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PII: S0014-3057(16)31674-3

DOI: <http://dx.doi.org/10.1016/j.eurpolymj.2017.04.024>

Reference: EPJ 7836

To appear in: *European Polymer Journal*

Received Date: 12 December 2016

Revised Date: 22 March 2017

Accepted Date: 17 April 2017

Please cite this article as: Abidi, M., López-Bernabeu, S., Huerta, F., Montilla, F., Besbes-Hentati, S., Morallón, E., Spectroelectrochemical study on the copolymerization of *o*-aminophenol and aminoterephthalic acid, *European Polymer Journal* (2017), doi: <http://dx.doi.org/10.1016/j.eurpolymj.2017.04.024>

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Spectroelectrochemical study on the copolymerization of *o*-aminophenol and aminoterephthalic acid

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Abstract

The electrochemical copolymerization of aminoterephthalic acid (ATA) and *o*-aminophenol (OAP) was carried out on platinum electrodes in acidic medium. The obtained material, poly(ATA-*co*-OAP), can be deposited by cyclic scanning of the potential in a wide potential range and shows significant electroactivity. However, it was observed that a copolymer with less overoxidation defects is obtained at inversion potentials where only OAP monomer (and not ATA monomer) is oxidized. The successful incorporation of unoxidized ATA monomers to the growing copolymer chain was confirmed by *in situ* FTIR spectroscopy and XPS, which suggested a monomer ratio close to 1:2 (ATA:POAP) within the obtained copolymer material. The redox switching of poly(ATA-*co*-OAP) in acidic medium involves reversible benzenoid-quinoid and phenoxazine-phenoxazone conversions but carboxylic groups do not participate actively on these transformations.

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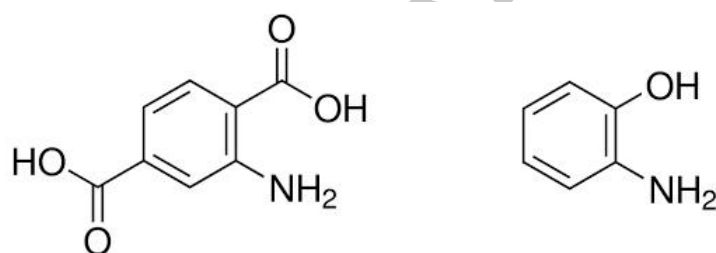
1. Introduction

Electroactive polymers can be prepared using either chemical or electrochemical polymerization methods. In both cases, electrochemically active groups (typically those containing O, N or S) can be incorporated into the polymer structure as a pendant group in monomer species (as in pre-functionalized polymers) or, alternatively, fixed into the polymer network in an additional step after polymerization (post-functionalized polymers). Like chemical polymerization, the electrochemical process is usually an oxidative polymerization although reductive polymerization is also possible under particular conditions. In most cases, electrochemical polymerization is preferable against the chemical route, especially if the polymeric product is intended for use as a polymer film electrode, as in thin-layer sensors, because the control of the oxidation potential is a prerequisite for the production of high-quality polymers [1]. After chemical polymerization, the material is usually obtained in an oxidized, conducting state containing counterions, which are incorporated from the solution used in the synthesis procedure. However, it is easy to change the oxidation state of the polymer prepared by potential cycling. In addition to pre- or post-modification, copolymerization of different monomers is one of the most efficient routes to modify the properties of conducting polymers [2,3] and this strategy produces often copolymers with properties being intermediate between different parent homopolymers.

As an example, the polymerization of *o*-aminophenol (OAP) has been extensively studied because of the formation of an electroactive polymer, POAP, with potential applications in biosensors or corrosion protection [4–6]. It is agreed that POAP is a ladder polymer composed of phenoxazine-type units showing redox activity, moderate electrical conductivity and chemical stability that strongly depends on the applied potential [7–9]. In order to exceed its limitations, *o*-aminophenol has been widely used as a co-monomer for copolymerization with aniline. Poly(ANI-*co*-OAP) retains part of the properties of polyaniline and also offers new characteristics [10–12], as the improved redox response at pH over 10, which is mainly attributed to the reversible redox activity of the -OH group contained in the copolymer chain.

A large number of different monomers have been used for copolymerization with aniline. Among them, those containing negatively charged ionizable groups such as sulfonic and carboxylic have deserve great attention because they provide polyaniline chains with self-

doping properties that extend the limited pH range for which polyaniline is electroactive and delivers enhanced physicochemical properties [13–15]. In a series of previous contributions, we electrochemically synthesized homo-polymers from aminobenzoic acid [16,17] and aniline-based copolymers, poly(ANI-*co*-ABA) [5,18]. These copolymers show enhanced electroactivity at higher pH and were used as electrocatalytic substrates for the oxidation of ascorbate molecules. On the other hand, aminoterephthalic acid (ATA) is an interesting comonomer containing a -COOH group attached to the aromatic ring. Copolymers formed from aniline and aminoterephthalic acid were chemically synthesized in our laboratory, showing good electroactivity in aqueous acid medium [3]. In this context, the aim of the present work is to investigate the possibility of electrochemically synthesizing electroactive copolymers containing both *o*-aminophenol and aminoterephthalic acid units. The chemical structure of the obtained materials will be characterized by using spectroscopic techniques such as *in situ* FTIRS and XPS.



Scheme 1. Chemical structures of aminoterephthalic acid, ATA, and *o*-aminophenol, OAP.

2. Experimental

Analytical grade *o*-aminophenol and aminoterephthalic acid (Aldrich) were used without further purification. D₂O was from Aldrich chemicals, 99.9% atom %D. The polymerization solutions were 1 M HClO₄ prepared from Merck Suprapure concentrated acid and ultrapure water. The polycrystalline platinum working electrode (0.3 cm² of geometrical area) was thermally cleaned and subsequently protected from the laboratory atmosphere by a droplet of ultrapure water of 18.2 MΩ cm obtained from an Elga Labwater Purelab system. Then, it was transferred to the working solution (previously deaerated by bubbling N₂) where it was immersed at controlled potential. Cyclic voltammograms were recorded at a constant sweep rate of 50 mV s⁻¹ and at room temperature. A reversible hydrogen electrode (RHE) immersed in the working solution was used as the reference electrode and the counter electrode was a platinum wire.

