

# Effect of pH on the preparation of self-assembled films of poly(*o*-ethoxyaniline) and sulfonated lignin

Leonardo G. Paterno<sup>a</sup>, Luiz H.C. Mattoso<sup>b,\*</sup>

<sup>a</sup>*Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, São Carlos, 13560-970, SP, Brazil*

<sup>b</sup>*Embrapa Instrumentação Agropecuária, CNPDIA/EMBRAPA, C.P. 741, São Carlos, 13560-970, SP, Brazil*

Received 24 August 2000; received in revised form 5 December 2000; accepted 7 December 2000

## Abstract

Self-assembled films of Poly(*o*-ethoxyaniline) (POEA) doped with HCl alternated with sulfonated lignin (SL) were successfully produced under different pHs and their kinetics of formation studied. The adsorption at lower pHs is faster due to the greater electrostatic attraction between the POEA and the SL covered substrate, but a lower amount of POEA is deposited due to charge repulsion of additional POEA chains and conformational steric hindrance. At higher pHs the adsorption of POEA takes longer but it is greater due to the contribution of hydrogen bonding interactions, lower charge repulsion between POEA chains and a more compact polymer conformation. Adsorption of POEA/SL multilayers could be carried out in different types of substrates. Atomic force microscopy (AFM) employed to investigate the morphology of the alternated layers showed that POEA layers exhibited a granular rough aspect, while SL layers presented a much smoother surface. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polyanilines; Self-assembly; Adsorption

## 1. Introduction

In the last years the self-assembly technique [1–3] has become an important approach to fabricate different architecture of ultra-thin films of organic materials in a simple and controlled manner. An additional advantage lies in the low cost of the experimental apparatus with which films can be fabricated in relatively short-time intervals. The method basically consists of oppositely charged polyions on the alternate adsorption [4], although it has also been extended to nonionic polymer molecules [5,6]. There has been some debate in the literature about the types of interactions governing the adsorption process in the layer-by-layer deposition [4–7]. It was initially considered to be basically governed by electrostatic interactions between ionic groups [4,7], but recently the possibility of being applied for nonionic hydrogen bonding polymers has been demonstrated [5,6]. In the present work, we have investigated the formation of self-assembled films of poly(*o*-ethoxyaniline), POEA, a water soluble polycation in the conducting state and sulfonated lignin (SL), which behaves as a polyanion. By studying the effect of pH on the preparation of POEA and SL self-assembled films we were able to observe that

both electrostatic and hydrogen bonding interactions as well as polymer conformation can be important for this system depending on the solution pH. Furthermore, the alternated layer-by-layer deposition could be carried out with different substrates. It is well known about the importance to investigate the film morphology in the literature. Electron microscopy has not been accurate enough to visualize the structure of ultra-thin films, mainly due its poor depth resolution. Alternately, atomic force microscopy-(AFM) has been employed [8] to study the morphology of conducting polymer films, not only due to its great vertical resolution but also because it allows the measurement of other interesting parameters, such as roughness, grain size and surface cross-section. Therefore, in this work AFM has also been used to investigate the morphology of POEA/SL self-assembled films.

## 2. Experimental details

POEA was chemically synthesized using ammonium peroxydisulfate, 1.0 M hydrochloric acid and excess of monomer according to the method described elsewhere [9]. SL in sodium salt form was purchased from Melbar Lignin Products (Brazil). Substrates were Suprasil™ quartz and BK7 optical glass slides (8 × 20 × 1 mm<sup>3</sup>) previously

\* Corresponding author. Tel.: +55-162-742477; fax: +55-162-725958.  
E-mail address: mattoso@cnpdia.embrapa.br (L.H.C. Mattoso).

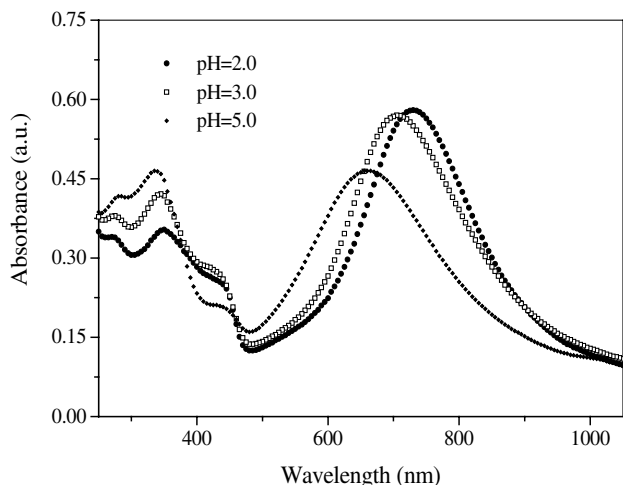


Fig. 1. UV-vis absorbance spectra of HCl-doped POEA solutions at different pHs, as indicated. Solution concentration = 0.04 g/l.

