and 75:25. It presents similar conducting properties as polyaniline in acid medium. The conductance of the prepared polymer shows significant improvement compared to polyaniline in weak acidic to neutral media. The resulting product is able to be derivatized by mild reactions with molecules bearing a carboxylate or a carbonyl group. We show that approximately 20% of the added functional groups can be easily modified.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Aniline; *o*-Aminobenzylamine; polyaniline; Conductivity; Copolymerization; Derivatization

## 1. Introduction

One of the main limitations in the development of molecular devices based on conducting polyaniline (PANI), e.g. sensors, is the absence of functional groups that allow chemical derivatization of the polymer to construct more complex devices. Physical immobilization has been used in many opportunities but when systems become more complex, a precise control of the composition and stability is needed.

Several groups have attempted substitutions on the polyaniline backbone [1–8]. Among them, Barbero and co-workers [1,2] have produced a comprehensive work on the functionalization of polyaniline, taking different strategies: electrophilic substitution, nucleophilic substitution

and copolymerization of aniline with substituted anilines; they were able to obtain polymers with different conducting properties. Mikhael et al. [3] also carried out the N-alkylation and the N-acylation of PANI. Chang et al. [4] prepared poly(*o*-aminobenzylphosphonic acid) and their sodium salts by chemical methods; they obtained a polymer whose conductivity does not show any dependence with pH up to pH 6, even though its conductivity is three orders of magnitude lower than conventional acid-doped polyaniline. Chen et al. [5] synthesized a water soluble polymer using a sulfonic acid, derivatizing the N atom of the linear chain of PANI. With a similar strategy, our group partially modified PANI with propanesultone for the construction of sensors based on conductivity changes [6]. In all these cases, the main objective was to achieve conductance independence from the pH and/or changes in the solubility; most of these polymers are not suitable for the further modification. On the other hand, Horwitz et al. [7,8] succeeded in polymerizing aniline derivatives

\* Corresponding author. Tel.: +54 11 45763358; fax: +54 11 45763341.  
E-mail address: [battagli@qi.fcen.uba.ar](mailto:battagli@qi.fcen.uba.ar) (F. Battaglini).

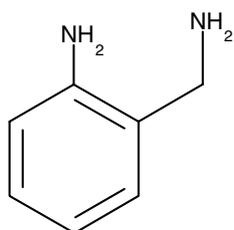
with ruthenium and iron complexes, even though the conductive properties of these new polymers were not investigated.

In this work, we present the electrochemical synthesis of a polymer bearing functional groups with similar conducting properties as polyaniline. Further derivatization of this polymer can be easily performed and may lead to application to sensors [6,9]. One of the advantages of the electrochemical synthesis is the possibility of being performed in very small areas, consequently allowing the development of electrode arrays or nanodevices.

To synthesize a polymer useful for derivatization and with similar characteristics as PANI, the following criteria must be accomplished: (a) the introduced functional group should be able to react in mild conditions (b) the resulting polymer should have similar redox potentials and conductivity properties as polyaniline; (c) the polymer should maintain its properties after being derivatized on the introduced functional group.

In a previous work [10], we have used *o*-aminobenzylamine (ABA) (structure shown in Scheme 1) with the purpose of preparing a polymer with similar characteristics to PANI. The advantage of using this reagent is the presence of a methylene group between the amino group and the ring, which attenuates the effect of the new amino group introduced on the electronic density in the aromatic ring. In addition, the primary aliphatic amino group is more reactive than an aromatic amino group for further derivatization. In spite of all these considerations, ABA polymerization yields an insulating polymer. Also, in the same work, we carried out the copolymerization of ABA and aniline in a ratio of 85:15, which yields a polymer with both characteristics: the presence of functional groups and the conductivity properties of PANI.

In the present work, we present results obtained with a series of polymers electrochemically synthesized from solutions of ABA:aniline in different ratios. The new materials are characterized by cyclic voltammetry, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), to elucidate their structure and electronic properties. It is found that solutions of ABA:aniline in a ratio ranging from 90:10 to 75:25 produces a copolymer with a ratio of ABA:aniline = 1:1. We consider the formation of a copolymer between the two molecules more likely than the formation of a blend of two polymers (polyaniline and polyaminobenzylamine), even though at this



Scheme 1. Structure of *o*-aminobenzylamine.

stage we cannot present a conclusive evidence. The conductivity of this new material is tested at pH 4.7 and 7.0, showing an improvement with respect to the behavior of PANI in the same conditions. Derivatization with molecules bearing a carboxylate group is presented; the obtained results are discussed in terms of possible applications as semiconductors and building blocks for sensor materials.

