Research Article

Electrochemical Synthesis of Polyaniline/Poly-O-Aminophenol Copolymers in Chloride Medium

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Received 11 January 2011; Revised 21 April 2011; Accepted 30 April 2011

Academic Editor: Hamilton Varela

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The copolymerization of o-aminophenol (OAP) and aniline (ANI) on Pt and ITO electrodes was studied using cyclic voltammetry in 0.1 M HCl/0.4 M NaCl solution. The films were characterized by SEM, cyclic voltammetry, and UV-Vis spectroscopy. The properties of the copolymer were compared with PANI and POAP films. The results strongly suggest that the growth of PANI-POAP films does not consist of the simple buildup of layers of homopolymers on the electrode surface as a result of OAP or ANI oxidation products in the monomer mixture, but that a new conducting polymer is formed by copolymerization.

1. Introduction

The polymerization of substituted anilines has been studied with an aim to achieve the formation of soluble polymeric films in order to improve processability while maintaining electric properties [1]. However, the electropolymerization of benzyl monomers containing both −NH2 and −OH groups is more recent and less well explored [2]. O-aminophenol monomer (OAP) is an aniline derivative that has been shown to hold two groups in the benzenic ring: an amine and a hydroxyl group, which supply many more coordination sites [2]. There is controversy in the literature with regard to dimeric structures formed after chemical and electrochemical oxidation of OAP in aqueous medium. Electrophilic reactions may occur at the meta or para position of the −NH2 group of OAP, yielding two types of heteroamnic. structures. While chemical oxidation of OAP yields the formation of 2-aminophenoxazine (APZ) [3–6], redox reactions involving the B structure (phenoxazine units) have been proposed for electrochemically prepared POAP films [7–10] (Scheme 1).

However, most conducting polymers suffer from some limitations. For example, polyaniline (PANI) with alkyl substituents presents limitations that are imposed on the conductivity of the produced polymer despite its solubility being improved when compared with PANI. Efforts have been made towards the design of new conducting materials. In this way, the conductivity of polyanilines and the solubility of substituted polyanilines can be achieved by copolymerization [11].

Copolymerization allows chemical modification as well as the introduction of specific functional groups to side substituents to control the physicochemical properties of materials [12]. The copolymerizations of sulfonated aniline and aniline have been successfully carried out [13–15]. There are many examples of polyaniline-type copolymers: copolymers of aniline and o-toluidine [16–18], aniline and 2-ethylaniline [11], aniline and o-anisidine [17, 19], aniline and o- and m-phenylenediamine [20, 21], aniline and N-butylaniline [22], aniline and o-alkoxysulfonated 23, aniline and pyrrole [23], and aniline and thiophene 25. These various copolymers are synthesized under different conditions, by chemical or electrochemical methods, in order to achieve the desired properties.

In 2002, the first studies of the copolymerization of OAP and PANI appeared with the objectives mainly being to improve the solubility of PANI and the electric conductivity of POAP. In recent years, many other works have been published in order to study the different properties of this
copolymer [24–26]. Hua and Ruckenstein [27] synthesized a novel water-soluble copolymer of aniline and aminophenol (AP) grafted with oligo-(oxyethylene) (PEO) side chains (AP-g-PEO). The copolymerization and copolymer compositions were changed using various feed mole ratios AP-g-PEO/aniline and oligo-(oxyethylene) side-chain lengths. The copolymer of poly((AP-g-PEO-750-co-aniline) with a feed mole ratio of 3/1 was water-soluble and exhibited relatively high conductivity (0.12 S/cm). Several authors have observed that the monomer concentration ratio, acid concentration, and applied potential strongly affect the copolymerization rate and the properties of the copolymer [27–29]. Zhang et al. [28] concluded that optimal conditions for the copolymerization involve the scan potential range being controlled between −0.10 and 0.95 V (versus SCE), with a solution consisting of 0.34 M aniline, 0.012 M m-aminophenol, and 2.0 M H₂SO₄. A nanostructured network of poly(aniline-co-o-aminophenol) has been synthesized in the presence of ferrocenesulfonic acid, and fiber size in the nanostructures can be controlled by the number of cycles during copolymerization [30]. Also found in the literature are applications of these copolymers as sensors of uricase [31], arsenate [32], 3,5-dicarbonyl compounds [33], hydrogen peroxide [34], and ascorbic acid [35]. However, the studies found in the literature involve the synthesis of PANI-POAP copolymer from sulfuric acid monomer solution and its copolymer. Solutions consisting of 0.1 M aniline, 1 mM o-aminophenol, and 0.1 M aniline + 1 mM o-aminophenol in 0.1 M HCl/0.4 M NaCl solutions were used for polymerization of the homo- and copolymers, respectively.