washed according to the method described by Kern [10]. A plastic substrate namely TERPHANE™, poly(ethylene terephthalate) from Rhodia-Ster/Brazil, was also used for comparison. Stock aqueous solutions (in Milli-Q water) of POEA at 0.4 g/l or  $1 \times 10^{-3}$  M (based on the tetramer unit mass, 692 g/mol) and of SL at 0.3 g/l or  $1 \times 10^{-3}$  M (based on the C9 unit mass, 298 g/mol) were used at different pHs. Films were obtained by the self-assembly method described elsewhere [4,11], which consists of POEA and SL layers in the alternate deposition during an immersion time of 3 min. UV-vis spectroscopy (Hitachi U2001 model) was employed to monitor the polymer adsorption process at wavelength of 455 nm, which is the isobestic point [12] for calculating the adsorbed amount of polymer at the different pHs, as shown in Fig. 1. Films were scanned by AFM, in a Digital Nanoscope III instrument, on the tapping mode.

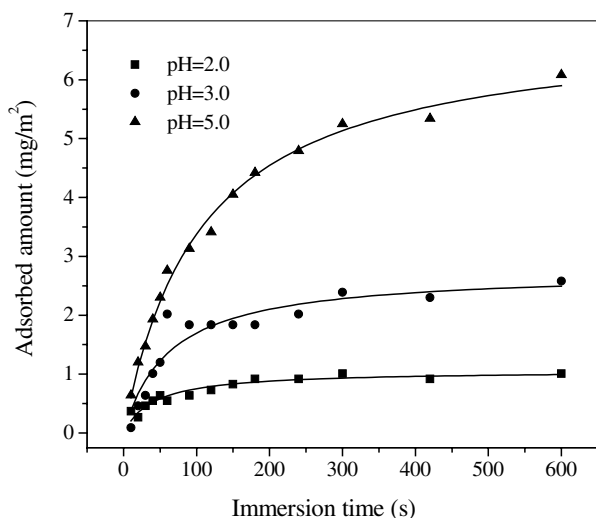


Fig. 2. Kinetics of adsorption of the first layer of HCl-doped POEA films at different solution pHs, as indicated. Solution concentration = 0.04 g/l. Quartz substrates.

Table 1

Maximum amount of material adsorbed ( $\Gamma_{\max}$ ) and characteristic time ( $\tau$ ) values obtained from fitting of adsorption isotherms of the first layer of HCl-doped POEA onto quartz substrates at different pHs according to Eq. (1)

Solution pH	$\Gamma_{\max}$ (mg/m <sup>2</sup> )	$\tau$ (s)
2.0	1.1	41
3.0	2.8	63
5.0	6.9	105

The spring constant of the cantilever was in the range 20–100 N/m. The images were obtained in a scan rate of 1 Hz with a silicon tip. The surface roughness was calculated using the power spectral density (RMS) obtained for each layer by arithmetical media of three distinct areas ( $1 \mu\text{m} \times 1 \mu\text{m}$ ) for each sample.

### 3. Results and discussion

The investigation of the adsorption kinetics of self-assembled films is important not only to determine the optimal time scale for the polymer layer deposition but also to infer about the mechanism of the adsorption process. Fig. 2 shows the time dependence of the adsorbed amount of the first layer of POEA deposited onto quartz substrates at three pH values. The adsorption process is relatively fast occurring since the first few seconds of immersion of the substrate within the polymer solution and reaches a plateau of saturation after a certain time dependent on the solution pH. According to Lvov and Decher [1] this type of behavior is due to the mechanism of formation of the polymer layer which is based on two stages: (i) at the fast first stage, polymer chains are anchored to the substrate, and (ii) at the longer second stage, the chain packing relaxes to a denser one. In a simplified way, a quantitative analysis of these isotherms can be done using the following equation:

$$\Gamma = \frac{\Gamma_{\max} t}{\tau + t}, \quad (1)$$

where  $\Gamma$  is the amount of material adsorbed ( $\text{mg/m}^2$ ) in the time  $t$ ;  $\Gamma_{\max}$  the maximum amount of the material adsorbed ( $\text{mg/m}^2$ ) when  $t$  goes to infinite;  $t$  the deposition time (s); and  $\tau$  is the characteristic time (s).