## 2. Experimental

### 2.1. Materials

Microperoxidase (MP-11), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS) were from Sigma, all other chemicals were analytical grade. Aniline was purified by distillation at reduced pressure.

### 2.2. Equipment

Electrochemical experiments were performed in a Pine AFRDE5 bipotentiostat. Acquisition of the data was accomplished with a National Instruments acquisition card. A three-electrode electrochemical cell was used. Ag|AgCl|3 M NaCl reference electrode (BAS) was used in all experiments (all potentials in this work are referred to Ag|AgCl, unless otherwise stated). A platinum foil was used as the counter electrode.

Infrared spectroscopy experiments were performed *ex situ* in a Nicolet 560 Magna II FTIR, with dry air purge. The detector was a refrigerated MCT/A. A commercial accessory kit (Spectra Tech) for diffuse reflectance was used to place the gold electrode into the spectrometer. Special electrodes that allowed disassembly were used. Different thicknesses were tried until optimum transmittance was obtained. Measurement of ABA spectrum was performed by transmittance on a KBr pellet.

The XPS experiments were performed in an ultrahigh vacuum (UHV) multitechnique Imaging XPS system (Thermo VG Scientific ESCALab 250), equipped with a hemispherical analyser (of 150 mm mean radius) and a monochromatic Al K $\alpha$  (1486.60 eV) X-ray source. The high sensitivity of this instrument obtained at a routine instrumental energy resolution of 0.5 eV FWHM at 20 eV pass energy allowed us to characterize spectral features in the core-shell regions. No charge compensation was found to be necessary for the samples studied in the present work. For XPS experiments, we used a specially designed working electrode, which consists of a 3 mm diameter gold disk in a teflon holder that allows the subsequent disassembly and extraction of the gold disk.

### 2.3. Copolymerization of aniline and *o*-aminobenzylamine

Electrochemical polymerizations were carried out from solutions with a total co-monomer concentration of

0.52 M in 1.8 M  $\text{H}_2\text{SO}_4$  in all cases. The potential was cycled between  $-0.2$  and  $1.2$  V.

#### 2.4. Conductivity (resistance) measurements

Home-built dual carbon band electrodes were used [6]. Measurement of resistance of the polymers synthesized on the band electrodes was carried out modifying a technique presented by Wrighton and co-workers [11]. It consists of a cell of two working electrodes (WE), the dual carbon bands, one reference electrode and one counter electrode. The two carbon bands are  $20\ \mu\text{m}$  apart from each other, separated by an insulating gap. The polymer grows on both WE until the two bands are joined by it. Then the modified electrodes are immersed in a solution at a defined pH. One of the WE (WE1) is kept at a constant potential with respect to the reference while the potential of the other WE (WE2) is swept up and down by  $20\ \text{mV}$  with respect to WE1. The current flowing through the cell is the result of the electrochemical processes, plus the current that flows between the two WE due to the potential difference between them. By analogy with a physical transistor, the current flowing between the two working electrodes is called the “drain current”, the potential of WE1 with respect to the reference is the “gate voltage”, and the potential of WE2 referred to WE1 is the “drain voltage”. The current measured in any of the working electrodes is the sum of the current produced by a redox process and the current forced to flow between the two WE by the drain voltage (drain current). For such small potential changes ( $20\ \text{mV}$ ), contribution to the current produced by the redox processes can be neglected, relative to the drain current. The current flowing through the polymer can be assumed to be the result of electronic conduction of the film, which is inversely proportional to the resistance. A source of error in the determination is the capacitive current, which can be avoided by stopping the voltage sweep in the positive (or negative) limit until the value of the current is constant.

#### 2.5. Modification with carboxylic acids

The corresponding carboxylic acid (ferrocene acetic acid or microperoxidase) is dissolved in phosphate solution with a pH around 9 to assure better solubility. Once it is dissolved, the pH is adjusted to 6.5. Then, EDC and NHS are added to the solution to reach a concentration of 100 and  $20\ \text{mM}$ , respectively. Once all reagents were added, pH was again adjusted to 6.5 and kept for 30 min for carboxylate activation. Then, the pH was readjusted to 7.5 and the modified electrode was introduced in the solution and left overnight at room temperature. After that, the electrode was rinsed with distilled water, and then characterized by XPS.

