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Article

# Influence of the pH and Substrate Immersion Time on the Adsorption of Poly(*o*-ethoxyaniline) in Self-Assembled Films

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Filmes ultrafinos de poli(*o*-etoxianilina)-POEA foram depositados sobre lâminas de quartzo pela técnica de automontagem a partir de soluções aquosas desse polímero em pH 3 e 5. A influência das condições de preparação sobre a quantidade de POEA adsorvida foi avaliada por meio de espectroscopia UV-Vis, microscopia de força atômica e voltametria cíclica. Verificou-se que em pH 5 a quantidade de POEA adsorvida é sempre maior que em pH 3, independentemente do tempo de imersão do substrato na solução polimérica. Imersões sucessivas do substrato na solução de POEA contribuíram para um aumento significativo da quantidade de polímero adsorvido. Quando as imersões foram realizadas em tempos longos o processo de adsorção atingiu um equilíbrio em cerca de 3 min. Por outro lado, se imersões sucessivas são feitas em curtos períodos de tempo, a quantidade de POEA nos filmes pode ser aumentada indefinidamente o que indica a existência de um processo de não-equilíbrio.

Ultra-thin films of poly(*o*-ethoxyaniline)-POEA were deposited onto quartz slides by the self-assembly technique from aqueous solutions of this polymer in pH 3 and 5. The influence of the experimental conditions on the amount of POEA adsorbed was evaluated by UV-Vis spectroscopy, atomic force microscopy and cyclic voltammetry. It was observed that in pH 5 the amount of POEA adsorbed is always greater than that in pH 3, regardless the time of substrate immersion into the polymeric solution. Repeatedly immersions of quartz substrate into the POEA solutions contributed to an increase on the amount of polymer adsorbed. When long time immersions were made the adsorption process reached a maximum around 3 minutes. However, if repeatedly short time immersions were adopted the amount of POEA adsorbed could be increased indefinitely indicating the existence of a non-equilibrium process.

**Keywords:** conducting polymers, poly(*o*-ethoxyaniline), self-assembled films, thin films

## Introduction

The fabrication of ultra-thin films of conducting polymers using the self-assembly technique (SA) has become very popular in the last years.[1] This technique is based on the spontaneous adsorption of molecules from solutions onto a solid substrate and it has been used for the deposition of mono and multilayer films from different classes of materials, including polyelectrolytes, conducting polymers, proteins, fullerenes, etc.[2,3] Among the advantages offered by using SA technique on the preparation of ultra-thin films we can include the low cost of experimental apparatus, short-time intervals for film fabrication and the control over the film properties by manipulating the experimental conditions.[2,3] The films obtained present very low thickness (around tens to hundreds of angstrons), smoothness and exhibit structural organization at the molecular level.[2,3] Prototypes of molecular electronic devices such as light emitting diodes,[4] gas and taste sensors[5,6] and biosensors[7] have already been produced by using the SA technique.

After the first work proposing the use of SA technique for the fabrication of films from colloidal materials in 1966 by Iler[8] and its extension to polyelectrolytes[9] and to conducting polymers,[10] several papers came up to explain the main factors responsible for the molecular adsorption and the film formation. However, a general

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mechanism can not be proposed for the large variety of materials that can be deposited by this technique.[2,3] In fact, the literature data has shown that for each kind of material deposited a different adsorption process can take place. Even when the same material is considered, in diverse experimental deposition conditions, varied mechanisms can be observed. The understanding of the mechanisms of adsorption for a certain material can be very useful to optimize time of film fabrication, control over the film thickness and properties, etc.

In the case of SA films of polyaniline and its derivatives, for instance, both electrostatic attraction and hydrogen bonding can act on the adsorption process.[11-15] The predominant mechanism will depend on the pH of polymeric solution. In our previous work we have observed that in pH 3 the adsorption of poly(*o*-ethoxyaniline) on quartz is driven by electrostatic attraction due to the protonated nitrogen atoms; however, if the solution pH is increased to 5 hydrogen bonding becomes more important.[14] In this case, the amount of polymer deposited on the film increases when the pH is increased as a result of reduction of charge repulsion and conformational hindrances.[14] Also, Raposo *et al.* have observed that the adsorbed amount of poly(*o*-methoxyaniline) on glass can be regulated by the time and number of immersions of the substrate into the polymeric solution.[16] In general, repeatedly immersions in short times followed up of washing/drying increase the amount of material deposited. For this system, the polymer adsorption process may not reach a saturation plateau if successive short-time immersion steps are adopted instead of long-time ones.[17]

In this contribution the effect of substrate immersion time on the amount of poly(*o*-ethoxyaniline), POEA, adsorbed in self-assembled films from aqueous solutions in two different pHs is investigated. The amount of POEA adsorbed was measured by using UV-Vis spectroscopy. The thickness and morphology of POEA films were investigated by atomic force microscopy. Cyclic voltammetry was used to evaluate the film electroactivity and to relate it to the different immersion times studied.