Table 1 gives the values of  $\Gamma_{\max}$  and  $\tau$  obtained for three pH values.  $\tau$  represents the beginning of the saturation plateau and increases about 2.5 times as the pH goes from 2 to 5, indicating that the absorption is taking longer to be concluded. Interestingly, the maximum amount of POEA absorbed ( $\Gamma_{\max}$ ) also increases significantly from 1.1 to 6.9  $\text{mg/m}^2$  upon increasing the pH from 2 to 5. It is well known in the literature [13–15] that the protonation degree (or doping state) of polyanilines increases as the concentration of proton in the solution increases, i.e. pH decreases. A scheme of the protonic acid doping process is given in

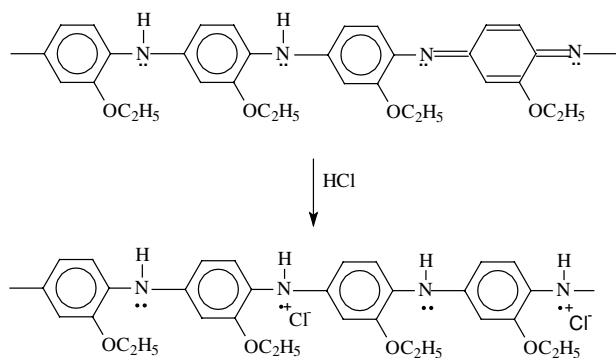


Fig. 3. Schematic protonic acid doping of a POEA tetrameric unit.

Fig. 3. Consequently, a more protonated polymer has a greater electrostatic attraction (driving force) to the substrate, resulting in a shorter  $\tau$  consistent with our results. On the other hand, the extended conformation exhibited by the highly charged POEA chains and the charge repulsion between them inhibit the approximation of additional POEA chains, resulting in an early stabilization of the adsorption and consequently lower amount of POEA adsorbed (lower  $\Gamma_{\max}$ ), as it will be discussed in detail later in this paper.

The pH dependence of the adsorption is confirmed during the film growth, i.e. multilayer formation, as shown in Fig. 4. The amount of POEA adsorbed increases linearly with the number of bilayers, being higher at higher pHs. This result cannot be explained on the basis of the original paradigm of the self-assembly technique [4,7], in which the adsorption process is attributed exclusively to electrostatic attraction. If that was the case the adsorption at lower pH should lead to a higher amount of material adsorbed since the polymer has a larger amount of positively charged sites. In addition the adsorption at pH = 5, where the POEA is only slightly

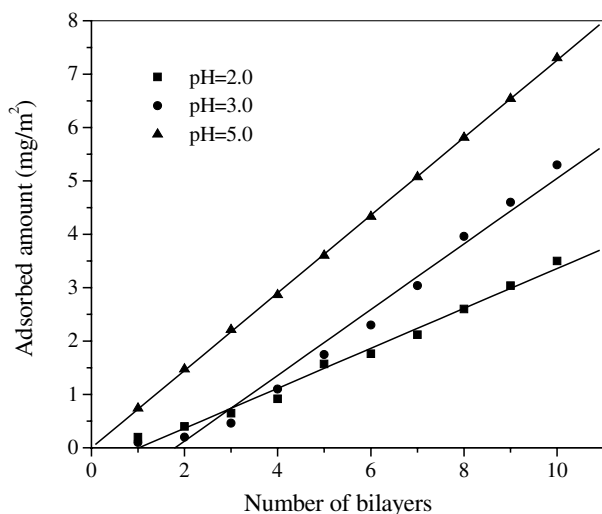


Fig. 4. Build-up of self-assembled films of HCl-doped POEA layers alternated with SL layers at different solution pHs, adsorbed onto quartz substrates. Solution concentration = 0.04 g/l. Immersion time for each layer = 3 min.

doped, should be negligible, contrary to what was observed in the present work. As a matter of fact, recent work in the literature [5,6,16–18] corroborates our observation, demonstrating the possibility of other types of interactions in different polyanilines solution systems.