As a blank test to ensure that the carboxylic acids were bound and not adsorbed, the same experiment was carried out with a polyaniline modified electrode.

### 3. Results

#### 3.1. Redox and conductivity properties

In an attempt to obtain a polymer with characteristics similar to those of PANI and primary amino groups ( $-\text{CH}_2\text{NH}_2$ ) hanging from the backbone, the electrochemical polymerization from a solution of ABA and aniline in a ratio of 85:15 was used, cycling the potential between  $-0.2$  and  $+1.2$  V, since polymerization of ABA is not observed at potentials lower than  $0.9\ \text{V}$  [10].

It is interesting to compare the growth of a polymer from this mixture with the growth of PANI from an aniline solution in the same monomer concentration and cycling between the same potential limits. Fig. 1 shows the voltammogram for PANI after two cycles at  $50\ \text{mV s}^{-1}$ . It can be observed that the two typical redox processes for PANI plus a peak at ca.  $550\ \text{mV}$  due to the side reactions observed when the polymerization process is carried out at potentials higher than  $0.75\ \text{V}$  vs Ag/AgCl. On the other hand, the growth of a polymer from a solution ABA:aniline = 85:15 presents distinct features, like growth rate and potential of the redox processes.

Fig. 2 shows the growth of the polymer until the peak currents are similar to those obtained for PANI (Fig. 1), this process takes 23 cycles in contrast to the 2 required for PANI. It is also interesting to analyze the way in which the polymer growth; in the first scan a flat line is observed until  $0.9\ \text{V}$ , for the second scan a peak ca.  $0.5\ \text{V}$  is apparent, similar to the one observed for ABA [10], and there is no indication of aniline polymerization, at this stage the growth is slow. By the 6th cycle, a peak ca.  $0.25\ \text{V}$  begins to be observed. In cycles 12 and 15 both peaks are well defined and the growth becomes faster. By the cycle 23, the peak current for the first redox process is practically

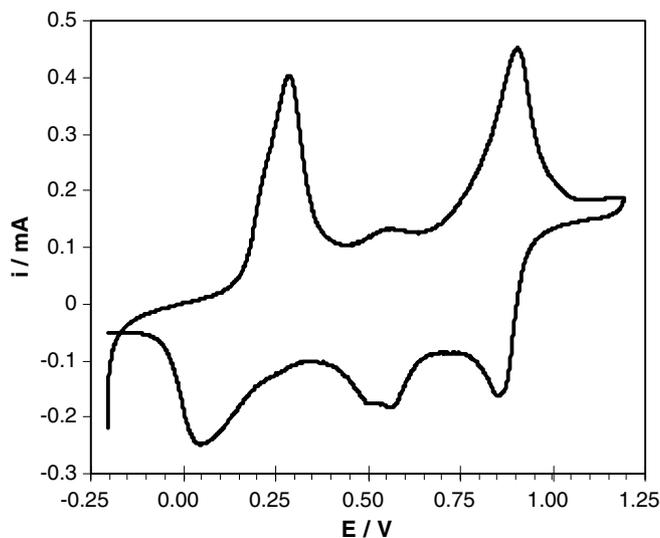


Fig. 1. Cyclic voltammogram of PANI in 1.8 M sulfuric acid obtained from a solution 0.52 M in aniline after 2 scans. Sweep rate:  $50\ \text{mV s}^{-1}$ . Working electrode: glassy carbon, area:  $0.071\ \text{cm}^2$ .