The polymerization and copolymerization of monomers were performed by using repeated potential cycling at a scan rate of 50 mV s⁻¹, and the cyclic voltammograms (CVs) were recorded simultaneously with the synthesis. The polymer/copolymer film-coated electrode was then placed in a monomer-free background electrolyte (0.1 M HCl and 0.4 M NaCl), and CVs of the film-coated electrode were recorded after obtaining the stable cyclic voltammetric pattern.

A Shimadzu 2401 PC UV-Vis spectrophotometer was used to record the UV-Vis spectra of PANI, POAP, and PANI-POAP films deposited onto an indium-doped tin oxide (ITO) glass electrode. Polymerization was carried out in the conditions specified above. Before all measurements were taken, the deposited polymer films on the electrode (which were extracted from the solution in the reduced state) were washed with 0.1 M HCl and dried in a vacuum for 24 hrs. Surface morphology of these films were examined by a Philips XL-30 scanning electron microscope (SEM). The FTIR spectra of the PANI and PANI-POAP film samples were taken using a Nicolet Impact 410 FTIR spectrophotometer.

### 3. Results and Discussion

#### 3.1. Electrochemical Polymerization of Aniline, O-Aminophenol, and Its Copolymer

Solutions consisting of 0.1 M aniline, 1 mM o-aminophenol, and 0.1 M aniline + 1 mM o-aminophenol in 0.1 M HCl/0.4 M NaCl solutions were used for polymerization of the homo- and copolymers, respectively. The polymerization and copolymerization of monomers were performed by using repeated potential cycling at a scan rate of 50 mV s⁻¹. Figures 1(a)–1(c) show the typical cyclic voltammograms recorded during electrochemical synthesis of the polymer in the presence of ANI, OAP, and ANI/OAP, respectively.

Typical CVs indicative of pure ANI polymerization are shown in Figure 1(a). During the anodic sweep, an anodic peak at 1.1 V appears in the first cycle, and then three anodic peaks (Iₓ, IIₓ, IIIₓ) appear in subsequent cycles. In the cathodic sweep, the presence of three corresponding broad reduction peaks is labeled: Iᵧ, IIᵧ, and IIIᵧ. Their peak currents increase quickly with an increase in the number of possible cycles. This indicates that polyaniline film grows very quickly as the electrolysis proceeds, which is caused by autocatalytic polymerization [36, 37]. The peaks can be attributed to: regarding the first peak at 0.2 V (peak Iₓ), formation of radical cations (polaronic emeraldine); regarding the second, benzoquinone formation, occurring at 0.5 V (peak IIᵧ); and regarding the third, formation of diradical dications, commencing at approximately 0.6 V and reaching a maximum at 0.75 V (peak IIIᵧ) [38]. After electrolysis,
a green film was formed on the working electrode after 15 cycles.

Figure 1(b) shows the electro-oxidation of OAP when cycling the potential between $-0.2$ and $1.10$ V at scan rate $50$ mV s$^{-1}$. Initially, two redox couples were observed. The anodic peaks were found at $0.31$ V (peak II$\text{a}$) and at $0.62$ V (peak III$\text{a}$), and the corresponding two cathodic peaks at $0.27$ V (peak II$c$) and $0.59$ V (peak III$c$). A redox pair at $0.12$ V/0.04 V (I$\text{a}$/I$c$) began to appear after a few scans and the current increase during continuous cycles. According to Barbero et al. [7], peaks a$\text{2}$ and a$\text{3}$ were due to the oxidation of OAP to the radical cation ($OAP^{\text{•+}}$) and its further oxidation to the dication, respectively. By contrast, peak a$\text{1}$ only resulted from the formation of radical cations (POAP$^{\text{•+}}$) from the polymer and/or oligomers. On further potential cycling, the oxidation current (peaks II$\text{a}$ and III$\text{a}$) decreases rapidly owing to the low conductivity of POAP, which hinders the diffusion of OAP through the polymer matrix [7, 37]. The redox peaks I$\text{a}$/I$c$ nonetheless increased steadily with an increasing number of scans, showing the gradual yet continual formation of electroactive POAP films. In contrast to PANI deposition, POAP films formed very slowly, and only after 90 cycles was a thin film found on the working electrode. It changed color from dark brown in the oxidized state to light yellow in the reduced state.

Like the homopolymerization of OAP and ANI, electrol-ysis of mixed solutions containing both OAP and ANI was carried out by cycling the potential between $-0.20$ V and different upper potential limits. Cyclic voltammograms recorded during potentiodynamic copolymerization on a Pt electrode of ANI with OAP for 0.1 M HCl + 0.4 M NaCl + 0.1 M ANI +1 mM OAP are shown in Figure 1(c). A close comparison of these CVs reveals that voltammetric curves of copolymers are more distinct than homopolymers, indicating that the film deposited during oxidation of the ANI + OAP mixture is different from that of ANI or OAP oxidation. The PANI-POAP film deposited is brownish-blue which is different from the color of both homopolymers, and it can be observed after 20$^\circ$ cycles, which is a shorter time than that obtained for POAP alone.

