Polyanilines with Pendant Amino Groups as Electrochemically Active Copolymers at Neutral pH

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One of the most promising fields of application of polyaniline (PANI)-based modified electrodes is the construction of biosensors. However, PANI itself is not electroactive in neutral media. This problem can be solved by copolymerization of aniline with other monomers. Herein, we present a study of the electrosynthesis and electrochemical performance of copolymer films of 3-aminobenzylamine and aniline. These films are both stable and electroactive in acid and neutral media. They can even be employed as mediators of ascorbic acid oxidation, showing variable electrocatalytic activity depending on the copolymer composition. The presence of different proportions of pendant amino groups was confirmed by using XPS. These groups are responsible for the increased electroactivity in neutral solution. The copolymer films studied here can be used as versatile building blocks in the construction of bioelectroactive assemblies.

1. Introduction

Owing to their excellent electronic and electrochemical properties, organic conducting polymers (CPs) have attracted significant attention from the scientific community in recent decades.[1,2] Particularly, polyaniline (PANI) has been one of the most studied CPs, owing to its high electronic conductivity, low cost, simple synthesis, and chemical stability.[3–5] One of the most promising applications of PANI is the construction of biosensors[6] and biodevices,[7] as it can provide a suitable environment for the immobilization of biomolecules and it can also act as an electron mediator or physicochemical transducer to convert a chemical signal into an electrical signal.[6,8,9] Both mediation and transduction depend critically on PANI conductivity and/or electroactivity, which are known to be excellent in acid media, but poor in neutral solution. This is a clear disadvantage for most bioelectrochemical devices, as they need to operate around neutral pH. However, several strategies have recently been employed to improve the electronic connectivity in neutral media, such as the incorporation of metal nanoparticles,[10,11] graphene,[12–14] and even redox mediators[15] within the polymer matrix. The extension of the pH range of electroactivity has been achieved by using a variety of methods, including post-polymerization N-alkylation,[16] and the incorporation of polyanions[17,18] or complex anionic molecules that act

as dopants.[14,19] Each of these methods yield more complex materials or composites and most of them require additional synthetic steps.

The presence of amine groups in PANI has been employed for further covalent functionalization in the construction of biodevices. The formation of a phosphoroamidate bond between terminal amino groups and phosphate groups of artificial single-stranded DNA/RNA oligonucleotides (aptamers) has led to the construction of a variety of aptasensors.[12,20] Other usual covalent modification utilizes the amine groups of PANI to form amide bonds with carboxylic groups of the biorecognition molecule.[10,11]

An alternative way to improve the electroactivity of PANI in neutral solutions has been the polymerization of substituted anilines, whose additional chemical moieties act as self-dopants in the resulting PANI.[21] This method does not require additional modification steps and, when polymerization is performed by an electrochemical method, the amount of polymer can be precisely controlled.

Interesting examples of substituted anilines are aminobenzylamines, which bear an additional pendant amino group. These amino groups are protonated at neutral pH, conferring additional charges to the polymer chains, which improve the proton doping level and, probably, the electroactivity. Additionally, these pendant primary amines could easily be modified to introduce further chemical moieties or biorecognition elements in a higher extension than that reached in PANI. The chemical richness and versatility of primary amino groups can make these substituted anilines a promising case for the synthesis of multifunctional materials.[22]

Unfortunately, some years ago, it was shown that aminobenzylamines do not properly electropolymerize in acid media,[23] whereas the incorporation of 2-aminobenzylamine (2-ABA) into a PANI film diminished its electroactivity in acid media.[24] Furthermore, its incorporation was not possible beyond a few vol-

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tammetric cycles, indicating that the electropolymerization of the 2-ABA homopolymer does not proceed to a large extent.[24] However, more recently, the polymerization of both 2-ABA[25, 26] and 3-aminobenzylamine (ABA)[27] in acid solution has been reported to produce stable films that can then be employed for adrenaline and uric acid sensing. Also, 4-aminobenzylamine has recently been shown to electropolymerize on graphene in LiClO$_4$ aqueous solution.[28] Hence, in this work, we first studied the case of ABA to clarify this apparent contradiction about the electropolymerization of aminobenzylamines.

On the other hand, a common strategy to produce polymers from monomers with a low tendency to homopolymerize is to use copolymerization with a similar co-monomer of higher reactivity. In this sense, aniline (ANI) has been extensively employed as a co-monomer with other less reactive aniline derivatives.[29–33] These copolymerization processes can be performed with the scope of improving some characteristic of PANI, that is, water solubility,[29] or to gain new functionalities such as ion binding,[30] biocompatibility,[31] and analyte-sensing capacity,[32, 33] among others. In particular, some films of copolymers including ANI and other similar substituted monomers have shown increased electroactivity in neutral solutions.[34, 35] Another important reason for preparing copolymer films lies in the possibility that not only the resulting materials display better properties than the homopolymers, but that these properties can be adjusted by tuning the proportions of the co-monomers. Although some works about the copolymerization of ANI and aminobenzylamines have been reported,[23, 36–38] no systematic studies have been performed in this direction.

Therefore, in this work, we further studied the electro-co-polymerization of ABA and ANI on Au electrodes with the aim of producing stable films with a controlled thickness. This method constitutes an easy procedure to obtain a simple material that presents good electroactivity in neutral solutions, as required for mediation and transduction functions and, therefore, becomes suitable to be employed in the construction of more complex bioelectrochemical assemblies.