In situ FTIR spectra were recorded in a Nicolet 5700 spectrometer equipped with a liquid nitrogen-cooled MCT detector. The sample compartment was purged from CO₂ and water vapor throughout the experiment using a purge gas generator from Peak Scientific PG28L. The working electrode was a mirror-polished polycrystalline platinum disc, 8 mm in diameter, obtained from Good Fellow Metals (purity 99.99%). A platinum wire electrode was used as the counter-electrode and a RHE as the reference electrode. The thin-layer spectroelectrochemical cell was made of glass and was provided with a prismatic CaF₂ window beveled at 60°.

XPS spectra were obtained with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatized Mg-K α (1253.6 eV) radiation source of 300 W and a hemispheric electron analyzer equipped with nine channeltron electron multipliers. The pressure of the analysis chamber during the scans was about 5×10^{-7} Pa. After the survey spectra were obtained, higher resolution survey scans were performed at pass energy of 50 eV. The intensities of the different contributions were obtained by calculation of the integral of each peak, after having eliminated the baseline with S form, and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. Bond energies were referred to the C 1s line at 284.4 eV, obtaining values with a precision of ± 0.2 eV.

3. Results and discussion

3.1. Electrochemical behavior of ATA and OAP monomers on Pt electrodes

In this section, we will examine first the electrochemical response of aminoterephthalic acid and *o*-aminophenol individually. The oxidation of each monomer species in the absence of the other will assist in the selection of appropriate conditions for copolymer formation, particularly on setting the upper potential limit during electro-copolymerization. In addition, the voltammetric profiles recorded for the individual monomers will be used to define similarities and differences between the redox behavior of obtained copolymers and homopolymers.

The electrooxidation of 10 mM ATA was carried out on a platinum electrode in 1M HClO₄ by cyclic scanning of the potential between 0.06 and 1.45 V. Fig. 1a shows that the oxidation of this species starts at a potential as high as 1.18 V and displays a maximum at 1.34 V that continuously decreases with the number of cycles. Then, it seems that this intense

anodic peak yields some non-electroactive adsorbed product on the electrode surface, as deduced from the absence of any coupled reduction wave during subsequent reverse scans. In fact, after the experiment, the surface of the platinum electrode appeared covered by a yellowish film that was then washed with ultrapure water and transferred to a new test solution containing 1M HClO₄ as the background electrolyte. A cyclic voltammogram recorded for this film in the absence of monomer species is presented in Fig. 1b, where the characteristic profile of a platinum electrode covered with an almost electroinactive thin layer of polymeric product can be clearly observed (the curve is similar to the polycrystalline electrode without a deposit). Therefore, it can be inferred that contrary to its parent compound *o*-aminobenzoic acid [16], the electrochemical oxidation of aminoterephthalic acid does not yield an electroactive polymer on the electrode surface.

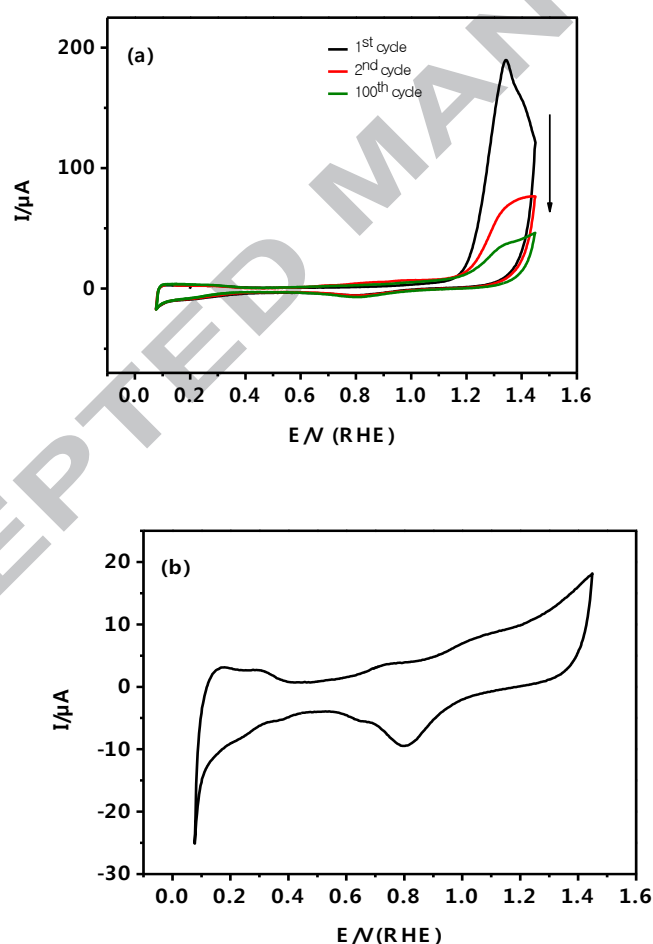
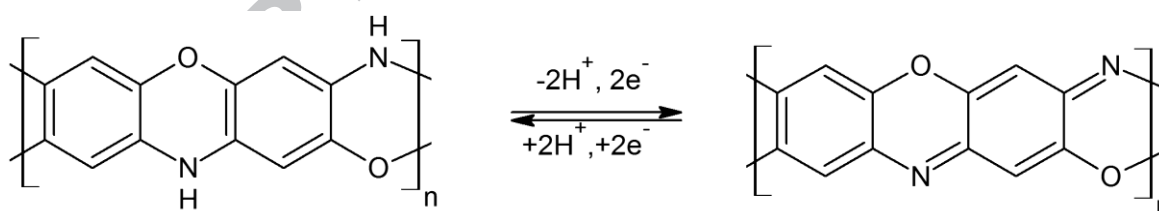


Fig. 1. a) Cyclic voltammograms recorded for a Pt electrode during the electrochemical oxidation of 10 mM ATA in 1M HClO₄ solution. 1st cycle (black line), 2nd cycle (red line), 100th cycle (green line). **b)** Voltammetric response of the modified electrode in 1M HClO₄ background solution free of monomer.