## Experimental

POEA was chemically synthesized in the emeraldine salt form according to the method described elsewhere.[18] Its chemical structure is shown in Figure 1. The substrates Suprasil® quartz slides (30x10x1 mm) were previously cleaned using the method described by Kern.[19] Glass slides (10x5x1 mm) covered with an indium tin oxide layer supplied by ASAHAI (Japan) were used for cyclic voltammetry studies. Hydrochloric acid was purchased from Sigma-Aldrich (USA) and used as received. All the water used in this work was purified in a Millipore Milli-Q system. An aqueous stock POEA solution $1x10^{-3}$ mol $L^{-1}$ was used for all the experiments.

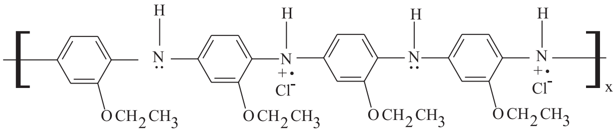

**Figure 1.** Chemical structure of poly(*o*-ethoxyaniline) (POEA) in the emeraldine oxidation state, salt form.

The investigation of the effect of substrate immersion time on the POEA adsorbed amount in two different pHs (3 and 5) was carried out in the following way: the substrates (quartz or ITO glass) were immersed for a pre-determined time into the POEA solution, washed in aqueous solution of HCl in the same pH and dried with a fan. After that, the absorbance in 455 nm was measured by UV-Vis spectroscopy. This wavelength was chosen since it represents an isosbestic point for POEA whose absorbance value does not change with the pH, only with the polymeric concentration, according to reference 11. The immersion times adopted were the following: a) 24 steps of 30 s each and b) 6 steps of 30s + 6 steps of 60s + 6 steps of 120s + 6 steps of 240s, for the same substrate; c) 10s, 30s, 60s, 120s and 240s for different substrates. All the experiments were carried out at 25°C.

UV-Vis spectroscopy data were collected using a Shimadzu spectrophotometer, model UV-1601 PC. Atomic force microscopy (AFM) images were obtained in a Digital Instruments microscope, model Nanoscope III A, in tapping mode using a silicon tip attached to a cantilever of spring constant 70 N/m and resonance frequency of 280 kHz. The cyclic voltammetry (CV) experiments were carried out under nitrogen atmosphere using a potentiostat/galvanostat EG&G/PARC instrument, model 283, driven by the EG&G/PARC PowerSwite software. The scan rate used was 50 mV $s^{-1}$ in the range between -0.2 and +0.6 V. Saturated calomel electrode (SCE) was used as reference and a platinum foil (Degusa) as a counter electrode.

## Results and Discussion

The adsorption process in self-assembled films of polyaniline derivatives is very dependent on the experimental conditions used for film fabrication. The time scale used for the substrate immersion into polymeric solutions is an important factor which was investigated in this work.

Figure 2 presents adsorption isotherms for POEA layers on quartz slides using different immersion times, from

POEA solutions in two pHs, 3 and 5. The number of immersions at the end of the experiments represented by Figures 2a and 2b was the same, *i.e.*, 24. For the isotherms presented in Figure 2a, obtained in pH 3, we can see that the amount of POEA adsorbed increases differently in the two time scales investigated; for short immersion times (24 steps of 30 s) the amount increases rapidly and it does not reach a saturation plateau. However, when longer immersion times were adopted the same is not observed. Instead, we note a very slow increase of the amount of POEA, which becomes almost constant when the time of immersion is increased to steps of 120 s. Plus, the overall amount of POEA adsorbed is greater in the films deposited using shorter immersion times. The adsorption studies carried out at pH 5 show similar characteristics, as we can see in Figure 2b. However, the overall amount of POEA adsorbed is much greater than at pH 3 and additionally after 24 immersions it is slightly greater in the film deposited by shorter immersion times than in longer immersion times. At pH 5 we can see more clearly the effect of time scale on the film formation when the immersion time is increased. For each time scale investigated, a particular rate of film formation (ratio between amount of material deposited and time of substrate immersion) can be qualitatively identified, according to the differences on the slope of the curve (see insert in Figure 2a), which shows, in general, that the rate decreases as the immersion time increases.