2. Results and Discussion

2.1. Electropolymerization of ABA

As mentioned in the Introduction, the electroactivity and stability of the homopolymer of ABA is not clear from previous studies.[23, 25, 27] To clarify this point, we first studied the voltammetric synthesis of the homopolymer of ABA. The electrolysis of an acidic ABA solution starts at more positive potentials than those used for ANI;[23] therefore, the electrosynthesis carried out by using cyclic voltammetry was performed from −0.2 to 1 V versus SCE in 0.5 M H$_2$SO$_4$. As show in Figure 1, there are two pairs of peaks in the voltammetric response during the electrosynthesis. The first pair of peaks at about 0.3 V resembles that of the first redox couple of PANI derivatives.[39] However, there is another anodic peak at about 0.57 V, with a cathodic peak at 0.43 V. This last redox couple could possibly be attributed to electroactive soluble products, as indicated by several facts. Firstly, the current of these peaks diminishes after
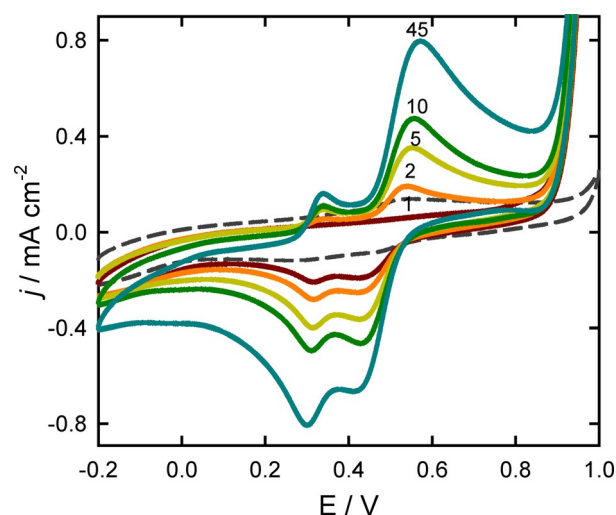

Figure 1. Voltammetric synthesis of PABA on a gold electrode at 0.05 V s^{-1} in 0.1 M ABA in 0.5 M H$_2$SO$_4$. The numbers of the successive cycles are indicated in the plot. The dashed line is the voltammetric response in monomer-free acidic solution after 45 cycles of electrosynthesis.

shaking the solution in the cell. Additionally, the ABA solution becomes slightly purple near the working electrode after polymerization, which indicates the presence of soluble products. Furthermore, when the ABA solution was replaced by pristine 0.5 M H$_2$SO$_4$ solution, the voltammetric current drastically decreased, even in the first new voltammetric cycle (Figure 1).

The final voltammetric response in monomer-free acid solution was practically the same when 2, 5, 10, and 45 cycles of electropolymerization were employed, with an integrated voltammetric charge of about 100 μC cm^{-2}. This indicates that the adsorbed material is only formed in the first cycles, and subsequent increases in current density could be attributed to the formation, and possibly electrochemical transformation, of soluble products. So, just a small amount of polymer remains attached to the surface, and it is not possible to synthesize films of polyaminobenzylamine (PABA) of different thicknesses through electropolymerization in acid solution.

Nevertheless, the voltammetric response in monomer-free acid solution shows some remaining redox peaks that can be better observed at high sweep rates (Figure 2). The analysis of different sweep rates indicates that it behaves as a confined reversible redox couple (Figure 2). The redox potential determined as the average of the anodic and cathodic peak potentials is 0.503 ± 0.002 V for this PABA film in 0.5 M H$_2$SO$_4$. This potential is close to that reported for poly(2-aminobenzylamine) in acid solution.[23] The first redox couple at about 0.3 V appears only as a shoulder of the main peaks.

