

# Influence of Different Dopants on the Adsorption, Morphology, and Properties of Self-Assembled Films of Poly(*o*-ethoxyaniline)

LEONARDO G. PATERNO,<sup>1</sup> LUIZ H. C. MATTOSO<sup>2</sup>

<sup>1</sup> Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, São Carlos, 13560-970, SP, Brazil

<sup>2</sup> Embrapa Instrumentação Agropecuária, CNPDIA/EMBRAPA, C. P. 741, São Carlos, 13560-970, SP, Brazil

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**ABSTRACT:** Self-assembled films of poly(*o*-ethoxyaniline)—POEA alternated with sulfonated lignin (SL)—were successfully produced, and their kinetics of formation and growth investigated for different dopants (hydrochloric acid, methanesulfonic acid, *p*-toluenesulfonic acid, and camphorsulfonic acid). These films were characterized by ultraviolet-visible spectroscopy, atomic force microscopy, surface potential, and electrical resistance measurements. It has been observed that the bulkiest dopants led to a greater time for the polymer deposition and greater amount of material adsorbed. This can be explained by the lower mobility and lower solvation of the bulkiest dopant counterions, which led to a higher screening effect of the charges present in the POEA chains and therefore to a more compact molecular conformation. The morphology of the POEA films were also greatly affected by the type of dopant used, being rougher for the bulkiest dopants. The POEA films also exhibited different electrical responses upon ethylene exposure depending on the dopant, indicating a promising use for gas sensor applications. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1309–1316, 2002

**Key words:** polyaniline; derivatives; self-assembly films; adsorption; dopant

## INTRODUCTION

In the last few years organic ultrathin films produced by the self-assembly technique have been extensively investigated mainly because they can exhibit a variety of properties of technological importance, depending on the type of organic material used.<sup>1,2</sup> Self-assembled films from conducting polymers are among the most studied, due to their high potential on the development of molec-

ular electronics devices such as light-emitting diodes,<sup>3</sup> chemical and biological sensors,<sup>4</sup> and transistors.<sup>5</sup>

The self-assembly technique<sup>6</sup> consists basically on the alternate adsorption of opposite charged macromolecules onto solid substrates from aqueous solutions via electrostatic attraction. However, it has been demonstrated recently that the adsorption of macromolecules can be also driven by other types of interactions, such as hydrogen bond<sup>7,8</sup> and biospecific recognition,<sup>9</sup> which open up the possibility to produce self-assembled films from a great variety of materials.

Polyanilines emerge as potential materials for the fabrication of self-assembled films due to their selected properties such as environmental stability, solubility, high electrical conductivity, and

Correspondence to: L. H. C. Mattoso (mattoso@cnpdia.embrapa.br).

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ease of doping. Several research groups have been investigating the adsorption phenomena for polyanilines, showing that electrostatic attraction<sup>10,11</sup> and hydrogen bonding<sup>7,8</sup> play an important role in the adsorption phenomena. It has been also shown in the literature<sup>12,13</sup> that the type of dopant used for polyanilines can promote great changes in chain conformation, polymer morphology,<sup>14,15</sup> and electrical properties<sup>12–16</sup> for cast films, but this has been not yet studied for ultrathin films produced by the self-assembly technique. The aim of the present work is to investigate the influence of different dopants (hydrochloric acid, methanesulfonic acid, *p*-toluenesulfonic acid, and camphorsulfonic acid) on the adsorption, morphology, and electrical properties of self-assembled films of poly(*o*-ethoxyaniline) as studied by ultraviolet-visible (UV-vis) spectroscopy, atomic force microscopy (AFM), surface potential, and electrical resistance measurements.

## EXPERIMENTAL

All chemicals used were analytical grade. *o*-Ethoxyaniline was purchased from Aldrich and was previously distilled before use. Hydrochloric acid (HCl), methanesulfonic acid (MSA), *p*-toluenesulfonic acid (TSA), 10-camphorsulfonic acid (CSA), ammonium persulfate, and ammonium hydroxide were purchased from Aldrich, and used as received. Ethylene 99.9% purity was purchased from White Martins Special Gases. Sulfonated lignin in the sodium salt form was purchased from Melbar Lignin Products.

Poly(*o*-ethoxyaniline) was chemically synthesized using ammonium persulfate, 1.0M hydrochloric acid, and excess of monomer according to a method described elsewhere.<sup>17</sup> The substrates used were Suprasil quartz slides (8 × 20 × 1 mm) previously washed according to the method described by Kern<sup>18</sup> and interdigitated gold microelectrodes (model IME 1050.5 series, 50 pairs of digits, 10 μm spacing, 0.1 μm height) supplied by Abtech (Pennsylvania, USA).