The electrochemical oxidation of 10 mM OAP was also carried out in 1M HClO₄ solution on the platinum substrate. First, a single voltammetric sweep from 0.06 up to 1.45 V was done in order to examine the voltammetric profile of OAP in the same potential window as in Fig. 1a for ATA monomer. The result is shown in Fig. 2a, for which the onset of OAP electrooxidation is observed at 0.78 V. In addition, two overlapped anodic peaks appear at 0.89 and 1.12 V on this voltammetric curve, the first one being more intense than the second one. Contrary to Fig. 1a, and during the first reverse scan, some cathodic features can be clearly observed in the 0.2 -0.6 V potential range. These are related with the formation of an electroactive polymeric deposit (POAP) on the platinum electrode. The voltammetric features of deposited POAP are strongly dependent on the upper potential limit employed during the electrochemical synthesis. In Figs. 2b to 2d, the electrochemical responses in 1M HClO₄ solutions of POAP deposited by cycling up to 0.95 V (b), 1.1 V (c) and 1.45 V (d) is shown. Cyclic voltammogram of film synthesized at 0.95 V exhibits two overlapped redox processes, showing that the redox transition of this polymer from its reduced to the completely oxidized state occurs via two consecutive reactions. On the contrary, for POAP film deposited at 1.1 V, only one redox transition is observed. The redox transition of this material has been usually ascribed to the reversible oxidation of phenoxazine rings in a ladder structure, as shown in Scheme 2. Both observations are in agreement with our previous results obtained for POAP synthesized under potentiostatic or potentiodynamic conditions [8,19].



Scheme 2. Accepted redox switching in acidic medium of a POAP segment involving phenoxazine – phenoxazone transitions [8,19].

However, if a limit potential as high as 1.45 V is applied during electropolymerization, the obtained POAP shows a markedly different electrochemical behavior. On the one hand, the currents associated with the redox peaks are lower and, on the other, an additional redox process develops. The potential of the first anodic peak in Fig. 2d is about 0.4 V, a value similar to those observed in Figs. 2b and 2c. However, the second anodic transition occurs at

0.55 V. Obviously, such a value is too positive to correspond to the same transitions occurring when the polymer was synthesized at moderate potentials. The result strongly suggests that POAP deposited at 1.45 V gets structural, electrochemically active defects on the polymer chain, probably due to an overoxidation appearing at potentials above those of phenoxazine-phenoxazone transitions. We will address this question later, during the discussion on the structure of ATA-OAP copolymer.

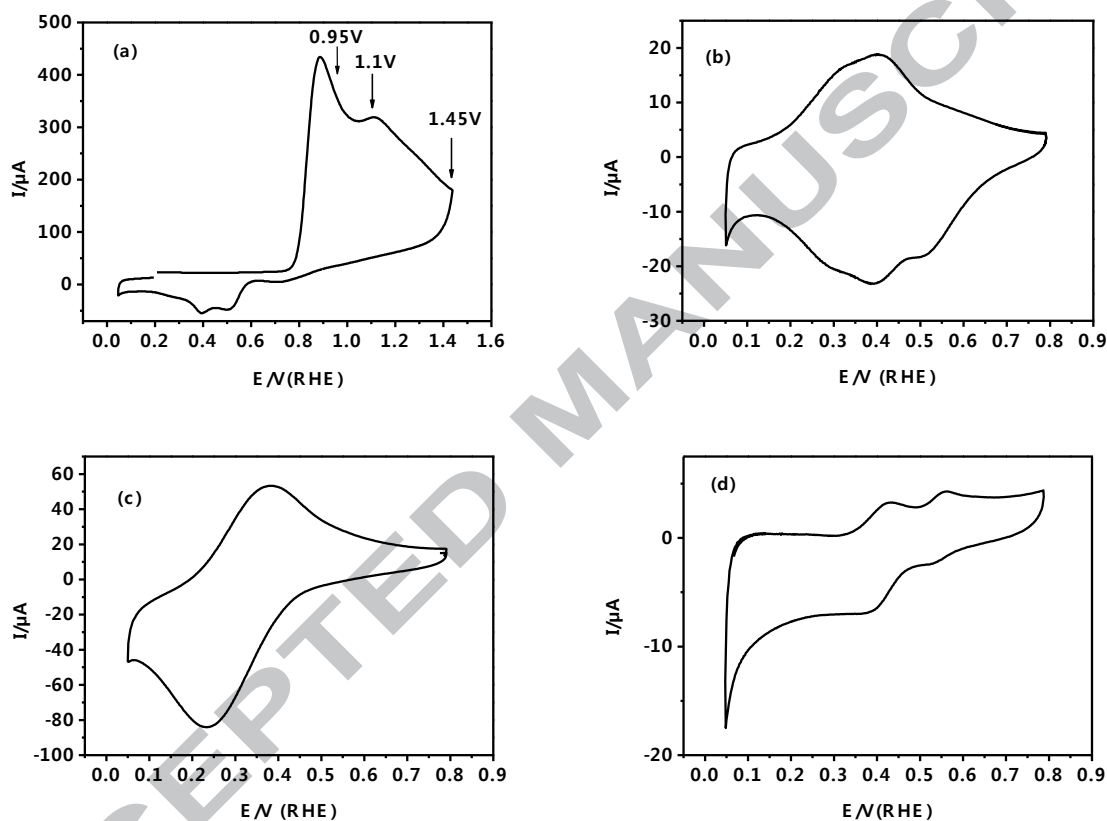


Fig. 2. (a) First potential cycle recorded for a Pt electrode during the electrochemical oxidation of 10 mM OAP in 1M HClO₄ solution and the steady voltammograms of the polymeric materials obtained after 100 polymerization cycles at different positive potential limits: 0.95 V (b), 1.1 V (c) and 1.45 V (d). Test solutions 1M HClO₄.