According to results reported here, the main problem of the electrosynthesis of PABA is the solubilization of the intermediate products. PABA has pendant amino groups, so it is expected to be much more soluble in acid media than PANI, which is insoluble, even in highly acidic solutions. Oligomers formed during the oxidative scan can either diffuse to the bulk solution or adsorb onto the electrode. This last possibility is the only option in the case of PANI, owing to its low solubility.
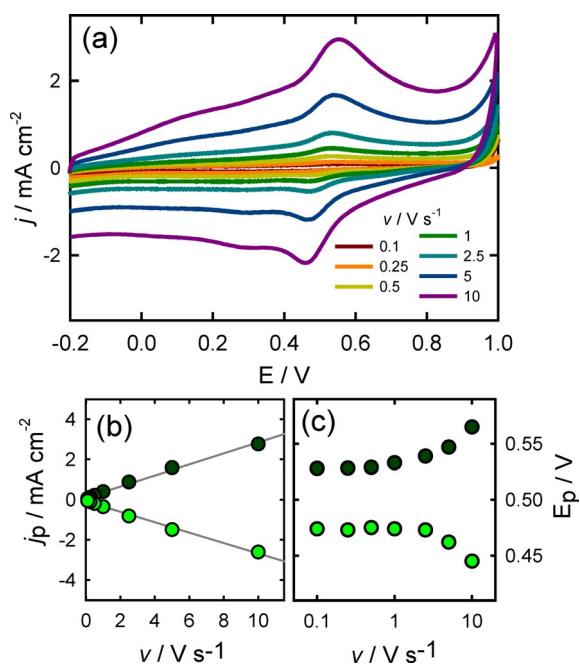
Figure 2. a) Voltammetric response of a PABA-modified Au electrode in 0.5 M H$_2$SO$_4$, $v = 0.1$–10 V s^{-1}. b) Peak current density and c) peak potential as a function of the sweep rate.
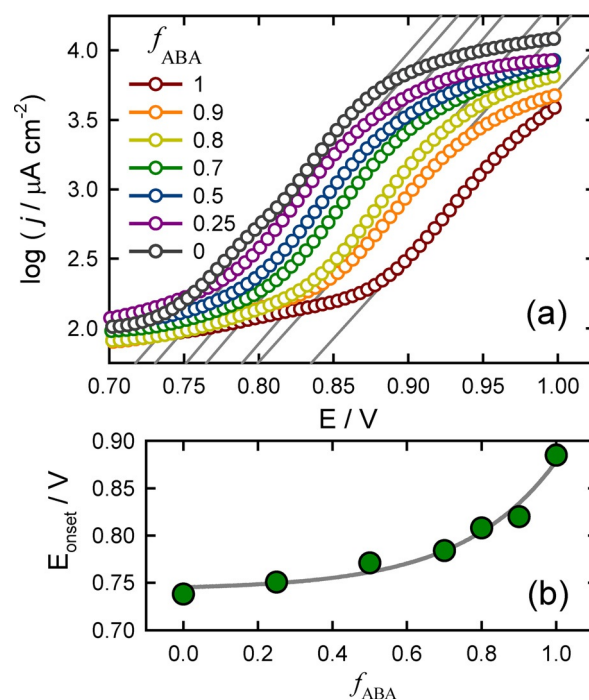
Figure 3. a) Pseudo-polarization curves of acidic 0.1 M solutions of ABA and ANI of different ABA ratios recorded at $v = 0.05$ V s^{-1}. b) Onset potentials for the oxidation of the solution as a function of the ABA ratio.

Even if some adsorption of PABA on gold takes place, any further adsorption of positive oligomers is hindered once the surface becomes positively charged.

As mentioned in the Introduction, a wide-spread strategy to modify the properties of a polymer is to copolymerize the monomer with other similar co-monomers. The natural co-monomer in this case is ANI.

2.2. Copolymerization of ABA and ANI

In this section, we study the copolymerization of ABA and ANI, carried out by using cyclic voltammetry in acid media, keeping the total monomer concentration and the voltammetric parameters (potential limits and sweep rate) constant for the different feed ratios (f_{ABA}).

Figure 3a shows the pseudo-polarization curves recorded during the first positive potential scan in the electrosynthesis solution with different proportions of ABA and ANI. From the extrapolation of the linear portion of the semi-logarithmic plot, the onset potential for the oxidation of the solution can be determined. In this case, the value at which the current density is 100 µA cm^{-2} was computed (Figure 3b). As the proportion of ANI increases, the oxidation potential of the solution decreases. Higher overpotentials are attained during the cyclic voltammetry and this has two main consequences: 1) the amount of polymer deposited after a complete cycle is larger for solutions richer in ANI, and 2) over-oxidation is more significant in the case of films richer in ANI, as indicated by the high relative intensity of the so-called "middle peak". Figure 4 shows the voltammograms of the second cycle of the electrosynthesis for different values of f_{ABA}. The redox couple of PABA is also pres-
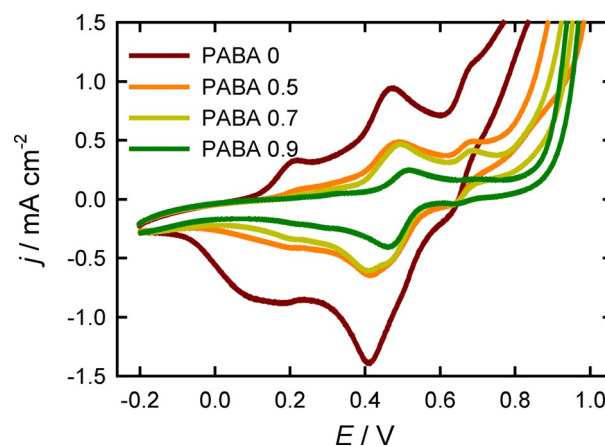
Figure 4. Voltammograms of the second cycle of the electrosynthesis of copolymers in solutions of different fractions of ABA in 0.5 M H$_2$SO$_4$.
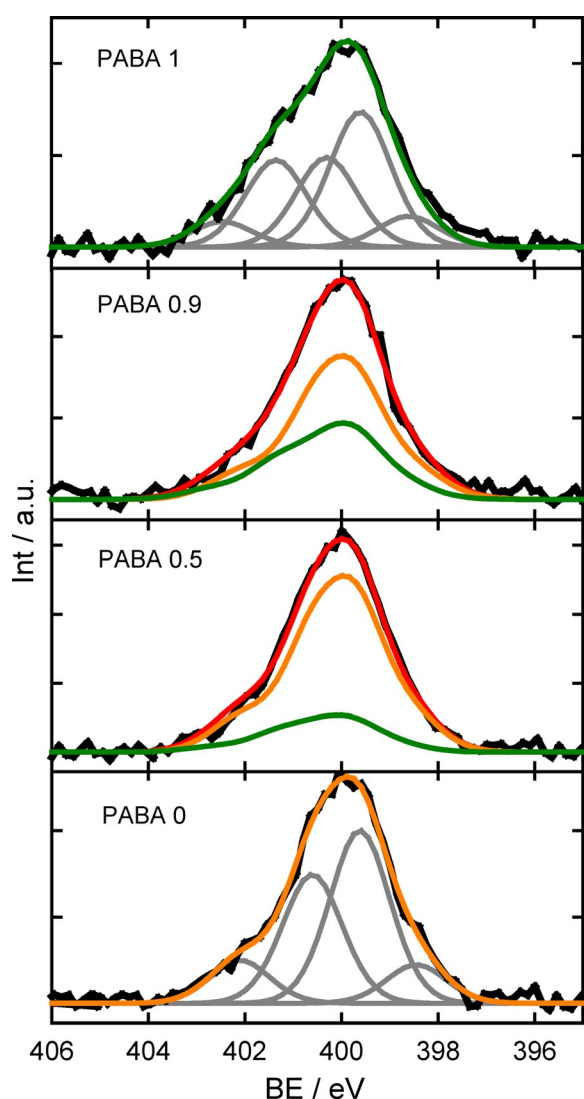
ent as the main peak for PABA 0.9 at 0.5 V. As f_{ABA} decreases, a new peak at about 0.44 V appears. Both peaks are discernible in the case of PABA 0.7 for the cathodic wave. This last peak is dominant in the case of PABA 0 and has been referred as the middle peak of PANI. The presence of this middle peak has received several explanations. It has been proven that this peak is related to the formation of cross-linked PANI chains through the direct reaction of the aniline nitrenium cations generated in the polymerization or through a direct reaction between two polymer chains.[40] However, the middle peak has also been attributed to the redox reactions of dimers,[41] oligomers,