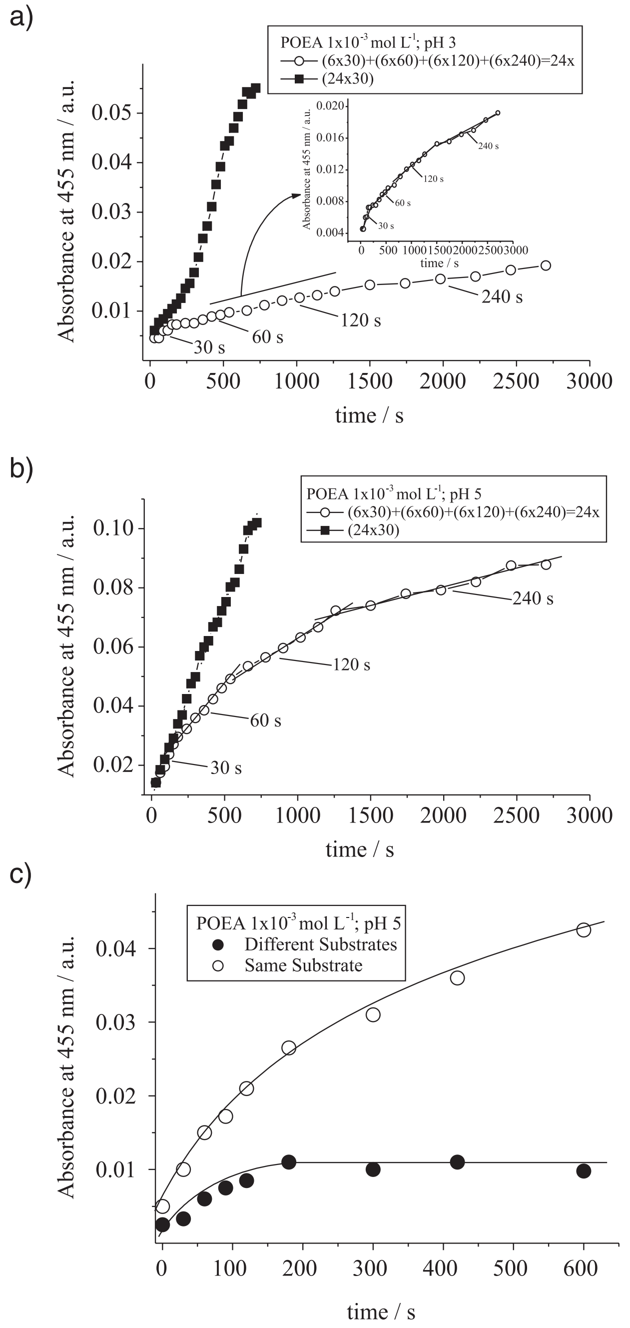

**Figure 2.** Variation of the maximum absorbance of POEA films, measured in 455 nm, with the immersion time of the quartz substrate. Films obtained from aqueous solutions containing 1x10$^{-3}$ mol L$^{-1}$ of POEA at (a) pH 3 and (b,c) pH 5. The time scale used is indicated. Experiment carried out at 25 °C.

The effect of time scale on the adsorption of POEA layers can be attributed to two main effects: the time scale itself and the washing and drying processes. In shorter immersion times the POEA molecules have a short time to stay in contact with the substrate surface and to attach themselves to form a molecular layer, so the amount of POEA adsorbed after each immersion is obviously smaller. The short time prevents the system to reach the equilibrium what means that the adsorbed amount of material is greater than the amount of desorbed one. The adsorption of poly(*o*-methoxyaniline) exhibited a similar behavior according to the work done by Pontes *et al.*,[17] what corroborate our hypothesis. Also, the shorter immersion time helps to prevent the competitive adsorption of water molecules, which in longer times would have more chance to attach to the substrate surface, reducing the number of sites for POEA adsorption. The water adsorption is very significant in these systems and according to the work done by Raposo *et al.*[13] an energy is spent to remove water molecules from the substrate surface and to replace them by polymer chains. Besides, during the washing process both POEA and water molecules which are not very well adsorbed, are removed releasing sites for other molecules in a next immersion. Consecutively, the film is dried and the water molecules entrapped among the polymeric chains are extracted. As a consequence the hydrodynamic volume of adsorbed polymer chains is decreased what results in less space occupied on the substrate surface.