In Figure 1(c), an anodic peak appears at $1.05$ V for the first cycle. This peak is caused by the oxidation of amino
groups from both monomers, since the ANI oxidation peak is at 1.1 V (Figure 1(a)) and oxidation of OAP occurs near 0.9 V (Figure 1(b)). In successive sweeps, there are three anodic peaks, with a shoulder at 0.2 V, and four cathodic peaks. The fact that there are four cathodic peaks on the reverse scan of the first cycle is a first indication that the deposition in this case is different from that of POAP and ANI.

After several cycles, four main redox pairs were observed and the current of redox peaks gradually increased with the number of cycles. The voltammetric behavior is different from that of PANI growth, with an additional redox pair (IVa/IVc) present at 0.28/0.26 V. This extra pair of redox peaks would be caused by redox of the copolymer itself. This observation strongly suggests that the growth of PANI-POAP film does not consist of the simple buildup of layers on the electrode surface as a result of ANI or OAP oxidation products in the monomer mixture, but that a new conductor polymer is formed. The same behavior was observed by different authors in sulfuric acid [27–30].

In Figure 1(c), it can also be observed that the redox peaks Ia/Ic are smaller than those observed in the same potential in Figure 1(a) (peaks Ia/Ic). The peaks IIa/IIc become more prominent in Figure 1(c) than in Figure 1(a). These results indicate an easier redox reaction of polyaniline side chains [38], which overlap the peak of benzoquinone formation. The broader anodic peak IIIa is observed at 0.58 V, which is related to the overlap of peak IIIa of Figure 1(a) and peak IIIa of Figure 1(c). The current density of peak IIIa is larger than that of peak IIIa of Figure 1(b), indicating that OAP is easily oxidized to the radical cation (OAP⁺).

3.2. Voltammetric Responses of PANI, POAP, and Its Copolymer. The voltammetric responses of PANI, POAP, and PANI-POAP films deposited on a Pt electrode were recorded in the supporting electrolyte (0.1 M HCl and 0.4 M NaCl), Figure 3. The CVs of the response and formation of polymer films are similar. In the case of POAP, the peak a3 observed in Figure 1(b) disappears completely, indicating that formation of radical cations (polarons) and dications (bipolarons) was not achieved in the polymer due to the difficulty in charge and electron delocalization along POAP polymer chains, which are known to be partly cross-linked [7].

The PANI films showed a typical redox response with three redox couples, as reported in the literature [39, 40]. The first and third redox couples are due to the interconversion reactions of PANI upon varying the potential (leucoemeraldine/emeraldine and emeraldine/pernigraniline, respectively). The middle peaks have been assigned to redox reactions involving an overoxidized PANI structure, indicating polymer degradation.

For PANI-POAP films, the CVs of response and polymerization are similar and both present four redox couples as previously discussed. However, by comparing the three curves present in Figure 2, it is possible to observe different responses for the three films that are deposited. The redox processes attributed to the PANI film shift for cathodic and anodic values. This behavior again suggests that copolymer formation has taken place.

3.3. UV-Vis of PANI, POAP, and Its Copolymer Films. Figure 3 shows UV-Vis spectra of PANI, POAP, and PANI-POAP films on ITO electrodes recorded in HCl 0.1 M and NaCl 0.4 M. The films were deposited in the same conditions shown in Figure 1.

PANI film presents UV-Vis spectra characteristic of the emeraldine base. There are three absorption bands at 317, 457, and 647 nm, which is a broad band. Bands with peaks at 317 and 457 nm correspond to the π–π* transitions in the
benzonoid rings, while the band at 647 nm is usually ascribed to an exciton, located in the quinoid ring [41].

The absorption spectrum of the oxidized form of POAP presents two absorption bands with peaks at 309 and 457 nm, which correspond to the π–π* transitions of the aromatic structure and the oxidized form of OAP [7], respectively. The band at 457 nm can also be attributed to the phenoxyzine of the polymer [7].

The UV-Vis spectrum of the copolymer shows the same bands observed for the PANI and POAP films, indicating that the same transitions observed in homopolymers occur in the copolymer. The UV-Vis spectrum of the copolymer is similar to that obtained for POAP films since both present a brown color. On the other hand, the absorbance of the band at 457 nm, which corresponds to the formation of the intermediate state during the electrooxidation of the leucoemeraldine state, presents a higher intensity when compared with that observed for the homopolymers. The absorption band at about 317 nm for PANI shifts to about 303 nm for PANI-POAP films. This shift can be caused by the presence of the substituent–OH groups in the copolymer chain. The absorption results obtained from electrochemical polymerization of the mixture of ANI and OAP clearly show the incorporation of OAP into the polymer during polymerization.