3.2. Electrochemical copolymerization of ATA and OAP

The results presented in the last section, strongly suggest that the anodic limit potential could play a significant role on the electrochemical copolymerization of both monomers. To gain insight into this point, copolymers were deposited using different limit potentials, from 0.95 V up to 1.45 V. Fig. 3a shows the first potential cycle recorded for a Pt electrode in an

acidic solution containing an equimolar mixture of OAP and ATA. The electrode was immersed at 0.06 V and the potential scanned up to 1.45 V. Arrows on this curve show the four points selected as anodic limit potentials to carry out copolymerization. Figs. 3b to 3e show the voltammetric responses, recorded in 1M HClO₄ test solution free of monomers, of those copolymers obtained after 100 electropolymerization cycles up to 0.95 V, 1.1 V, 1.25 V and 1.45 V, respectively. A first inspection of these curves makes it clear an effect of the potential limit on the voltammetric profile. The material formed up to 0.95 V (Fig. 3b) was a thin, almost transparent film showing a redox activity equivalent to that obtained in Fig. 2b, after the homopolymerization of OAP up to the same potential limit. Therefore, it seems that an effective copolymerization is not occurring at so mild conditions (it should be noted that 0.95 V is too low a potential to oxidize ATA monomers). The most significant difference between the voltammograms in Fig. 2b and Fig. 3b seems the higher overlapping observed for the redox transitions of the former, an observation that can be explained in terms of the lower coverage reached by that material in Fig. 3b.

However, the electrochemical response of the deposited material changes significantly when the potential limit for the electropolymerization is extended up to 1.1 V. Such a potential value is still under the onset of ATA electrooxidation, but Fig. 3c shows two separate redox transitions at 0.42/0.27 V and 0.65/0.56 V. The voltammetric profile recorded is quite different to that obtained after OAP homopolymerization under similar conditions (compare with Fig. 2c). Consequently, it seems that copolymerization can be successfully performed at 1.1 V thanks to the incorporation of unoxidized ATA monomers to the polymer growing chains. Interestingly, the potential of the first process in Fig. 3c fits well with the couple of reversible peaks observed in Fig. 2c for POAP homopolymer and, therefore, could be tentatively ascribed to the phenoxazine-phenoxazone transition. Since no overoxidation of the polymer occurred at 1.1 V, the second redox process in Fig. 3c should be necessarily attributed to the presence of ATA centers within the polymer chain. This result is clearly in contrast with the lack of homopolymerization of ATA under the same electrochemical conditions (Fig. 1b).

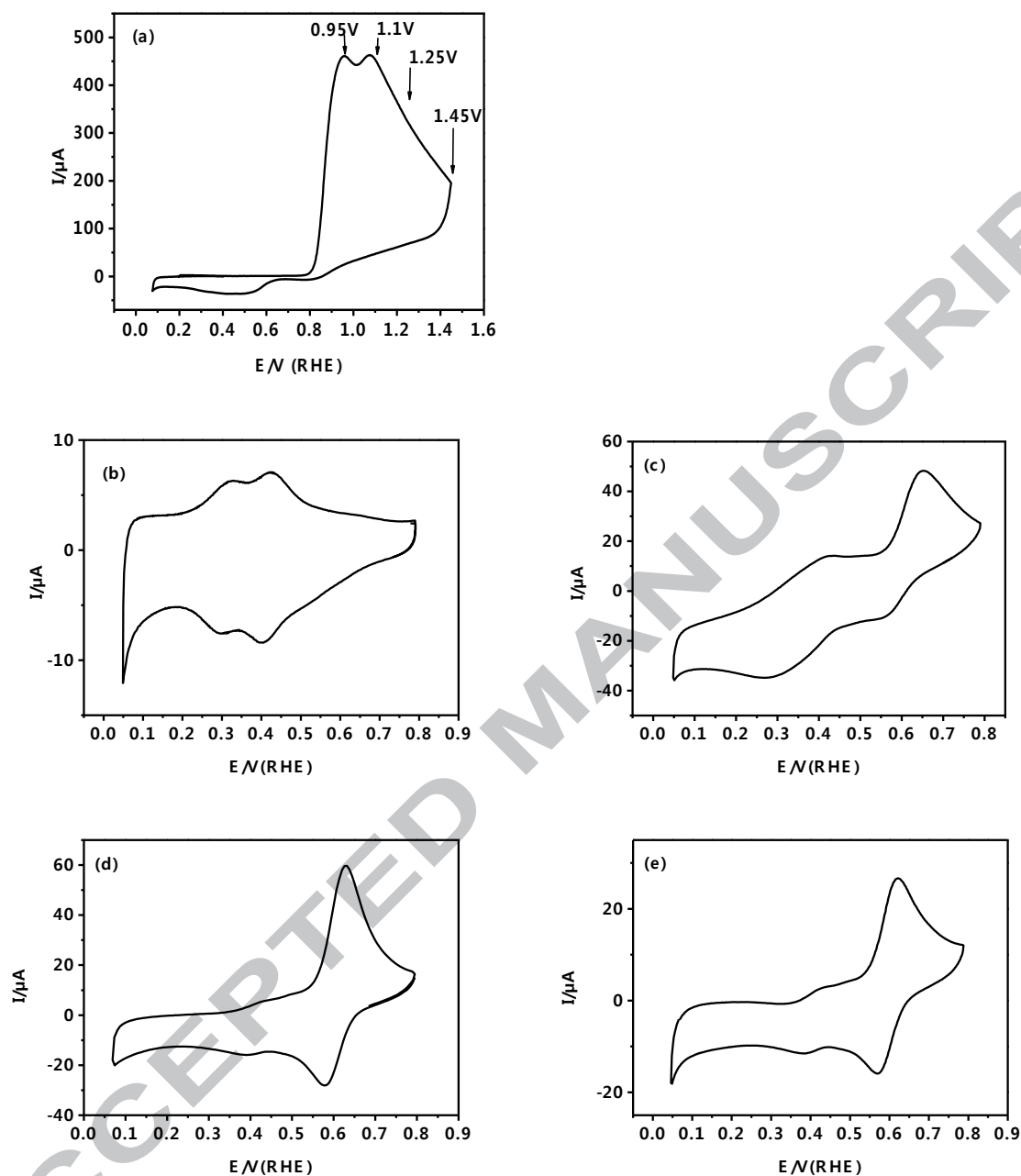


Fig. 3. a) First potential cycle recorded for a Pt electrode during the electrochemical oxidation of a mixture 10 mM OAP + 10 mM ATA in 1M HClO_4 ; Steady voltammograms of the polymeric materials deposited after 100 polymerization cycles at: 0.95V (b), 1.1 V (c), 1.25 V and 1.45 V (d). Test solutions 1M HClO_4 .