The effects of immersion time adopted for POEA film fabrication and washing/drying processes can be further observed in a experiment comparing the adsorption carried out on a single substrate and on several substrates. In Figure 2c we note that using different quartz slides for each immersion time done in a continuos way, *i.e.*, without intermediate washing/drying, a saturation plateau is reached rapidly and the total amount of POEA adsorbed is very small. For a single substrate, washed and dried between each immersion, the amount of POEA adsorbed is much greater and does not seem to reach a saturation plateau for the time period studied.

The POEA amount from films prepared at pH 5 is greater than that from films prepared at pH 3 independently of the immersion time adopted, what is consistent with our previous work.[14] At low pH the POEA chains are highly protonated and the electrostatic repulsion induces a more expanded chain conformation; consequently the amount of POEA adsorbed is small since the repulsion will prevent the approximation of other chains and the consequent greater hydrodynamic volume of the chains, they will occupy a larger space on the substrate surface. When the pH is raised the electrostatic repulsion becomes less significant what allows other chains to approximate and to attach. The chains will occupy smaller space due to a more compact molecular conformation facilitating the adsorption of more polymer and their molecular packing on the substrate surface.[14]

The non-equilibrium characteristics of the polymer adsorption carried out in shorter immersion times allows to produce films from a same material without the necessity to introduce an intercalating polymer layer since the polymer film grows over itself. This situation is obtained at the both pHs investigated. At high pHs the POEA chains not significantly protonated will adsorb mainly through hydrogen bonding, via amine and imine sites, in agreement with the literature.[13-15,20] Hydrogen bonding allows the polymer to adsorb over itself without saturation under the conditions studied in Figure 2b and c. At low pHs although the hydrogen bonding might be also acting on the adsorption, the large number of protonated nitrogen atoms from POEA chains already attached would repel upcoming chains inducing an earlier interruption of the adsorption process.

AFM images of POEA films obtained in two different time scales of substrate immersion, at pH 5, are presented in Figure 3. The AFM image of a clean quartz substrate without any film deposited (Figure 3a) reveals a globular morphology with very low roughness. In Figures 3b and c are presented the AFM images for self-assembled POEA films prepared using different time scales for substrate immersion. As we can see, the film deposited using only one immersion of 120 s shows globules of POEA adsorbed, larger than those observed for the plain substrate. The coating is not uniform with some regions of the surface having more material than others. In the other hand, the POEA film deposited using 4 immersion steps of 30 s presents the same globular features, however, the substrate surface seems to be completely covered with a rougher but more homogeneous POEA layer. In fact, comparing the POEA film morphologies we can note that in longer immersion times the amount of material deposited is smaller than that deposited using shorter immersion times,

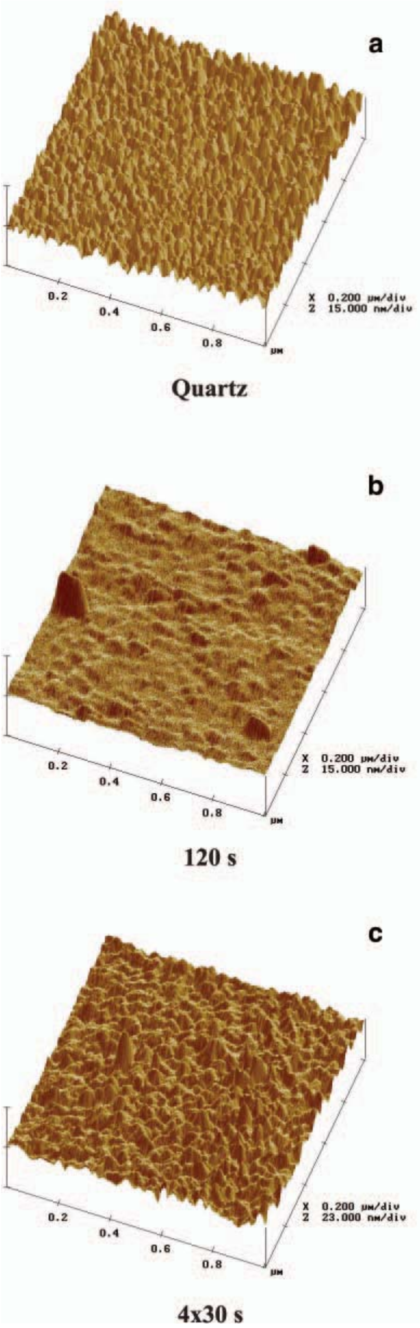

**Figure 3.** AFM images (1 $\mu$m$^2$) of POEA self-assembled films obtained at pH 5 using different time scale: (a) plain quartz substrate; (b) 120 s; (c) 4 of 30 s.

when the overall time of the substrate in contact with POEA solutions is the same in both cases.