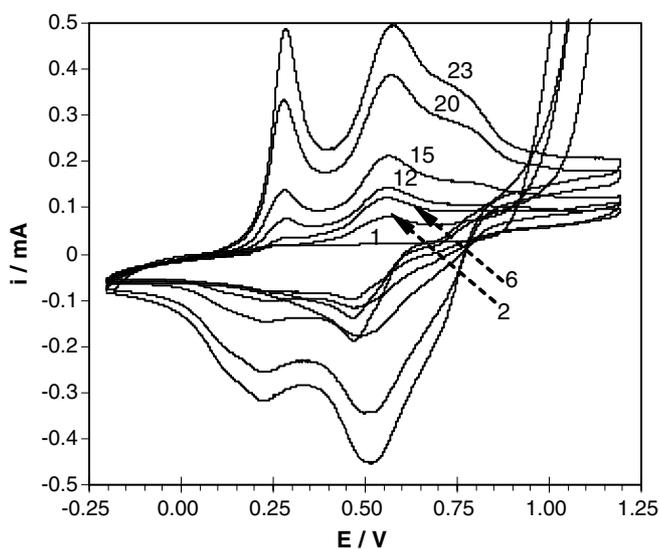


Fig. 2. Electrochemical polymerization from a solution containing 0.442 M ABA and 0.078 M aniline in 1.8 M sulfuric acid. The numbers indicate the scan cycle. Sweep rate:  $50 \text{ mV s}^{-1}$ . Working electrode: glassy carbon, area:  $0.071 \text{ cm}^2$ .

the same as the one observed for PANI (Fig. 1), but the shape of the whole voltammogram is clearly different. It can be observed a redox process at 0.25 V similar to the one observed in PANI and a more complex process between 0.5 and 0.8 V that could be attributed to two redox reactions, one manifested by a peak ca. 0.52 V and another by a shoulder ca. 0.7 V. No peak is observed at potentials higher than 0.8 V as it happens in PANI, where a quasi-reversible process is observed.

The behavior of the new polymer at higher pHs is depicted in Fig. 3. At pH 4.7 (Fig. 3(a)), the potential of the first anodic peak (and the corresponding cathodic peak) practically does not change; at pH 7 (Fig. 3(b)) a shift to more negative potentials is observed. The potentials for the second anodic peak (and the corresponding cathodic peak) are strongly dependent on the pH, similar to what it is observed for polyaniline.

Molecular transistors were built by copolymerization of ABA and aniline, in a ratio 85:15, onto dual carbon band electrodes. Measurement of the resistance of the polymers synthesized on the band electrodes was carried out modifying a technique presented by Wrighton and co-workers [11]. It consisted in fixing the potential of one of the microbands and sweeping the potential of the other some millivolts up and down. When a bias of 20 mV is applied, it can be assumed that the current flowing through the polymer is the result of the electronic conduction of the film. Fig. 4 shows the resistance of the prepared molecular transistor at different potentials. The new material presents conducting properties similar to PANI in 1.8 M sulfuric acid. Its resistance at pH 4.7 increases four times. When the same experiment was carried out with PANI the resistance increases 20 times. At pH 7.0 the resistance increases only 50 times, meanwhile for PANI, it increases 5000 times [6].

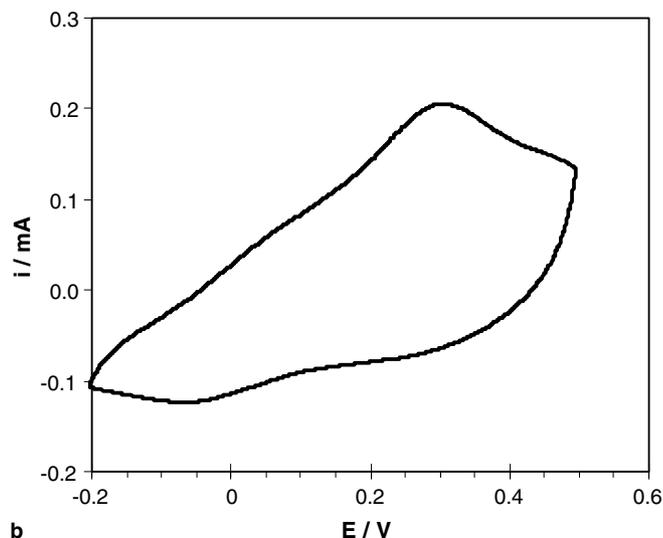
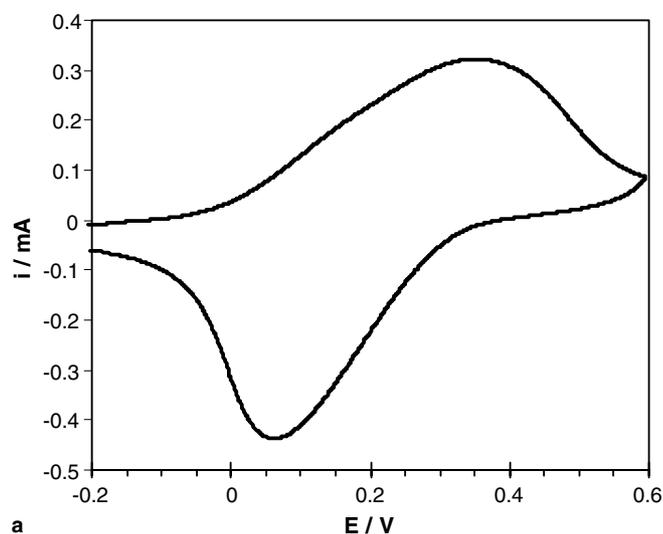