The recent work of Ikkala et al. [16,17], for instance, showed that films of polyaniline doped with camphor sulfonic acid cast from *m*-cresol solutions may form supramolecular structures due to a combination of three simultaneous interactions: firstly, the sulfonic acid is bonded to PANI due to proton transfer; secondly, the hydroxyl group in *m*-cresol is hydrogen bonded to the carbonyl group of the CSA molecule; and finally, the phenyl groups of the *m*-cresol and PANI are stacked, thus yielding enhanced mutual dispersion forces. Such interactions promote a more extended conformation of the PANI chains in the doped state [18], leading to improvements in solubility and conductivity. The contribution of hydrogen bonding interactions in polyanilines self-assembled films was further demonstrated by Stockton and Rubner [5]. They showed the possibility of preparing alternated layer-by-layer films of polyaniline with a variety of different nonionic water soluble polymers (poly(vinylpyrrolidone), poly(vinyl alcohol), poly(acrylamide) and poly(ethylene oxide)) by an adsorption process which was driven basically by hydrogen bonding interactions with the amine and imine sites of polyaniline.

We suggest that the adsorption of POEA chains under the conditions studied in the present work is governed by electrostatic and hydrogen bonding interactions, which are dependent on the solution pH and are affected by conformational variations of the polymer chains. At lower pHs the proton concentration in the solution is more leading to a greater doping level of the polyaniline derivative due to protonation, as demonstrated by MacDiarmid et al. [14]. In such conditions the POEA chains are in a more extended conformation due to the repulsion between the positively charged segments of the polymer backbone [18,19]. According to Kawaguchi and Takahashi [20] the increase in charge density within the polymer backbone should lead to an increase of the polymer adsorption to the substrate. However, other aspects such as the pH dependence of polymer conformation and hydrogen bonding interactions were not taken into account. Indeed, at high pHs, in addition to the lower electrostatic repulsion, a more compact polymer conformation and multiple bonding sites allow the adsorption of a larger amount of polymer.

It has been demonstrated for polyaniline that the polymer conformation depends strongly on its doping state [18,19]. Polyaniline acts as a polyelectrolyte, in which the electrostatic repulsion between similarly charged units of the polymer chain occurs and become greater as the polymer charge density (or doping level) increases upon pH decrease. Such intramolecular repulsion promotes a 'straightening-out' of the polymer chain going from a coil-like to a more extended conformation [18]. As a consequence at a first stage the adsorption is faster due to the high charge density which

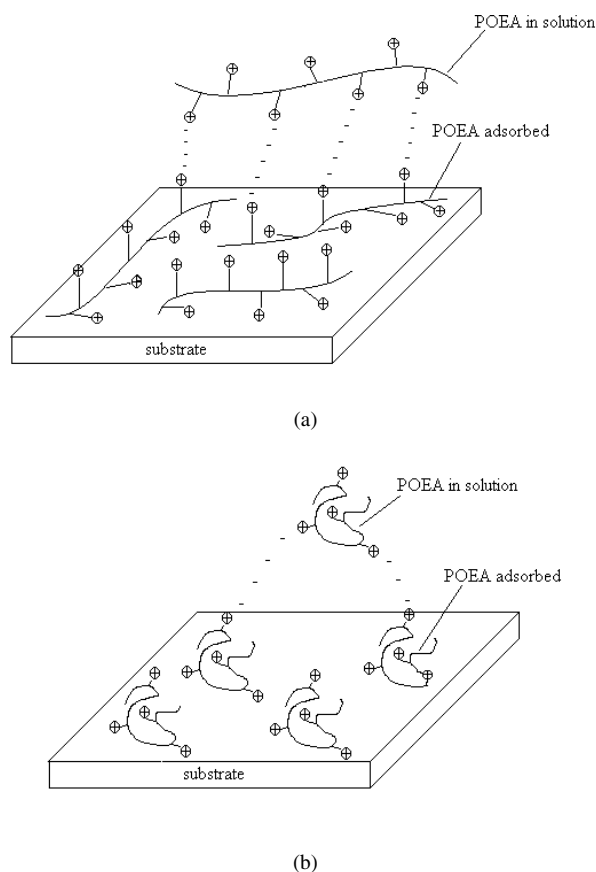


Fig. 5. Illustration of electrostatic and conformational contribution on the adsorption of POEA chains onto solid hydrophilic substrates by the self-assembly technique at two solution pHs: (a) pH = 2 and (b) pH = 5.