When the copolymerization potential window was extended up to potentials where the oxidation of both, ATA and OAP, takes place (1.25 V and 1.45 V), the deposited materials show very similar voltammetric profiles, as it can be observed in Figs. 3d and 3e. These cyclic voltammograms are dominated by two reversible redox transitions at 0.45/0.39 V and

0.63/0.58 V. Again, the low potential process seems related with phenoxazine structures and the high potential one with the presence of aminoterephthalic acid centers within the polymer chains. It is worth mentioning that current intensities of redox processes in Fig. 3d are significantly lower than in Fig. 3c (this is particularly noticeable for the second redox transition at 0.63/0.58 V) which means that a coupled copolymer degradation occurs during the electrosynthesis up to 1.45 V.

3.3. Spectroscopic characterization of poly(ATA-co-OAP)

In situ FTIR spectroscopy has been employed to monitor the redox transitions of poly(ATA-co-OAP). Fig. 4a shows a set of infrared spectra collected for this copolymer in 0.1M HClO₄/D₂O medium in the frequency range comprised between 1150 and 2000 cm⁻¹. The copolymer was deposited on a mirror-polished Pt disc using 1.1 V as the positive potential limit, in order to obtain a material with as few defects as possible. The filmed electrode was transferred to the spectroelectrochemical cell and then carefully pressed against the prismatic CaF₂ window at controlled potential. First, the reference spectrum was acquired at 0.1 V and then the potential was stepped sequentially to higher values (those indicated in Fig. 4a) where sample spectra were acquired. By referring each sample spectrum to the single reference, it is possible to follow spectroscopically the progress of the redox transformation.

In agreement with the voltammetric profile in Fig. 3c, when the applied potential reaches 0.3 V the copolymer begins to oxidize and a broad infrared feature appears at 1569 cm⁻¹. This frequency is assigned to the C=C stretching vibration in quinoid rings formed upon copolymer oxidation. The broad peak sharpens, intensifies and shifts to higher frequencies at increasing potentials and, simultaneously, new vibrational modes appear on the spectra. On the one hand, characteristic positive-going bands develop at 1255, 1484 and 1510 cm⁻¹. On the other, several downward bands are promoted by the applied potential at around 1330, 1360, 1400, 1644 and 1718 cm⁻¹. With regard to the upward bands, they come unambiguously from the reduced form of poly(ATA-co-OAP). In particular, the main absorption at 1510 cm⁻¹ and the shoulder at 1484 cm⁻¹ are clearly related with aromatic C-C stretching vibrations, for which the positive character illustrates the conversion of benzenoid into quinoid structures at increasing potentials. Besides, the positive-going feature at 1255 cm⁻¹ can be assigned to the C-O stretching vibration in aromatic phenoxazine rings [20]. The transformation of phenoxazine into phenoxazone structures upon oxidation makes this band visible as an

upward peak. Table 1 summarizes frequencies and assignments of these features and those corresponding to the oxidized state. Among the latter, significant absorptions originate from intermediate order C-N stretching modes, which appear usually in the spectral range 1300-1400 cm^{-1} in conducting polymer structures derived from aromatic amines [21]. At higher wavenumbers, the observed 1648 cm^{-1} band is clearly related with the C=N stretching in oxidized phenoxazine structures [9]. Finally, the successful incorporation of ATA monomers to the copolymer is confirmed by the weak negative-going band at 1718 cm^{-1} . This feature is assigned to the C=O stretching vibration of carboxylic groups and its low intensity reveals that these structures do not participate actively in the redox process [16]. In other words, most carboxylic groups are preserved as -COOH during the transformation of phenoxazine into phenoxazine. At this point, it is worth mentioning that no activation of additional vibrational modes occurred when the redox state of poly(ATA-co-OAP) was changed from the first voltammetric peak to the second one, at about 0.6 V. This observation is interpreted in terms of the homogeneity of the chemical structures implied in both redox processes. The case is conceptually similar to the redox transitions of polyaniline, for which leucoemeraldine to emeraldine and emeraldine to pernigraniline transformations involve the same IR vibrational modes, although they are related to different polaronic states [22,23].

It was shown in Figs. 2c and 3b that the voltammetric features of POAP homopolymer deposited at high anodic potentials are similar to those of poly(ATA-co-OAP) copolymer. Now, we will compare the vibrational features of both materials in order to reveal possible analogies between their chemical structures. Fig. 4b shows a set of *in situ* FTIR spectra collected for a POAP film deposited up to 1.45 V on a Pt disc electrode. Spectra were obtained at the same sample potentials than in Fig. 4a and the reference was acquired at 0.1 V as well. In parallel to the voltammetric results, the oxidation of POAP followed by FTIR spectroscopy looks shifted about 100 mV positive to that of copolymer. In spite of this, Fig. 4 shows the vibrational traits of both materials are essentially the same, and also similar to those of POAP deposited at less positive potentials [9]. The main IR features can be related to the presence of benzenoid-quinoid and phenoxazine-phenoxazine structures, although a significant difference can be observed between both set of experiments, which is the lack of absorptions related to either carbonyl or carboxyl groups on POAP. It should be taken into account that the additional voltammetric peak at 0.6 V in Fig. 2d (and its analogy with Fig. 3c) suggests that the overoxidation of POAP could promote structures containing -C=O. In fact, the intensity of the IR signal recorded in Fig. 4b is half that in Fig. 4a, which supports the

occurrence of POAP overoxidation during electropolymerization at extreme inversion potentials.