Fig. 3. Cyclic voltammograms of the polymerization product. (a) 0.1 M acetate buffer pH 4.75 and (b) 0.1 M HEPES pH 7.0, 0.1 M  $\text{KNO}_3$ . Sweep rate of  $50 \text{ mV s}^{-1}$ . Working electrode: glassy carbon, area:  $0.071 \text{ cm}^2$ .

It is worth mentioning, that the potential corresponding to the minimum resistance changes with pH, which follows the same trend as the potential for the first redox process.

### 3.2. Infrared spectroscopy results

Spectra of ABA, PANI, and the modified electrode obtained from an initial ratio of ABA:aniline = 85:15 in solution are presented in Fig. 5. The analysis of bands was made based on literature about the subject [4,12,13]. The most important features in the spectrum of the new polymer (Fig. 5(b)) compared to those of polyaniline (Fig. 5(a)) are: the stretching of methylenes at  $2850\text{--}2950 \text{ cm}^{-1}$ ; primary aliphatic amines at  $3300 \text{ cm}^{-1}$ ; CH bending due to 1.2.4 substitution of the ring (not present in polyaniline, but present in poly(*o*-toluidine)) at  $860\text{--}880 \text{ cm}^{-1}$ ; hydrogen bond at  $3000 \text{ cm}^{-1}$  (in the new material there is a high tendency to form intramolecular hydrogen bond), the structure in the

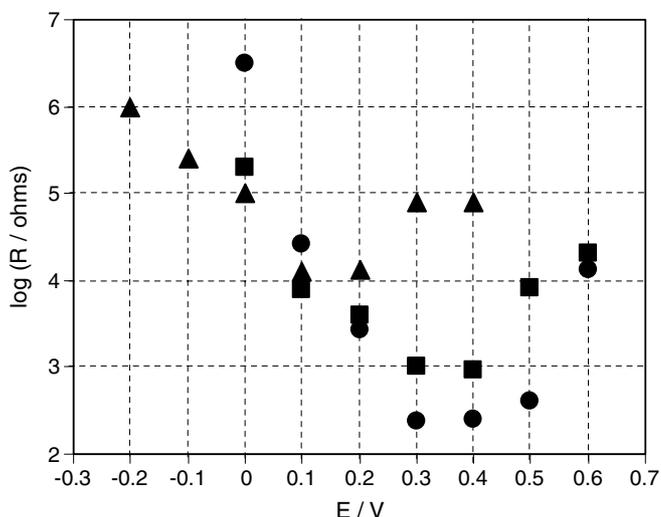


Fig. 4. Resistance of the polymerization product as a function of the gate potential at different pHs. ●, 1.8 M sulfuric acid; ■, 0.1 M acetate buffer pH 4.75, 0.1 M KNO<sub>3</sub>; ▲, 0.1 M HEPES pH 7.0, 0.1 M KNO<sub>3</sub>.

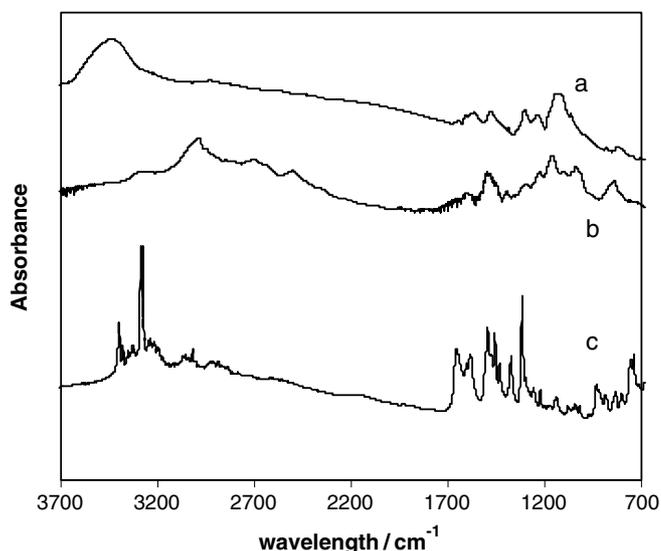


Fig. 5. Infrared spectra of: (a) PANI; (b) polymerization product and (c) *o*-aminobenzylamine (ABA) in a KBr pellet. The polymer samples were electrochemically grown in 1.8 M sulfuric acid and held at  $E = -0.2$  V.