leads to a greater electrostatic interaction (driving force) of the POEA to the SL modified substrate. However, at a second stage a smaller amount of polymer is adsorbed since the molecular packing and arrangement of the polymer chains become more difficult for an extended polymer chain than for a more coil-like structure which is obtained at higher pHs (lower charge density in the polymer backbone). In addition the intermolecular repulsion between POEA chains (in solution and those already adsorbed in the first stage) starts to become important since the charge density on the surface increases to a certain higher level due to the similarly charged POEA chains being adsorbed. A schematic representation of this effect is illustrated in Fig. 5.

Additionally, considering that the charge density of the SL does not change with pH, because the sulfonic group acts as a strong acid, at higher pH one will need more POEA chains (which possess a lower charge density) for overcompensating the SL charges than at lower pH. Since the SL macromolecule forms a rigid network the coil-like conformation exhibited by the POEA, at higher pH, favors the arrangement and adsorption of a larger amount of the polymer in this condition. It should be pointed out that the hydrodynamic volume of a coil-like is also smaller, contributing to a better polymer chain packing. The same idea

seems to be valid for the absorption of the first POEA layer to the substrate.

These results are consistent with other studies in the literature [21] showing that a larger amount of polymer is adsorbed in self-assembled films of poly(vinyl sulfate) and poly(allylamine) when the ionic strength of the polymeric solutions is increased. They propose that the addition of salt to these polymeric solution promotes screening of the electrostatic charges on the polymer chains, causing the intra- and inter-molecular electrostatic repulsion to decrease and leading to the rod-to-coil transition of the polyelectrolytes with the consequent increase in the amount of adsorbed polymer [21]. A similar effect known as Donnan effect, has also been observed during the synthesis [22] and doping [23] of polyanilines and derivatives, where a screening effect of the positively charged polyaniline sites occurs with the increase in the ionic strength of the solutions studied.

We believe, therefore, that the types of interactions which seems to be involved on the adsorption of the POEA and SL under the conditions studied are electrostatic interactions (between the ionized sulfonic groups of SL and the positively charged species of doped PANI, namely radical cations, see Fig. 3) which dominates the rate of the polymer adsorption at lower pHs, whereas at higher pHs the contribution of hydrogen-bonding interactions (between hydroxyl, carbonyl, ether and sulfonic groups of SL and amine/imine groups of POEA), in addition to the lower electrostatic repulsion effect, more compact polymer conformation and multiple bonding sites, allow the adsorption of a greater amount of polymer. It should be noted that according to the literature [7], it is not the net surface charge which determines the adsorption, but rather the possibility to form a significant amount of bonding sites between the polymer and surface groups, even though these bonds are individually less strong than other types. As a consequence the films investigated in this work were very stable and the polymer chains would not desorb even after the extensive washing employed during their preparation procedure.

One great advantage of these polymer systems is that they can be deposited by the self-assembly technique in various types of substrates of different chemical nature including plastics and glasses, as illustrated in Fig. 6. It can be observed that a 10-bilayer film of POEA/SL can be deposited in three different substrates leading practically to the same absorbance and linear growth previously discussed, and therefore to the same amount of polymer adsorbed independently of the substrate. The dispersion in absorbance observed in the figure is within the experimental error of the self-assembly technique, indicating that the polymer growth is dictated by the interactions between the polycation and polyanion with very little influence of the substrate.

The self-assembled films appeared to be very homogeneous when analysed by optical or scanning electron microscopy up to a scanning range of 100  $\mu\text{m}$ . However, since the vertical resolution of these microscopes are limited to 20 nm