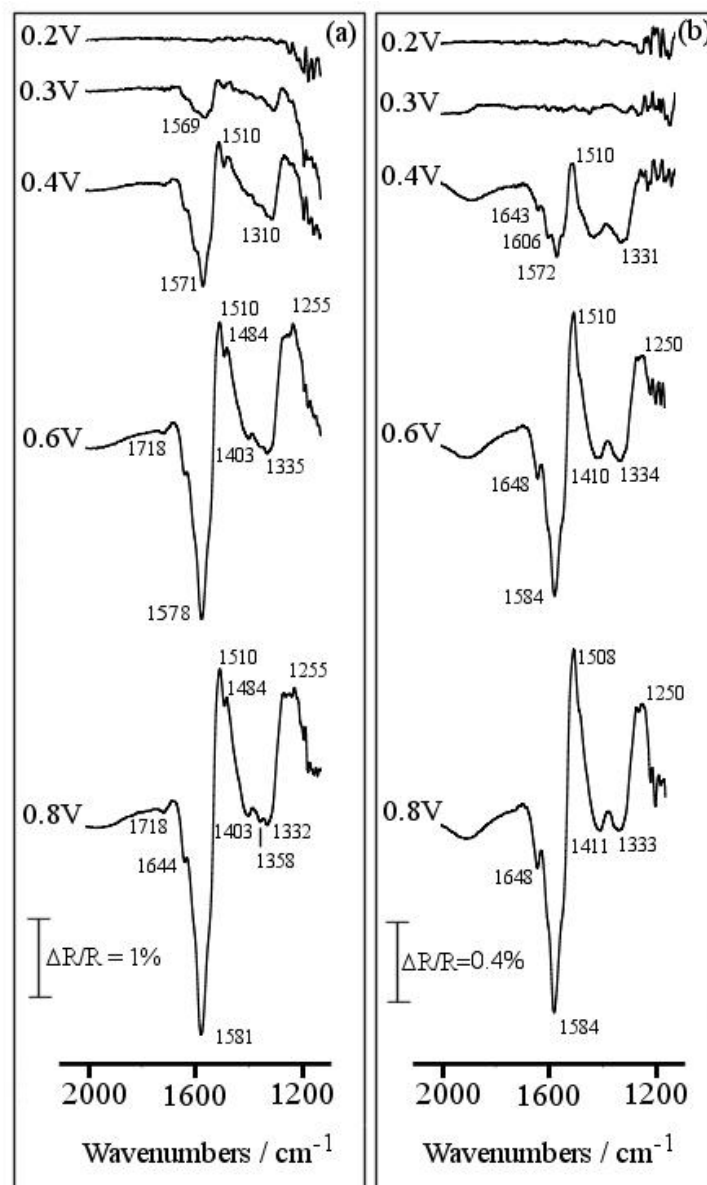


Fig.4. *In situ* FTIR spectra collected during the oxidation of: (a) poly(ATA-co-OAP) deposited potentiodynamically up to 1.1 V (100 cycles), and (b) POAP deposited potentiodynamically up to 1.45 V (100 cycles). Reference potential 0.1 V. Sample potentials indicated for each spectrum. 100 interferograms recorded at each potential. 8 cm^{-1} resolution. Electrolyte 0.1M HClO_4 in D_2O .

Table 1. Observed frequencies and proposed assignments for the vibrational bands of electrochemically deposited poly(ATA-*co*-OAP) and POAP derived from Fig. 4.

	Frequency / cm^{-1}		Assignment
	Poly(ATA- <i>co</i> -OAP) / 1.1 V	POAP / 1.45 V	
Reduced form	1255	1250	C–O str. Phenoxazine rings
	1484	-	C–C str. Aromatic rings
	1510	1510	C–C str. Aromatic rings
Oxidized form	1330-1360	1333	Intermediate order (C \approx N) str.
	1403	1410	C \approx N str. + C–C str.
	1581	1584	C=C str. Quinoid rings
	1644	1648	C=N str. Quinone-imines
	1718	-	C=O str. Carboxylic acid

XPS spectroscopy has been employed to characterize poly(ATA-*co*-OAP) electrodeposited up to 1.1 V. After 100 electropolymerization cycles, a CV similar to that shown in Fig. 3c was obtained and the filmed electrode was removed from the polymerization medium in reduced state. Then, it was thoroughly rinsed with ultrapure water, carefully dried under nitrogen and finally transferred to the UHV chamber. Fig. 5 shows the XPS spectra for C 1s, N 1s and O 1s core levels and Table 2 summarizes the proposed assignments for the observed signals. The best fit includes three contributions for each element. In particular, the C 1s signal shows two major peaks at 284.6 and 286.1 eV and a minor peak at 288.4 eV. The lower binding energy feature is clearly related to aromatic carbons, whereas that at 286.1 eV reveals the presence of aromatic carbons bound to nitrogen or oxygen, thus forming ether-like structures [19,21]. This result supports the occurrence of phenoxazine cyclizations suggested by the previous *in situ* FTIR experiments. Finally, the high binding energy peak at 288.4 eV strongly suggests the presence of carboxylic O–C=O carbons. Similar chemical shifts of about + 4.0 eV relative to the unsubstituted aromatic ring carbons were reported for C 1s signals coming from -COOH in parent aminobenzoic acids [24]. Carboxylic structures are located exclusively at ATA centers in poly(ATA-*co*-OAP) and, consequently, the incorporation of this monomer to the copolymer seems confirmed. The ratio of carboxylic carbon against total carbon derived from peak area in Fig. 5 is about 1:10. Obviously, this value warrants caution due to the potential presence of some adventitious carbon on the sample, but it results in an ATA:OAP monomer ratio of 1:2 for the synthesized copolymer chain. Taking into account that oxidized OAP monomers should be significantly more reactive than unoxidized ATA

monomers in the potential window employed during electropolymerization, 1:2 ratio seems an acceptable figure.