and degradation products including *p*-amino-phenol, quinone-imines, and *p*-benzoquinone.[42]

2.3. XPS Analysis of the Electrosynthesized Copolymers

The chemical composition of the copolymers was determined by using XPS. For this purpose, the Au substrates modified with the electrosynthesized copolymers were first cycled in 0.5 M H_2SO_4 and then washed with water. Finally, they were dried under vacuum.

To keep the discussion in focus, here we will only analyze the N 1s core region. However, details of the C 1s and O 1s core levels, fitting, and assignment can be found in the Supporting Information. Figure 5 shows the N 1s region of the XPS spectra of homo- and copolymers of ABA and ANI. XPS of PANI has been reported several times and its characteristics are well

Table 1. N 1s core components used for fitting the PANI and PABA spectra.

Component	PANI N 1s BE [eV]	Amount [%]	PABA N 1s BE [eV]	Amount [%]
$=N-$ neutral imine	398.5	10.2	398.6	8.4
$-NH-/-NH_2$ neutral amine	399.6	45	399.6	36.8
$-NH^{\bullet+}-$ polaron structure	400.6	33.6	400.3	24.3
$=NH^+-$ protonated imine	402.1	11.2	402.5	6.9
$=NH_3^+$ protonated 1° amine	–	–	401.4	23.6

known. The N 1s core-spectrum level of PANI (indicated as PABA 0) can be deconvoluted into four peaks (full width half maximum, FWHM = 1.5 eV) (Table 1). The lower binding energy (BE) component at 398.5 eV has been attributed to the neutral N backbone ($=N-$) bound to C.[43–46] The following component at 399.6 eV has been assigned to the neutral amine, which is expected to appear at a BE about 1 eV higher than the imine.[44,46] Charged nitrogen species are expected to appear at higher BEs than neutral ones, so the components at 400.6 and 402.1 eV have been referred to as positive nitrogen species.[44–47] The peak at about 400.6 eV has been assigned to oxidized secondary amines (delocalized polaron-type structure), whereas the peak at about 402 eV is attributed to the protonated imine (localized bipolaron-type structure).[44,46] Although the existence of polaron structures is widely recognized in CPs, it has been neglected in previous analyses of PABA by using XPS, which leads to an overestimation of the protonated primary amine contribution.[27]

As the components of PANI should also be present in the case of PABA, the fitting of the PABA N 1s signal (shown in Figure 5) was performed by adding only the new component to account for the protonated primary amine contribution. Typically, the contributions of protonated and neutral primary amines appear at about 401 and 399 eV, respectively.[48,49] The component at about 399 eV is already present in the case of PANI, so no additional peak was employed for neutral primary amines. As the intensity of the peaks was allowed to vary during the fitting routine, the component at 399 eV now accounted for both the neutral backbone amines and additional uncharged primary amines. The results of the fitting with these five components are shown in Figure 5 and Table 1.