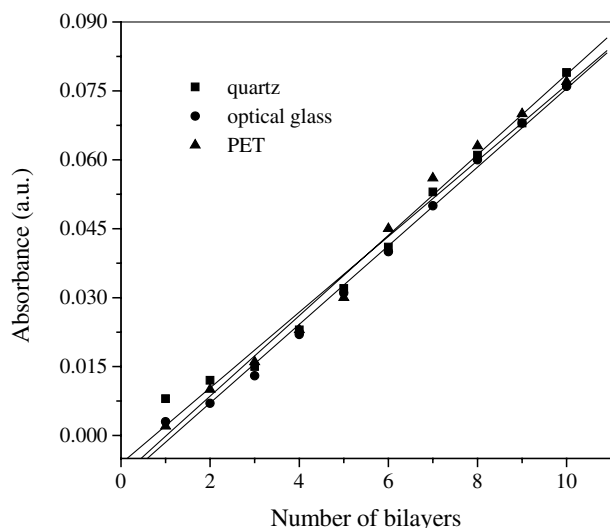


Fig. 6. Build-up of self-assembled films of HCl-doped POEA layers alternated with SL layers onto different types of substrates, as indicated, at pH 3.0. Solution concentration = 0.04 g/l. Immersion time for each layer = 3 min.

and the roughness of the thin film surface studied are below ca. 5 nm, the AFM was used to investigate their morphology systematically. Fig. 7 shows an AFM image of a 5 bilayer POEA/SL film prepared at pH 3, containing POEA as the uppermost layer. A granular formation is seen, whose grains width (estimated by the inter grain separation between 50 and 100 nm) are more than 10 times of the depth (3–4 nm), as indicated in the profile of Fig. 7(b) and (c). Such morphology is typical of polyanilines [24] and it has been observed in the literature by other authors [8,25]. According to Avlyanov et al. [8] films of polyanilines deposited on glass substrates by in situ polymerization also exhibit a granular formation with dimension very similar to ours. They suggest that the film growth results from the nucleation of particles on the surface where the lateral growth rate is high compared to their growth in height. This hypothesis is being further explored in our laboratory by carrying out AFM studies in a fluid cell apparatus.

The evolution of the morphology during the alternated layer-by-layer deposition was also analysed by AFM for each layer. As illustrated in Fig. 8, a rough granular surface appears for the POEA layer (RMS roughness of 0.80 nm), whereas a significantly flatter one is seen for the SL surface (0.26 nm). Fig. 9 shows that such feature is maintained for the subsequent POEA and SL layer deposited. A similar behavior was observed in the literature [26] for alternating layers of glucose oxidase and poly(ethyleneimine), where the subsequent adsorption of the polyion layer decreased the surface roughness of the protein layer significantly, due to bridging of protein molecules by the polyion chains. We believe that the same effect is occurring in our case. Recent molecular computational simulation of lignin [27] has indicated that its macromolecular network leads to the formation of a planar structure which can easily cover the rough

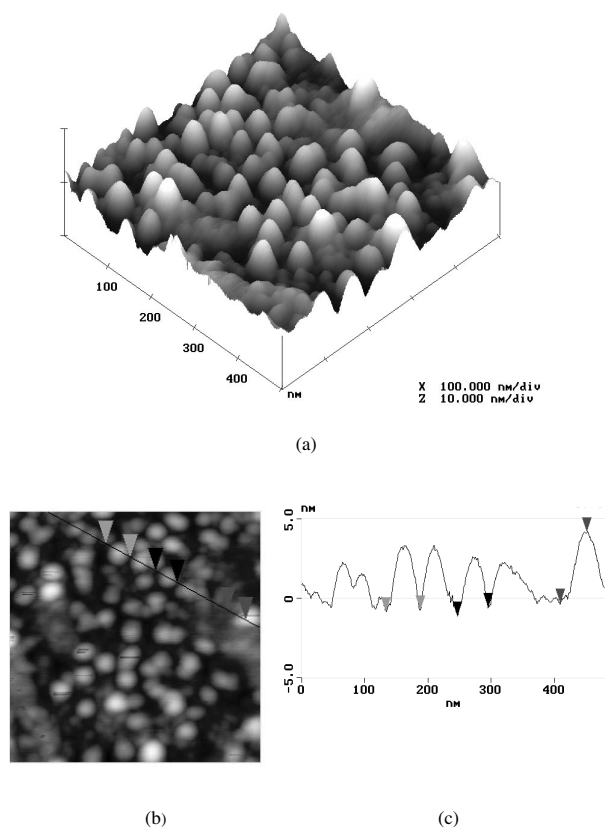


Fig. 7. AFM images of a five-bilayer film of HCl-doped POEA layers alternated with SL layers, showing the surface of the fifth layer of POEA. (a) 500 nm × 500 nm 3D image; (b and c) topographic profile.

surface of POEA. Radotic et al. [28] also showed a modular formation of a lignin precursor by STM which is similar to the images we obtained and corroborates our work. Lignin Langmuir–Blodgett (LB) films [29] also showed a surprisingly low RMS roughness, even lower than for LB films from the traditional amphiphile cadmium stearate. Therefore, it seems very likely that the rougher POEA surface obtained in each adsorption step is covered by the flatter SL layers. This is a nice way of decreasing the roughness of ultra-thin films, which is important for certain applications in nanotechnology where a smoother surface is usually required.