region from 1230 to 1350  $\text{cm}^{-1}$ , where more than two peaks appear as in the case of a polymer synthesized from *o*-aminobenzylphosphonic acid by Chan et al. [4]. This feature was attributed to the mechanical coupling by intramolecular hydrogen bond with the phosphonate. In our case, this would happen with the primary amino groups. The modified electrode also presents characteristics in common with the spectra of aniline and polyaniline [13]: the vibration of benzoid ring at 1500  $\text{cm}^{-1}$  and the vibration of quinoid ring near 1600  $\text{cm}^{-1}$ .

### 3.3. XPS results

To determine the composition of the material grown on the electrode surface, it is necessary to differentiate between

the N on the methyl group in ABA (aliphatic amino group) and the N atom on the backbone of the polymer (aromatic amino group). In the latter case, the N atom can be present in different oxidation states (amino or imino), depending on the degree of oxidation of the polymer. Furthermore, in both cases (aliphatic or aromatic) the N atom can be protonated or remain neutral. The signal due to N1s is very similar for both type of N atom. For example, the N1s features for the quinoid ( $-\text{N}=\text{}$ ) and benzoid ( $-\text{NH}-$ ) formed in the polyaniline backbone are located at 398.1 and 399.3 eV [14], respectively. Whereas for a N in a primary amino bound to an aliphatic C, it is observed at 398.5 eV [15]. In both cases, when the N atom is protonated the signal shifts to ca. 401 eV.

Fig. 6(a) shows the spectrum for pure polyaniline in the unprotonated reduced form. In the same conditions, the spectrum for the new material shows a second peak due

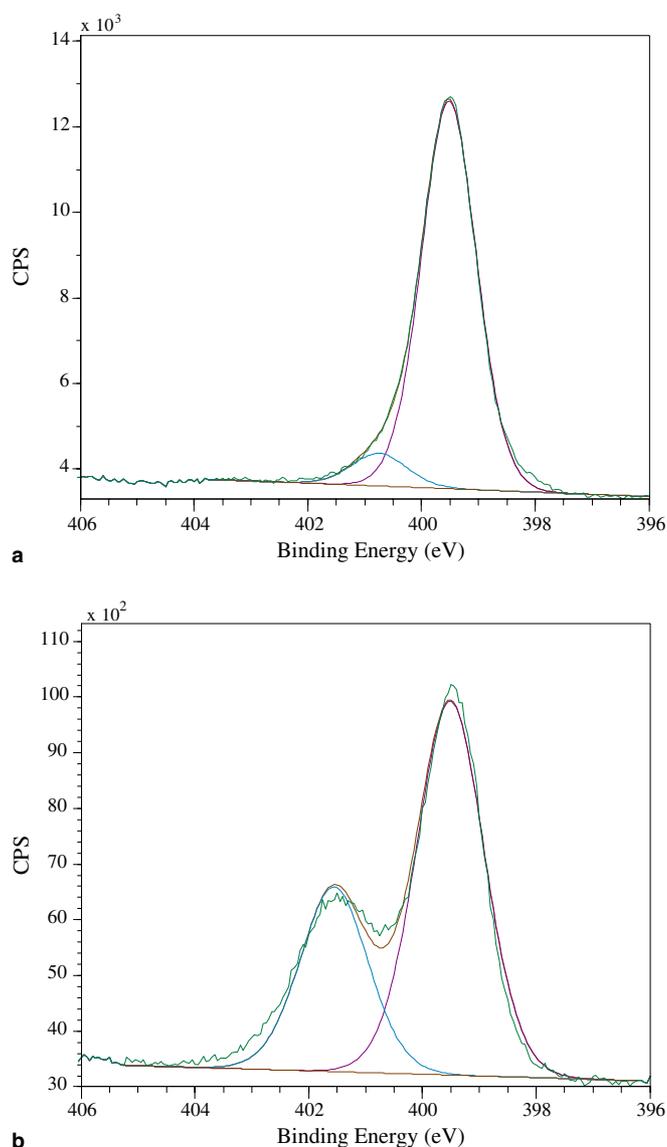


Fig. 6. XPS spectra of N1s for: (a) Polyaniline and (b) polymerization product. Charge deposit:  $8 \times 10^{-3} \text{ C cm}^{-2}$ .

to the N atom on the aliphatic C (Fig. 6(b)). In this case, the separation between the peaks is well defined, suggesting the capability of the primary amino groups to remain protonated. From this result a ratio ABA:aniline of 1:1 is estimated.