Owing to the low stoichiometric content of nitrogen in the copolymer sample, the N 1s spectrum appears noisier than C 1s. The best curve fit for this element shows two main contributions at 398.5 and 400.0 eV and a high-binding-energy shoulder near 402 eV. This residual component seems to correspond to positively charged N⁺ atoms [25], which are balanced by a small amount of perchlorate anions (not shown). In fact, the N⁺/N ratio derived from Fig. 4 is about 4%, which reveals a minor fraction of polymer chains could not be completely reduced in the moment of electrode withdrawal from the polymerization medium. According to our previously reported assignments for phenazine-like structures [21], the two lower BE peaks at 398.5 and 400.0 eV are ascribed to neutral nitrogen species, corresponding to amine (phenoxazine) and imine (phenoxazone) groups, respectively. This latter species may be resulted, mainly, from surface environmental oxidation of phenoxazine during electrode manipulation. On the other hand, the three deconvoluted contributions to the O 1s core level spectrum appear at 530.0, 531.2 and 532.6 eV in Fig. 5. The particularly low binding energy of the minor peak at 530.0 eV is a characteristic of oxygen attached to metals [26] and, therefore, it can only be explained by the presence of Pt-O species coming from the electrode substrate. The contribution at 531.2 eV seems to correspond to C=O in carboxylic groups attached to aromatic rings [19], while the high-energy peak at 533.6 eV is clearly assigned to oxygen singly attached to carbon atoms, as in phenoxazine structures [19,26]. Again, both types of oxygen environments are compatible with the incorporation of ATA centers to the ladder copolymer.

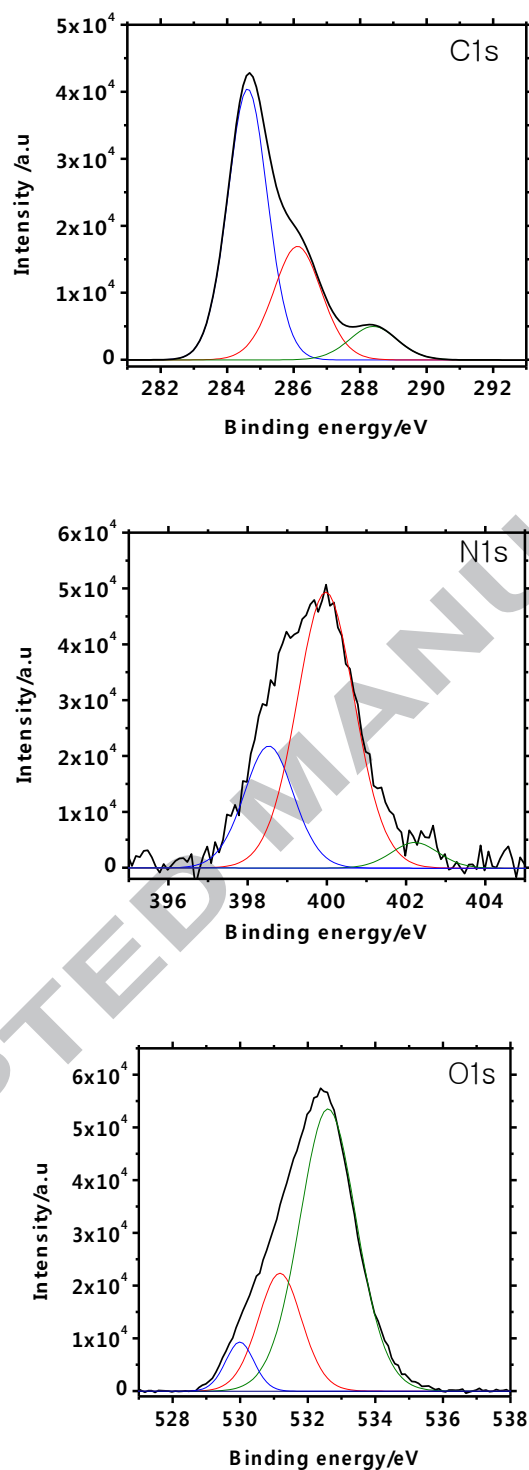
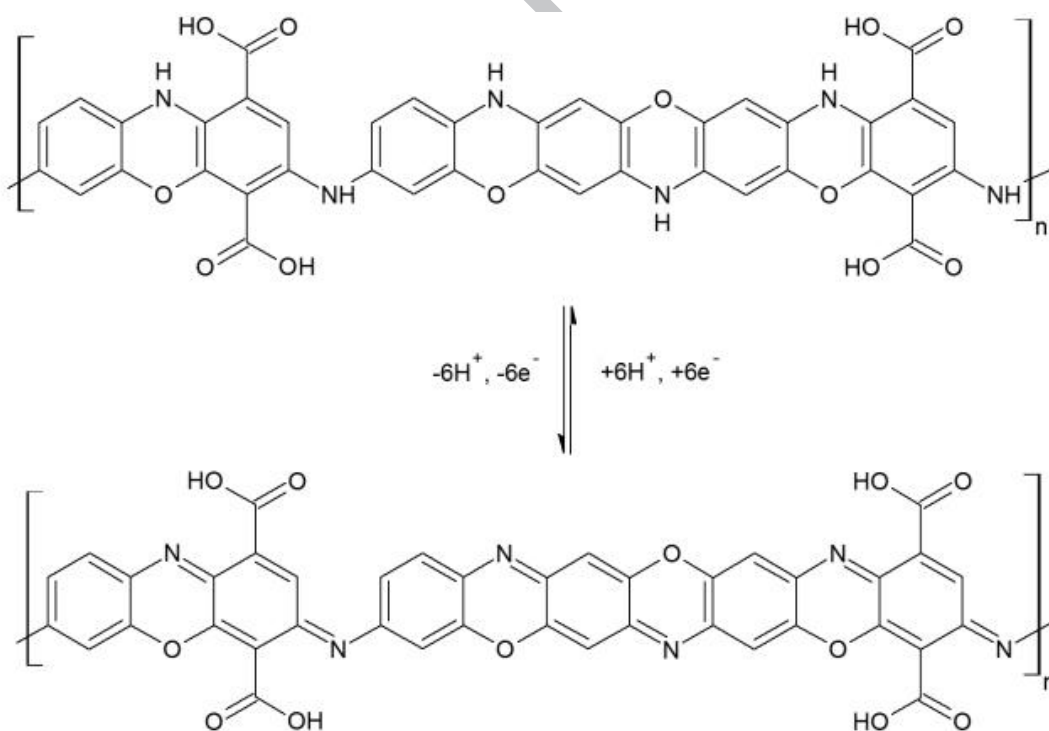


Fig.5: High resolution XPS signals for C 1s, N 1s and O 1s obtained from a poly(ATA-co-OAP) film electrodeposited on a platinum substrate using 1.1 V as the upper potential limit. The polymer was removed from the polymerization solution in its reduced state.