The N 1s core region was employed to determine the compositions of the electrosynthesized copolymers. Quantification by measuring C/N areas is not recommended, owing to the possibility of over oxidation and the undetermined atmospheric contamination that mainly affects the C 1s signal. The method used in this work for determining the chemical composition consists of fitting the region of N 1s of the XPS signal of each copolymer by employing two contributions, one for PABA and the other for PANI. These contributions were built with the same components used for the homopolymers and the relative intensities were kept constant (Table 1). Therefore,

Figure 5. XPS spectra of copolymers of ABA and ANI at different feed ratios. From top to bottom: f_{ABA} = 1, 0.9, 0.5, and 0. Black lines are experimental spectra, whereas grey peaks are the components used for fitting. Orange and green lines are the fits of PANI and PABA components, respectively, and the red lines are the global fits.

each spectrum was fitted by using a linear combination of the PANI and PABA contributions. To perform this computation, the only variable fitted was the ratio of the total integrated areas of PABA to PANI, which allows the copolymer composition to be obtained. The ABA fraction in the copolymers (F_{ABA}) as a function of the feed ratio was determined by this method, as presented in Figure 6. The solid line in the figure represents
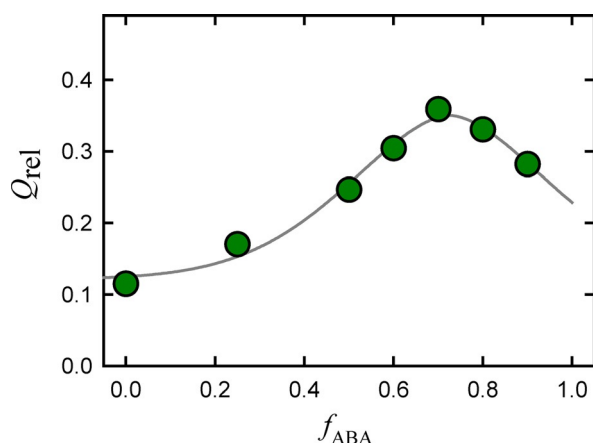
Figure 6. Copolymer composition as a function of the feed ratio, as determined with XPS. The solid line represents the fitting to the Mayo–Lewis model. The effective reactivity ratios for both monomers are reported in the plot.

the fitting to the Mayo–Lewis model. The expression for the terminal copolymerization (Mayo–Lewis) model is given by Equation (1):

$$F_{ABA} = \frac{r_{ABA}f_{ABA}^2 + f_{ABA}(1 - f_{ABA})}{r_{ABA}f_{ABA}^2 + 2f_{ABA}(1 - f_{ABA}) + r_{ANI}(1 - f_{ABA})^2} \quad (1)$$

where r_{ABA} and r_{ANI} are the rate constants for homopolymerization to copolymerization of each co-monomer.[50] This model has been applied to the voltammetric electrosynthesis of other CPs, such as copolymers of ANI with diaminobenzenesulfonic acid,[51] o-methoxyaniline,[52,53] and o-chloroaniline,[54] and also in the case of polypyrrole derivatives.[55] However, this model has been developed for bulk chemical copolymerization and some of its assumptions are not valid in the case of the electrochemical synthesis. Therefore, any further mechanistic conclusion from its application could be speculative.[53] Nevertheless, the electrochemical reactivity ratios obtained from voltammetric synthesis have been shown to correlate well with the chemical ratios of similar co-monomers.[53,56] These parameters do not have the usual meaning, but they still allow the differences in reactivity to be quantified and could be considered as effective reactivity ratios. In the present case, the values reported in Figure 6 account for the lower tendency of ABA to be incorporated to the copolymer.

Previous XPS results of thick films indicated that the composition (F_{ABA}) of copolymers of ANI and 2-ABA was about 0.5 for 2-ABA feed ratios in the range 0.75–0.9, and it was practically 0

for $f_{ABA} < 0.75$.[36] For those studies, higher potential limits were employed, so more oxidized polymer are expected to have been obtained. Additionally, as the incorporation of 2-ABA was indicated to be higher in the initial potential cycles,[36] thicker films are supposed to be richer in ANI than thinner ones, even for the same feed ratio. In our case, the lower effective reactivity of ABA results in a continuous increase in the ABA proportion in the copolymer, from 0 to approximately 0.4 as the feed ratio is increased (Figure 6). Nevertheless, this range of compositions allows a significant tuning of the electrochemical performance in neutral media, as shown in Section 2.4.