### 3.4. Copolymerization using different ratios

Solutions of ABA:aniline with different concentration ratios were polymerized, and the resulting products were analyzed by XPS. For comparison purposes, it is desirable that the polymerization conditions are as similar from one experiment to the other as possible. It has to be considered that the rate of growth of the resulting polymer increases as the proportion of aniline increases. Therefore, if the polymerization were to be carried out for the same amount of time, that is, the same amount of potential cycles, films of different thicknesses would be obtained. As a minimum thickness of film is necessary to obtain a good XPS signal, the extent of polymerization was chosen based on a similar amount of charges. So aniline and ABA solutions in H<sub>2</sub>SO<sub>4</sub> 1:10 were prepared, with total concentration of 0.52 M (sum of both reagents) but with ratios of ABA:aniline 90:10; 85:15; 80:20; 75:25; 70:30; 60:40; 50:50 and 0:100 (this last one corresponding to aniline alone, to use the XPS spectrum of polyaniline, polymerized under the same conditions, as the reference). The composition of the copolymers determined by XPS can be divided in two main groups: for samples between 90:10 and 75:25, the backbone N to pendant N ratio does not vary, being in all these cases ca. 66:33, which suggests a ABA:aniline ratio of 1:1 in the polymer. The other group is formed by samples in the proportion 60:40 or lower in ABA. A remarkable change in the composition of the resulting polymer is observed with a ratio of backbone-N to pendant-N of 92:8 for ABA:aniline = 60:40. For ABA:aniline = 50:50, practically pure polyaniline is obtained, which is consistent with the result obtained by cyclic voltammetry [10].

### 3.5. Covalent modification

Earlier, we have modified the polymer synthesized from a ratio ABA:aniline = 85:15 with ferrocene carboxyaldehyde with a 20% yield based on the aliphatic same primary amino groups present in the polymer [10]. In this work, we have modified the polymer through another reaction, commonly used in biochemistry, the coupling of a primary amino group with a carboxylate group using EDC/NHS as catalyst. As probes, we have chosen ferrocene acetic acid and microperoxidase 11 (MP-11). The last molecule is part of the active center of equine heart cytochrome c and has peroxidase activity. It contains 11 amino acids and a heme group in the center of which an Fe atom is coordinated. In addition to terminal carboxylate, the molecule contains other carboxylate groups on the heme group. Both compounds are useful for the construction of sensors [6,16], and the iron atom present in both of them is a good tracer

for XPS experiments. Its presence can be easily detected at 710 and 722 eV. The presence of Fe in the sample exposed to FeCp<sub>2</sub>CH<sub>2</sub>COOH was detected, representing a modification of 24% of the aliphatic amino groups. Furthermore, we could detect Fe in the polymer exposed to MP-11, despite its smaller proportion, which is expected since the greater size of the MP-11 molecule represents a modification of 17%.

## 4. Discussion and conclusions

The product of the copolymerization of *o*-aminobenzylamine and aniline is presented. When the process is carried out from solutions of ABA:aniline in a ratio from 90:10 to 75:25, a product with a stoichiometric ratio of 1:1 is obtained.

At this stage, we have no conclusive evidence whether we have obtained a copolymer or two entangled homopolymers; in any case, a material with different properties compared to polyaniline and polyaminobenzylamine (PABA) is obtained. The growth of the polymer evidences that the first layers are richer in ABA; after 12 cycles aniline begins to be incorporated in similar proportion and the growth rate of the polymer increases (Fig. 2), evidencing the incorporation of the two monomers. The voltammogram of the final product (cycle 23) is clearly different from the one corresponding to polyaniline grown in the same conditions (Fig. 1) and the one from polyaminobenzylamine [10].