#### 4. Conclusions

Self-assembled films of POEA doped with HCl alternated with SL were successfully produced and investigated under different pHs and substrates. A linear build-up was obtained for different substrates and solution pHs. The layer-by-layer deposition is governed by electrostatic and hydrogen bonding interactions, allowing the formation of films at pHs in the range from 2 to 5, with a larger amount of material adsorbed at higher pH. The adsorption at lower pH is faster due to the greater electrostatic attraction of the POEA to the

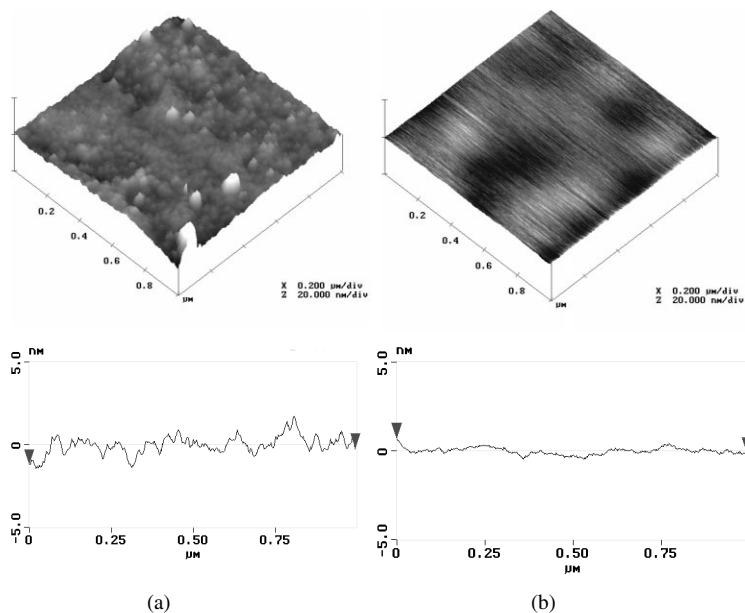


Fig. 8. AFM images of films of HCl-doped POEA layer alternated with SL. (a)  $1 \mu\text{m} \times 1 \mu\text{m}$  image of a film containing only one layer of POEA and its cross-section profile; (b)  $1 \mu\text{m} \times 1 \mu\text{m}$  image of a film containing one bilayer of POEA/SL and its cross-section profile.

SL covered substrate, but a lower amount of POEA is deposited due to charge repulsion of additional POEA chains and conformational steric hindrance. Conversely, at high  $\text{pH} = 5$  the adsorption of POEA takes longer, but it is greater due to the contribution of hydrogen bonding interactions, lower charge repulsion between POEA chains and a more compact polymer conformation. The adsorption of POEA/SL multilayers was independent of the type of substrate used. AFM demonstrated that the surface roughness varies with the number of deposited layers, being higher for POEA than for SL layers, as a result of the grain morphology of POEA layers and the smoother planar surface of SL layers, which covers the rough POEA layer in each alternated deposition.

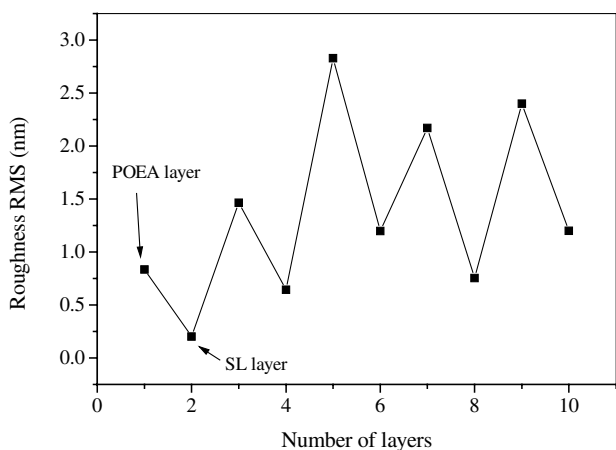


Fig. 9. RMS roughness variation for self-assembled films of POEA/SL as a function of the number of layers deposited. Odd layers correspond to POEA and even ones to SL.