2.4. Electroactivity in Acidic and Neutral Solutions

Cyclic voltammetry of films of different compositions was performed in both 0.5 M H_2SO_4 and 10 mM pH 7 phosphate buffer; the latter is widely employed in bioelectrochemical studies. Films of similar integrated anodic charge (1500 ± 400 µC cm^{-2} in acidic media) were employed. These films are at least 15 times thicker than the films of PABA obtained by homopolymerization, as detailed in Section 2.1. Figure 7 shows
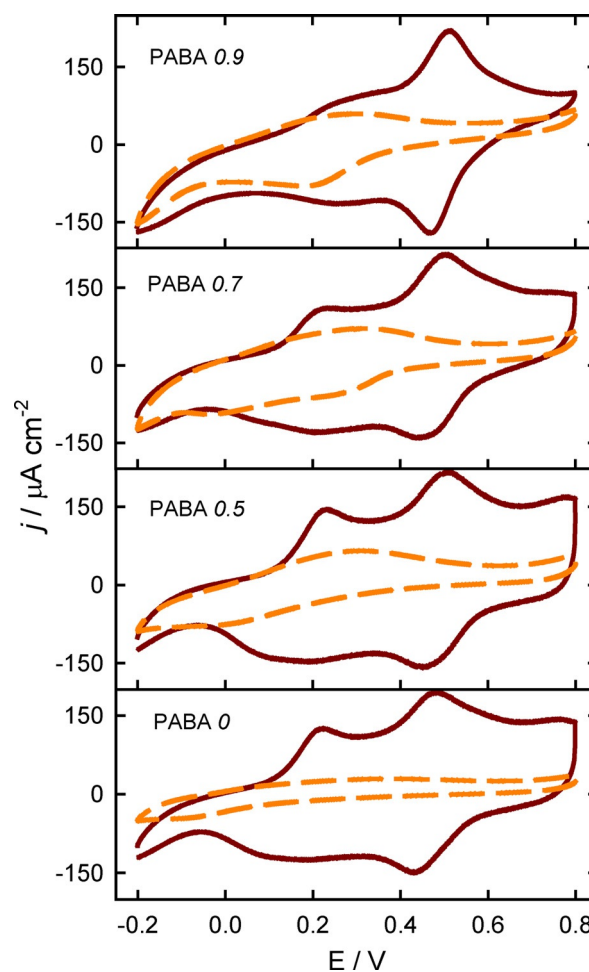
Figure 7. Voltammetric response of copolymers of ABA and ANI with different feed ratios at $v = 0.025$ V s^{-1} in 0.5 M H_2SO_4 (solid line) and 10 mM pH 7 phosphate buffer (dash line).
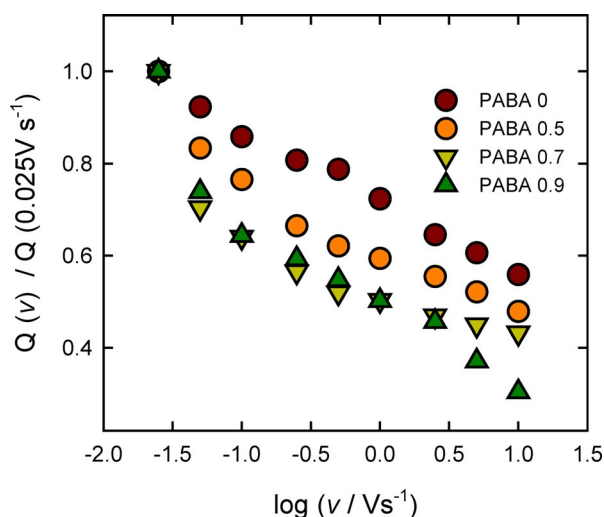
Figure 8. Integrated anodic charge of films relative to that measured at 0.025 V s^{-1} as a function of the logarithm of the sweep rate in 0.5 M H$_2$SO$_4$.

the voltammetric response in both media for films of different f_{ABA}.

All films are stable to potential cycling in acidic media. However, as the ABA fraction increases, the electroactivity in acidic media decreases. Figure 8 shows the anodic integrated charge relative to the value recorded at 0.025 V s^{-1}, as a function of the sweep rate. As the potential is scanned faster, fewer polymer units are able to transfer electrons and the anodic charge decreases. This effect is less notable when the electron transfer between the polymer redox units is fast, as it is in the case of PANI, which is known to have good electronic conductivity in acidic media. According to these results, electron transfer within the film is slower in the case of PABA copolymers, and probably so is their electronic conductivity.

The electroactivity of PANI films in neutral media is poor, and practically no defined peaks are observed. As the proportion of ABA increases, the electrochemical response of the copolymer films also increases. Figure 9 shows the relative anodic charge of films in neutral media (Q_{rel}).
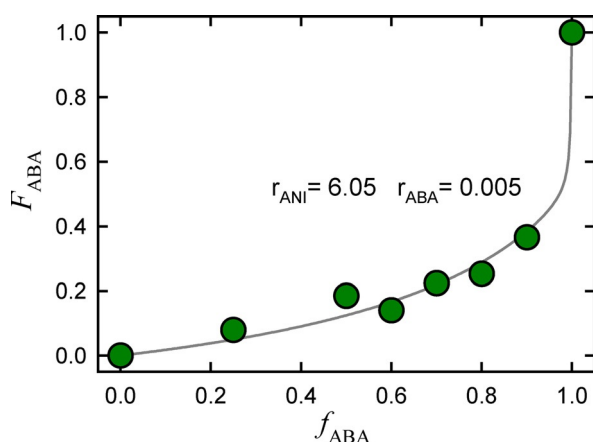
Figure 9. Fraction of the anodic voltammetric charge in acidic solution remaining at neutral pH (Q_{rel}) as a function of the ABA feed ratio. The solid line is supplied to guide the eye.

The loss of electroactivity of PANI at higher pH values seems to be related to the overlapping of the two redox processes, the low stability of the pernigraniline form toward the redox switching, and the low rate of reduction in these media. In the case of substituted polyanilines, the persistence of some redox activity at neutral pH has been related to the fact that the overlapping of the two redox processes in the copolymers is diminished with the incorporation of the pendant group, and pernigraniline is not formed.[24] In this sense, the presence of the pendant group modifies the first redox transition (leucoemeraldine to emeraldine) by shifting the redox potential to higher values, owing to the steric effect of the alkyl substituent that induces nonplanar conformations in the emeraldine chains.[39] In contrast, the emeraldine-to-pernigraniline transition shifts to lower potentials.[57] It has been suggested that the potential shift of this transition is caused by the electron donation effect of the alkyl group, which stabilizes the fully oxidized form, in which the steric effect would be less important.[58] Furthermore, it has been reported that the two redox processes overlap partially for ethyl substitution[58] and almost totally for propyl substitution.[57] The dependence of the first redox transition of PANI on the pH value is complex[59] and, although it initially shifts to lower potentials as the pH increases, it generally shifts to higher potentials.[60] The second redox transition also strongly depends on pH. In this case, it shifts to lower potentials as the pH increases.[61] The result is the overlap of both peaks at approximately neutral pH.[62]

The electroactivity of PABA copolymers in neutral solution was further tested by measuring the electrooxidation of ascorbic acid (AA) on these films, as shown in Section 2.5.