Table 2. XPS peak energies and proposed assignments for a poly(ATA-co-OAP) film electrodeposited up to 1.1 V on a Pt substrate.

Signal	Binding Energy / eV	Assignment
C 1s	284.6	C-C aromatic
	286.1	C-N-C + C-O-C
	288.4	HO-C=O
N 1s	398.5	C-N
	400.0	C=N
	402.2	C=N ⁺
O 1s	530.0	Pt-O
	531.2	C=O
	532.6	O-C-O

In this way, according to the combination of cyclic voltammetry, *in situ* FTIR and XPS results, it is derived that the most probable copolymer structure contains about two OAP monomers per each ATA ring, within a ladder structure as that depicted in the following scheme.



Scheme 3. Idealized reduced and oxidized forms of a short segment of poly(ATA-co-OAP) showing the POAP-derived ladder structure which contains phenoxazine-phenoxazone rings and carboxylic groups located at ATA centers.

4. Conclusions

The electrochemical polymerization of aminoterephthalic acid (ATA) in acid medium on platinum yields a thin, non-electroactive polymer attached to the electrode surface. In spite of the difficulty in obtaining an ATA-based homopolymer, this monomer was successfully copolymerized with *o*-aminophenol (OAP) to yield an electroactive material, poly(ATA-*co*-OAP). The copolymer can be deposited by cyclic voltammetry in a wide range of potentials, although the best copolymerization conditions seem those for which OAP monomer is oxidized at moderate potentials (1.1 V in the present study) and, besides, no oxidation of ATA is induced. In this way, unoxidized ATA units are incorporated progressively to the growing POAP chain forming a copolymer structure, which shows two reversible voltammetric waves in acidic medium. The formation of OAP radical cations at potentials below the onset of ATA electrooxidation facilitates the incorporation of neutral (unoxidized) ATA monomers to the growing polymer chain.

From the *in situ* FTIR results, it can be derived that the redox switching of POAP and poly(ATA-*co*-OAP) involve the same main chemical structures, namely benzenoid-quinoid rings and heterocycles containing both N and O (phenoxazine-phenoxazone). It has been also observed that carboxylic groups do not participate actively on the redox transformation of the copolymer. The combination of cyclic voltammetry and FTIR results suggested that the first redox process (related to the phenoxazine-phenoxazone conversion) is preserved in poly(ATA-*co*-OAP) irrespective of the anodic limit employed during copolymerization. However, the current intensity of the second redox process raises at increasing synthesis potentials and should be ascribed to the incorporation of ATA, although no individual response of these units can be observed by *in situ* FTIR. In other words, no activation of additional vibrational modes occurs when the potential is shifted from the first voltammetric peak to the second one. XPS results confirmed the successful incorporation of ATA units to the copolymer and suggested a monomer ratio close to 1:2 (ATA:POAP) within the copolymer material.

Acknowledgments

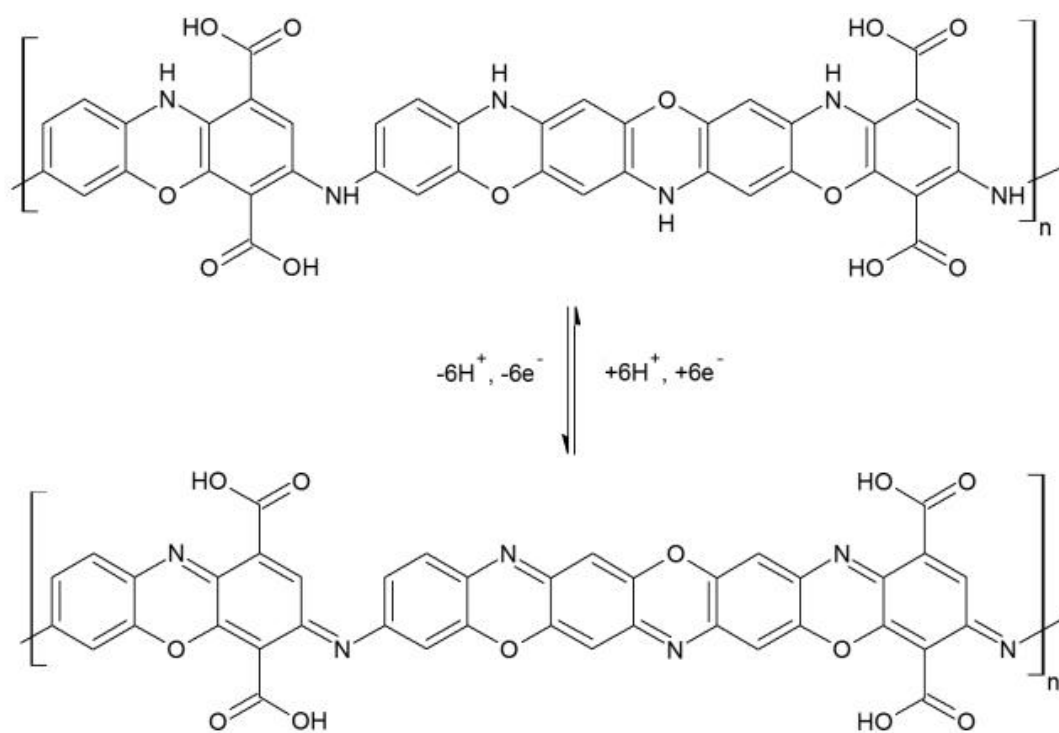
Financial support from the Spanish Ministerio de Economía y Competitividad and FEDER funds (MAT2016-76595-R). M. Abidi thanks the Ministry of Higher Education and Scientific Research of Tunisia for funding her stay at the University of Alicante.

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Graphical abstract



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Highlights

- The 2-aminoterephthalic acid (ATA) does not homo-polymerize in these conditions.
- During polymerization of 2-aminophenol (OAP), ATA is incorporated in the polymer.
- In situ FTIR spectroscopy and XPS confirm the incorporation of ATA in the polymer.
- The copolymer obtained is electroactive in acidic medium.

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