3.4. FTIR of PANI and PANI-POAP. To investigate the copolymerization of ANI and OAP, FTIR and UV-Vis absorption spectra were also employed to characterize the structure of PANI-POAP. Figure 4 shows the FTIR spectrum of PANI-POAP (curve 1), and for comparison, the FTIR spectrum of PANI (curve 2).

As seen in Figure 4, the FTIR spectra of copolymers seem to present the same picture as that of PANI, indicating that aniline units dominate the composition of the copolymer. However, there are some differences between curves 1 and 2.

This suggests that the copolymer chain is somewhat different from the polyaniline chain, since the former contains OAF. A peak at 1383 cm⁻¹, which appears on curve 2 but not on curve 1, may be attributed to the C–O–H deformation vibrations, since a peak at 1400 cm⁻¹ appears in the IR spectrum of o-aminophenol [35] and the IR spectra of phenols have an absorption peak at 1390–1310 cm⁻¹ [36]. Thus, the peak at 1383 cm⁻¹ in Figure 4 can be considered as evidence of the presence of the OAP unit in the polymer film. We can also notice that the two split peaks at 1210 and 1230 cm⁻¹ are observed in the IR spectrum of o-aminophenol [35], which may be attributed to the C–O stretching vibrations. However, only a very small shoulder at 1214 cm⁻¹ appears in Figure 4. This is due to the fact that a broad band centered at 1288 cm⁻¹ may mask the C–O stretching vibrations.

The other peaks observed for both PANI and PANI-POAP films can be attributed as follows: the peaks at 1583 and 1483 cm⁻¹ are attributed to the C=C stretching vibrations of the benzene ring and quinone ring vibrations [37, 38, 42]. The peak at 1303 cm⁻¹ is due to the C–N stretching of the polymer. The strongest band observed near 1100 cm⁻¹ and the band at 1235 cm⁻¹ are due to C–C stretching and C–C twisting, respectively, of the alkyl chain [43]. The peak near 800 cm⁻¹ is due to the N–H out-of-plane bending absorption. The C–Cl stretching peak arises in the range of 590–700 cm⁻¹ [44]. This confirmed the Cl-doping of the electrochemically synthesized polyaniline films in HCl.

3.5. Morphology of the PANI, POAP, and Its Copolymer Films. The images of PANI, POAP, and copolymer films are shown in Figure 5. The deposits of polymers were obtained on ITO electrodes in the same conditions as the UV-Vis spectra.

PANI exhibits a fibrous structure in Figure 5(a) and the fibrous deposit is not entirely uniform over the electrode, indicating that the fibers are preferred sites for further polymer growth. As can be seen, POAP films present a highly compact structure (Figure 5(b)). The SEM image of the PANI-POAP film, in Figure 5(c), reveals uniform films, which completely recover the surface, and a dense fine granular deposit. The change in surface structure indicates the strong effect of ANI units on the copolymer morphology.

4. Conclusions

The CVs of OAP-ANI copolymerization, on a Pt electrode, were compared with CVs for ANI and OAP polymerization. For ANI-OAP polymerization, four main redox pairs were observed and the current of redox peaks gradually increased with the number of cycles, indicating the growth of conducting polymer film in each cycle. However, for ANI polymerization, three characteristic redox pairs were recorded, whereas for the CV of OAP polymerization, only two redox pairs were marked. The color of the oxidized polymers varies: PANI-POAP film is brownish-blue and PANI film is green, while POAP film is brown. Based on the fact that the cyclic voltammogram of the resulting polymer is not a simple superposition of each individual polymer, and
the color of the resulting polymer is different from that of PANI and POAP, we can conclude that the resulting polymer obtained from electrolysis of the solution consisting of ANI and OAP is a copolymer, rather than a mixture of PANI and POAP.

Furthermore, differences in UV-Vis spectra can be noticed between the three films favoring the incorporation of OAP units in the copolymer. SEM analysis showed a change in morphology, from fibrous PANI films to dense fine granular PANI-POAP films, indicating the strong effect of ANI units on the copolymer morphology. The FTIR spectrum of PANI-POAP indicates that an electrochemical copolymerization of ANI and OAP took place in this study.

Copolymerization of ANI and OAP has been used as a good electrochemical sensor for different samples, and our preliminary results show that the material has electroluminescent properties, and it could, therefore, be used in polymer-based light-emitting diodes.

Acknowledgments

The authors are indebted to the Brazilian agencies CAPES, CNPq, and Araucária Foundation. The authors also wish to thank Mr. M. A. C. Berton and Mrs. Laiz Valgas de Castilhos of LACTEC for providing technical support in SEM experiments.

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