2.5. Electroactivity at Neutral pH and Ascorbic Acid Oxidation

The biological and industrial importance of vitamin C has promoted intense work in the field of the electrochemical sensing of AA.[63] A primordial feature required for AA sensing is good electroactivity in neutral solutions. In the case of PANI-based modified electrodes, it has been solved by either copolymerization[34] or template polymerization with polyanions.[17,18] Moreover, it has been reported that polyanilines with an enhanced middle peak show a better response to AA in neutral solution.[41] Here, the studies with AA do not pursue the objective of developing a sensor material, but test the ability of the copolymer films to interact with biologically relevant species and mediate the electron transfer in neutral solution.

Figure 10a shows the voltammograms of the oxidation of AA on different modified electrodes. The electrocatalytic effect of the PABA 0.7 film is evidenced by the position of the current peak, which is about 0.2 V lower than the peak on PANI-modified or unmodified electrodes. The response to increasing AA concentrations of copolymer films of different compositions is presented and analyzed in the Supporting Information. Figure 10b shows the voltammograms of the oxidation of AA on an electrode modified with a PABA 0.7 film. When the concentration of the diffusing species in solution is low enough, the rate-limiting step is the diffusion of AA from the solution,
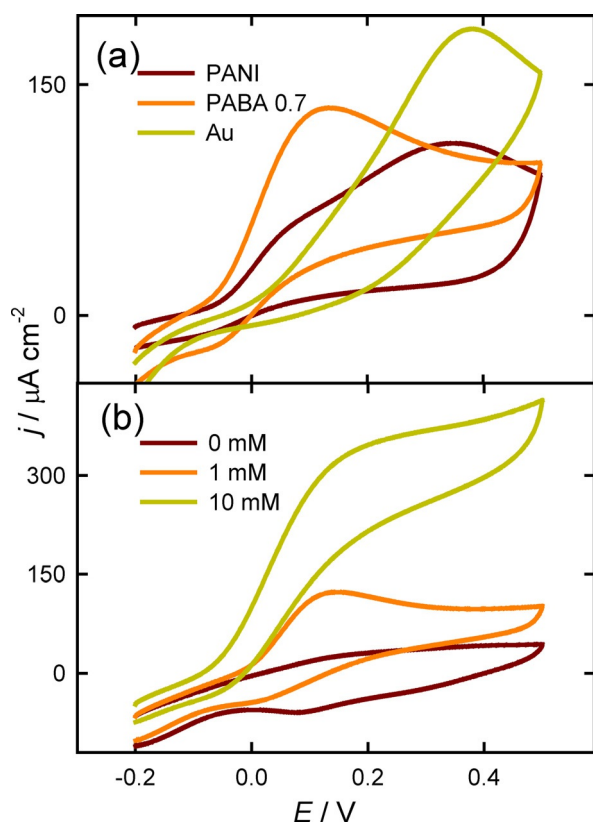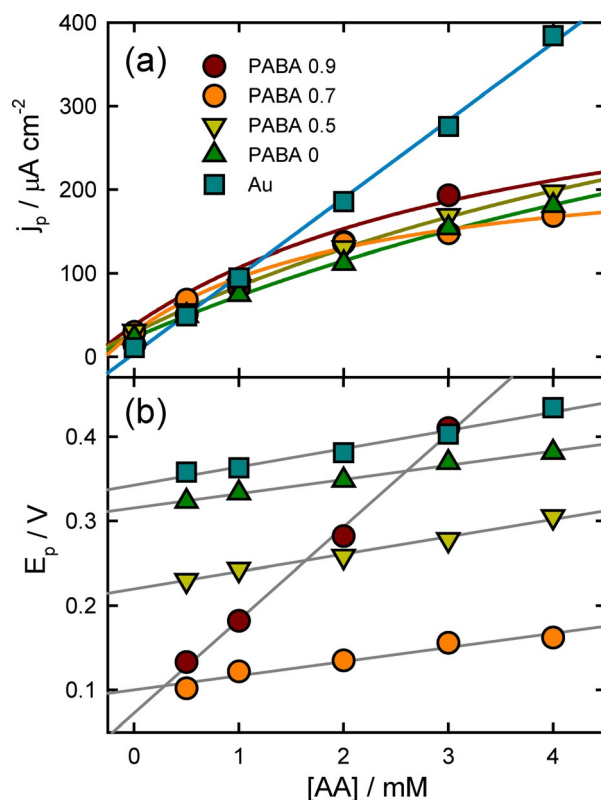
Figure 10. a) Voltammograms of different modified electrodes in 2 mM AA. b) Voltammograms of the electrode modified with the PABA 0.7 film in AA-containing solutions of different concentrations. All experiments were performed in 10 mM pH 7 phosphate buffer at $v = 10$ mV s^{-1}.