This polymer presents a conductivity comparable to that of polyaniline in acid medium, it was observed that the change of conductivity as a function of pH is different; at pH 4.7 the minimum resistance of this polymer increases only four times, while that for PANI increases 20 times. At pH 7.0, an increase in resistance of 50 times is observed, in contrast to 5000 found for PANI, thus allowing resistance measurements to be carried out with conventional equipments. This difference with PANI can be understood considering that in this type of polymers the conductivity is due to protonation and movement of charges. In the case of the polymer synthesized in this work, the primary amino groups introduced are protonated functional groups capable of sharing that proton with the backbone of the polymer. It also produces an increase in the amounts of counterions present in the polymer that helps the charge movement. This result is consistent with the evidence of hydrogen bond signal in IR spectroscopy and the XPS spectrum for N1s.

The chemical modification of the introduced primary amino group was evaluated by formation of a Schiff base in our previous work [10] and by amide formation from reactions with ferrocene acetic acid and MP-11 in the present work. In the first case, ferrocenealdehyde reacted with the polymer with a yield of 16%, while in the latter case of amide bond formation, the yields were 24% and 17% for ferrocene acetic acid and MP11, respectively. In both cases, around 20% of the primary amino groups can be derivatized, which is likely due to the interaction between

the chains of the polymer that produces a compact structure difficult to penetrate and react.

This new polymer can be useful for the construction of nanodevices since it can be electrochemically grown in very small areas and derivatized afterwards. Its conducting properties at pH 4.7 and 7.0 are to some extent better than those of PANI and it could be combined with other polymers, as poly(styrenesulfonate), to improve even more its conductance at neutral pH. For example, a sensor for glucose with the enzyme switch used by Bartlett and Wang [9] could be constructed by immobilizing a mediator on the amino groups instead of having it in solution, thus achieving a “reagentless” test.

### Acknowledgments

The financial support of ANPCyT (PICT 14308) and the Natural Sciences and Engineering Research Council of Canada are acknowledged.

### References

- [1] C. Barbero, H.J. Salvagione, D.F. Acevedo, D.E. Grumelli, F. Garay, G.A. Planes, G.M. Morales, M.C. Miras, *Electrochim. Acta* 49 (2004) 3671–3686.
- [2] H. Salvagione, M.C. Miras, C. Barbero, *J. Am. Chem. Soc.* 125 (2003) 5291–5292.
- [3] M.G. Mikahel, A.B. Padias, J.K. Hall Jr., *J. Polym. Sci. A: Polym. Chem.* 35 (1997) 1673–1679.
- [4] H.S.O. Chan, P.K.H. Ho, S.C. Ng, B.T.G. Tan, K.L. Tan, *J. Am. Chem. Soc.* 117 (1995) 8517–8523.
- [5] S. Chen, G. Hwang, *J. Am. Chem. Soc.* 117 (1995) 10055–10062.
- [6] D. Raffa, K.T. Leung, F. Battaglini, *Anal. Chem.* 75 (2003) 4983–4987.
- [7] C.P. Horwitz, Q. Zuo, *Inorg. Chem.* 31 (1992) 1607–1613.
- [8] C.P. Horwitz, Q. Zuo, *J. Electroanal. Chem.* 324 (1992) 79–91.
- [9] P.N. Bartlett, J.H. Wang, *Faraday Trans.* 92 (1996) 4137–4143.
- [10] D. Raffa, F. Battaglini, *J. Electroanal. Chem.* 504 (2001) 120–124.
- [11] E.W. Paul, A.J. Ricco, M.S. Wrighton, *J. Phys. Chem.* 89 (1985) 1441–1447.
- [12] Z. Ping, G.E. Nauer, H. Neugebauer, J. Theiner, *J. Electroanal. Chem.* 420 (1997) 301–306.
- [13] N.S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel, *J. Chem. Phys.* 92 (1990) 4530–4539.
- [14] A.Q. Zhang, C.Q. Cui, J.Y. Lee, F.C. Loh, *J. Electrochem. Soc.* 142 (1995) 1097–1104.
- [15] H. Tachibana, Y. Yamanaka, H. Sakai, M. Abe, M. Matsumoto, *Polymer* 42 (2001) 1995–2000.
- [16] A.E.G. Cass, G. Davis, G.D. Francis, H.A.O. Hill, W.J. Aston, I.J. Higgins, E.V. Plotkin, L.D.L. Scott, A.P.F. Turner, *Anal. Chem.* 56 (1984) 667–671.