The formation of polyaniline films from solutions has been investigated in the literature and, in general, it has been observed that at the beginning of deposition nucleation represents an important step.[21] After the nuclei are formed they start a radial growth through incorporation of more chains from the solution what gives the film a typical globular morphology.[21,22] The resulting globules can also be observed in both films presented in Figure 3 independently of the immersion time adopted but the recovering of the substrate surface is not the same. Considering that the films were deposited using an overall time of substrate immersion of 120s, in one step immersion the substrate surface is covered with a less dense POEA layer than in the other case. As we discussed earlier, in shorter immersion times, the amount of POEA adsorbed is small, since the substrate stays in contact with the polymeric solution for a shorter period of time. However, if we consider a film deposited by a repeatedly number of immersions in shorter time, the short time of substrate/solution contact and the drying process together lead to the formation of a dense POEA layer due to the adsorption of POEA on new sites. The removing of water also decreases the hydrodynamic volume of the polymer chains which occupying less space helps for the adsorption and packing of more material on the substrate surface. Considering the film produced in a single immersion step, all the contributions cited above are not present what explains the difference between the morphology of these two films.

In Figure 4 is presented the variation of average surface roughness of POEA films as a function of the time and number of immersions of the substrate into the POEA solution. During the first 60 s of immersion we observe a small increase of the surface roughness which becomes more pronounced when we used a larger number of repeatedly immersions in short times. This result can be related to the increasing of the amount of POEA adsorbed due to the successive immersion steps. It is very common to observe an increasing on the surface roughness of thin films as the amount of material deposited increases.[23] This effect is often attributed to the accumulation of defects through the film deposition which are more likely to be formed with the increasing of material deposited.

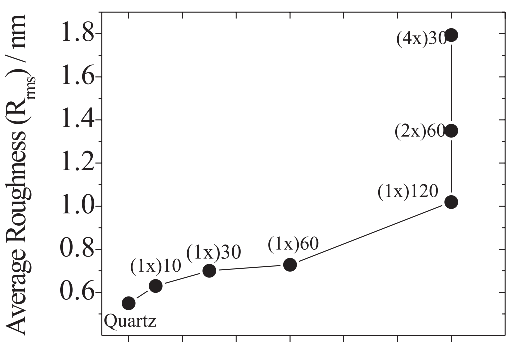

**Figure 4.** Average roughness ($R_{rms}$) values for self-assembled POEA films obtained by the use of different time scale, as indicated.

The amount of POEA adsorbed increases with the number of substrate immersions in shorter times and is confirmed by thickness measurements taken using the AFM microscope. The film thickness obtained for a film deposited using a single substrate immersion of 120 s was 1.3 nm, whereas for a film deposited using 4 immersions of 30 s the thickness measured was 10.1 nm, about 8 times larger. A profile of a step scratched on a film obtained obtained by 4 immersions of 30s is presented in Figure 5.

Figure 6 presents the cyclic voltammograms obtained in a 1.0 mol $L^{-1}$ hydrochloric acid aqueous solution for self-assembled POEA films deposited in a ITO electrode prepared by immersion in four different time scales: 1) 60 seconds (Figure 5a); 2) 120 seconds (Figure 5b); 3) (2x)60 seconds (Figure 5c); 4) (4x)30 seconds (Figure 5d). The shape of cyclic voltammograms are basically the same for all the films deposited. The peaks related to the

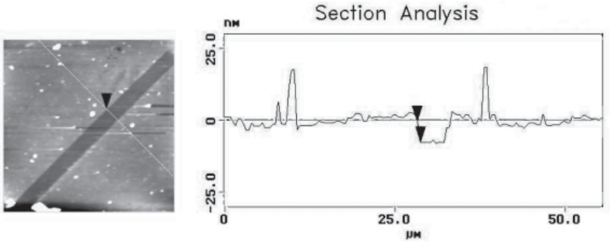

**Figure 5.** Cross-section analysis of a POEA self-assembled film obtained after 4 immersions of 30s from a $1x10^{-3}$ mol $L^{-1}$ POEA aqueous solution at pH 5.