Figure 11. Peak current density (a) and peak potential (b) for AA oxidation on PABA films.

and voltammograms show the typical dependence of diffusion-controlled, irreversible electrochemical reactions.[64] As the concentration of the diffusing redox species increases, this step becomes faster and other steps become rate limiting (Figure 11 a). The voltammograms show no peak, but a limiting value of the current (Figure 10 b).

On the polymer films, electrooxidation takes place at lower potentials (Figure 11 b). As mentioned before, this indicates that there is some electrocatalysis induced by the polymer films.[65] The effect is more noticeable in the films with higher proportions of ABA. This feature is desirable, for instance, in the construction of sensors, as lower oxidation potentials yield more selectivity towards other possible oxidizable interferences. The voltammetric results for AA oxidation strengthen the conclusion that copolymers synthesized from $f_{ABA} = 0.7$ have the best performance in neutral solutions. In the case of PABA 0.9, the noticeable shift in the peak potential as the AA concentration increases is probably caused by the lower conductivity in neutral solution that renders charge transport as being slower.

3. Conclusions

Polymerization of ABA into thick films is not possible by using cyclic voltammetry in acidic solution, probably owing to the high solubility of the polymerization products. Although some

amount of polymer is deposited on the electrode, it is not possible to tune the thickness of the film, which is usually one of the advantages of the electropolymerization technique. However, when ANI is added to the electropolymerization solution, stable films of variable thickness are obtained. The electroactivity in acidic media increases with the proportion of ANI, but films obtained from solutions with higher proportions of ABA present better electrochemical response at neutral pH values. The copolymer-film-modified electrodes are able to mediate the electrooxidation of ascorbic acid at pH 7, and the electrocatalytic effect depends on the film composition. Both the remaining electroactivity in neutral solution and the electrocatalysis of AA oxidation are higher for the copolymer with $f_{ABA} = 0.7$.

In summary, we have shown that it is possible to obtain stable PANI-based polymer films with a variable proportion of pendant amino groups by using an easy electropolymerization method. These films are electroactive at neutral pH and can be employed as mediators of redox processes involving biomolecules.

These results open the door to further studies involving the interactions between PABA films and other electroactive biomolecules, such as proteins and enzymes, and the chemical modification of pendant amino groups to add further chemical functionality to the films. In this sense, PABA copolymers are promising building blocks for the design of bioelectroactive assemblies.

Experimental Section

Chemicals

ANI, ABA (see Figure 12), and L-AA were purchased from Sigma–Aldrich. Potassium phosphate monobasic was obtained from Carlo Erba and sulfuric acid was purchased from Anedra. All chemicals were employed as-received, without further purification, except for ANI, which was vacuum distilled. All solutions were prepared with Milli-Q water.
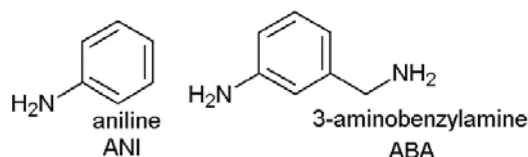

Figure 12. Chemical structure of monomers employed in this work.

Cyclic Voltammetry

Gold electrodes were prepared by sputtering a thin layer of Ti on glass substrates to improve the adhesion. The electrodes were cleaned with soft basic piranha solution ($1\,NH_4OH/1\,H_2O_2/7\,H_2O$) prior to the electrochemical experiments. Before the electrosynthesis of the polymer films, the Au electrodes were cycled in 0.5 M H_2SO_4 between -0.2 and 1.7 V. Electrochemical experiments were performed with a Teq potentiostat (Teq, Argentina). The electrochemical cell consisted of three electrodes in a Teflon-lined cell with 2 mL volume capacity. The Au working electrodes were sealed with an o-ring, defining an electroactive area of 0.145 cm^2. The counter electrode was a Pt wire and a saturated calomel electrode (SCE) was employed as the reference.

Copolymer films were electrosynthesized by using cyclic voltammetry from -0.2 to 1 V versus SCE at 0.05 V s^{-1} in 0.5 M H_2SO_4. The total monomer concentration was kept constant at 0.1 M and different ratios of ANI and ABA were employed. Copolymers were named as PABA X, where X is the molar ratio of ABA in the electrosynthesis solution (f_{ABA}). In this sense, PABA 1 or just PABA means the homopolymer of ABA and PABA 0 means PANI.

X-Ray Photoelectron Spectroscopy

XPS was performed by using a SPECS SAGE HR 100 system spectrometer. A MgKα (1253.6 eV) X-ray source was employed, operating at 12.5 kV and 10 mA. Survey spectra were obtained with a pass energy of 30 eV, whereas 15 eV was employed for detailed spectra of C 1s, O 1s, and N 1s regions. The takeoff angle was 90° and operating pressure was 810^{-6} Pa. Under these conditions, the BE resolution was determined to be 1.1 eV. Quantitative analysis of the spectra was carried out with the Casa XPS 2.3. 16 PR 1.6 software. Shirley baselines and Gaussian–Lorentzian (30 %) product functions were employed. To compensate surface-charging effects, the BE of the main component of the core level C 1s spectrum was set at 285 eV.[43] The FWHM was fixed for the different components of a given element. Survey atomic ratios were calculated from the integrated intensities of core levels after instrumental and photo-ionization cross-section correction.

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