## Acknowledgements

The financial support by FAPESP, CNPq and EMBRAPA (Brazil) is greatly acknowledged. The authors also wish to thank Dr Alan G. MacDiarmid from the University of Pennsylvania, USA, and Dr. O. Ikkala from Helsinki University of Technology, Finland for useful discussions.

## References

- [1] Lvov Y, Decher G. *Crystallogr Rep* 1994;39:628–47.
- [2] Decher G. *Science* 1997;277:1232–7.
- [3] Ulman A. *An introduction to ultrathin films: from Langmuir–Blodgett to self-assembly*. 1st ed. Boston: Academic Press, 1991 (440 p).
- [4] Decher G, Hong JD. *Ber Bunsenges Phys Chem* 1991;95(11):1430–4.
- [5] Stockton WB, Rubner MF. *Macromolecules* 1997;30:2717–25.
- [6] Pontes RS, Raposo M, Camilo CS, Dhanabalan A, Ferreira M, Oliveira Jr. ON. *Phys Stat Sol A* 1999;173:41–50.
- [7] Lowack K, Helm CA. *Macromolecules* 1998;31:823–33.
- [8] Avlyanov JK, Josefowick JY, MacDiarmid AG. *Synth Met* 1995;73:205–8.
- [9] Mattoso LHC, Manohar SK, MacDiarmid AG, Epstein AJ. *J Polym Sci: Part A: Polym Chem* 1995;33:1227–34.
- [10] Kern W. *Semicond Int* 1984;94–9.
- [11] Mattoso LHC, Paterno LG, Campana Filho SP, Oliveira Jr. ON. *Synth Met* 1997;84:123–4.
- [12] Raposo M, Mattoso LHC, Oliveira Jr. ON. *Thin Solid Films* 1998;327–329:739–42.
- [13] Huang WS, Humphrey BD, MacDiarmid AG. *J Chem Soc Faraday Trans* 1986;1(82):2385–400.
- [14] Ray A, Richter AF, MacDiarmid AG, Epstein AJ. *Synth Met* 1989;29:E151.
- [15] Mattoso LHC, MacDiarmid AG. In: Salamone JC, editor. *Polymeric materials encyclopedia*, vol. 7. 1st ed. New York: CRC Press, 1996. p. 5505.

- [16] Ikkala OT, Pietila L-O, Ahjopalo L, Osterholm H, Passiniemi PJ. *J Chem Phys* 1995;103(22):9855–63.
- [17] Ikkala OT, Pietila L-O, Passiniemi P, Vikki T, Österholm H, Ahjopalo L, Österholm J-E. *Synth Met* 1997;84:55–58.
- [18] MacDiarmid AG, Epstein AJ. *Synth Met* 1994;65:103–16.
- [19] MacDiarmid AG, Epstein AJ. *Synth Met* 1995;69:85–92.
- [20] Kawaguchi M, Takahashi A. *Adv Coll Inter Sci* 1992;37:219–317.
- [21] Lvov Y, Decher G, Mohwald H. *Langmuir* 1993;9:481–6.
- [22] Mattoso LHC, MacDiarmid AG, Epstein AJ. *Synth Met* 1994;68:1–11.
- [23] MacDiarmid AG, Epstein AJ. *Mat Res Soc Symp Proc* 1992;247:565–76.
- [24] Wessling B. In: Skotheim TA, et al., editors. *Handbook of conducting polymers*, 2nd ed. New York: Marcel Dekker, 1998 (Chapter 19).
- [25] Porter TL. *Surf Sci* 1993;293:81–5.
- [26] Onda M, Lvov Y, Ariga K, Kunitake T. *Jpn J Appl Phys* 1997;36:L1608–11.
- [27] Constantino CJL. PhD Thesis, Instituto de Física de São Carlos, Universidade de São Paulo, São Paulo, Brazil, 1999.
- [28] Radotic K, Simic-Krstic J, Jeremic M, Trifunovic M. *Biophys J* 1994;66:1763–7.
- [29] Constantino CJL, Dhanabalan A, Cotta MA, Pereira-da-Silva MA, Curvelo AAS, Oliveira Jr ON. *Holzforschung*, 200;54(1):55–60.