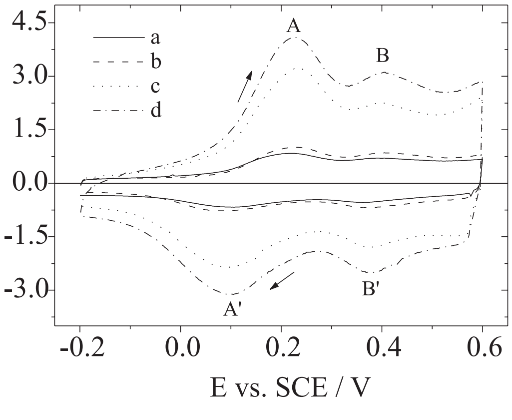

**Figure 6.** Cyclic voltammograms obtained in 1 mol $L^{-1}$ HCl of ITO electrodes recovered with POEA self-assembled films, prepared in different time scales: (a) 60 seconds; (b) 120 seconds; (c) (2x) 60 seconds; (d) (4x)30 seconds. Scan rate: 50 mV $s^{-1}$.

leucomeraldine-emeraldine conversion (between 0.10-0.22 V) and to emeraldine oxidation-reduction conversion (between 0.39-0.41 V) can be easily identified on all films and they are in agreement with those found for POEA in a previous work.[24] However, it can be also noted that the anodic charge related to the emeraldine oxidation-reduction increases when a larger number of immersions in shorter times were used. Figure 7 shows the variation on the anodic charge ratio ($Q_{(4x)30\ sec.}/Q_{timescale}$) as a function of the time scale for substrate immersion. These data confirm the increase of the amount of POEA adsorbed as the number of immersions made in shorter time increases. Since the anodic charge increases with the number of active sites which undergo a redox process these active sites must increase in number as the amount of material adsorbed increases.

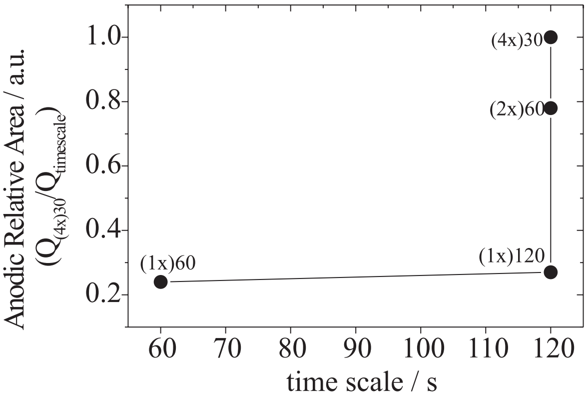

**Figure 7.** Anodic relative area for the POEA films as a function of the used time scale, which was obtained from the cyclic voltammograms showed in Figure 6.

## Conclusions

The effect of substrate immersion time on the amount of poly(*o*-ethoxyaniline), POEA, adsorbed in self-assembled films from aqueous solutions was investigated in two different pHs. According to the data presented the amount of POEA adsorbed increased when repeatedly short-time immersions of the substrate into the POEA solution were made. The effect was attributed to a non-equilibrium process which takes place when the contact time between substrate and POEA solution is shorter. Also the washing/drying process has an important contribution to the increase of the amount of POEA adsorbed since water molecules and poorly adsorbed POEA chains can be removed, releasing more sites for additional polymer adsorption. The amount of material adsorbed could be also increased by increasing the solution pH, independently of the time scale adopted for the substrate immersion. In higher pHs the hydrogen bonding is the most important driven force acting on the adsorption process and it is also responsible for the continuous growth of the polymer film.

AFM images and cyclic voltammograms confirmed the increasing of the POEA adsorbed as we increased the number of immersion steps in shorter times. A more uniform coating is formed when the POEA films were produced using short immersion times. The anodic charge related to the emeraldine oxidation/reduction process increased as the number of immersions in short times increased, confirming that a greater amount of material is deposited.

Finally, the fabrication of POEA films using short immersion times is characterized by a non-equilibrium and non self-limiting process, which allowed us to obtain thicker films without the necessity of introduction of additional intercalating polymer layer. This flexibility can be very useful on the preparation of thicker conducting polymer films for applications in sensors and in other electronic devices.

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