Stock aqueous solutions (using ultrapure water from a Milli-Q system) of POEA at 0.4 g/L or 1.10<sup>-3</sup>M (based on the tetramer unit mass, 611 g/mol) and of SL at 0.3 g/L or 1.10<sup>-3</sup>M (based on the C9 unit mass, 298 g/mol) were prepared. Films were obtained by the self-assembly method described elsewhere,<sup>6,19</sup> which consists in the alternate deposition of POEA and SL layers by the immersion of substrates in the polymeric solu-

tions for 3 min. UV-vis spectroscopy (Hitachi U2001 model) was employed to monitor the polymer adsorption process at a wavelength of 700 nm. The films obtained were analyzed by atomic force microscopy in a Digital Nanoscope III instrument, on the tapping mode. The spring constant of the cantilever was in the range 20–100 N/m, and a silicon tip was used. Images were obtained in a scan rate of 1 Hz. The surface roughness was calculated by the power spectral density (RMS) and average roughness (Ra) obtained for each layer by arithmetical media of three distinct areas (1 × 1 μm) for each sample.

Solutions of POEA doped with different types of dopants were prepared in the following manner. The as-synthesized HCl doped POEA polymer powder had to be firstly wet with acetone and then dissolved by adding water under continuous stirring during 18 h. This solution was then dedoped by the addition of NH<sub>4</sub>OH 0.1N and then redoped with the desired dopant at pH 3.

Films adsorbed onto gold-coated glass substrates were characterized by surface potential measurements. The samples were scanned by a vibrating gold probe (a gold disk of 20 mm<sup>2</sup>; frequency of vibration: 20 Hz) connected to a Trek 320B electrostatic voltmeter approximately 1–2 mm above the films' surface. The DC electrical resistance was measured for films deposited onto the interdigitated microelectrodes, containing only one layer of POEA doped with the different dopants described above. The electrical measurements were carried out before and during the exposition to ethylene contained inside of a Pyrex glass chamber (1 L) on static mode at 25°C and 60% of relative humidity. The electrical resistance was monitored as a function of exposition time by a HP34401A high precision digital multimeter connected to a computer.

## RESULTS AND DISCUSSION

Solutions of POEA doped with different types of dopants could be successfully prepared in aqueous media, according to the procedure described in the Experimental section. The absorptivity (m<sup>2</sup>/g) was calculated, by doing different calibration curves at different polymer concentrations and using the Lambert–Beer equation, which was different for each dopant as presented in Table I.

The amount of POEA adsorbed was calculated considering the absorptivity of POEA for each dopant, and it is plotted as a function of polymer

**Table I Absortivity Values for Poly(*o*-ethoxyaniline) Doped with the Different Acids Indicated, in Aqueous Solutions at pH 3**

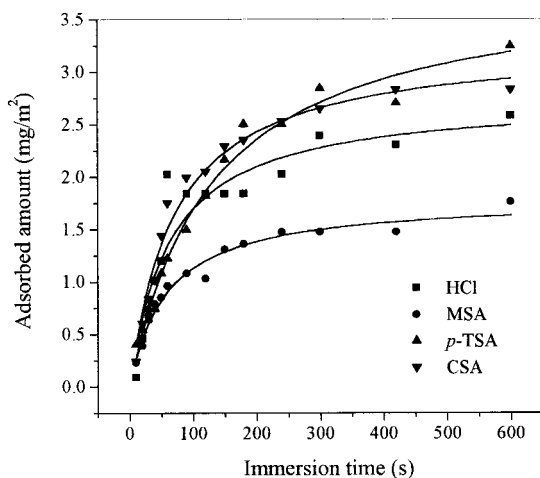
Dopant Type	Absortivity (m <sup>2</sup> /g)
HCl	1.56
MSA	1.76
TSA	1.48
CSA	1.66

adsorption time in Figure 1. Although the shape of the curves are very similar, it can be observed that the total amount of material adsorbed and the time of saturation depend on the dopant used. A quantitative analysis of these isotherms can be done in a simplified manner using the equation below:

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

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

One observe that the bulkiest dopants (CSA and TSA) lead to a greater time for the polymer deposition and amount of material adsorbed, i.e., greater  $\tau$  and  $\Gamma_{\max}$  (Table II). A possible explanation is based on morphological and mobility implications caused by the dopant on the polymer. It

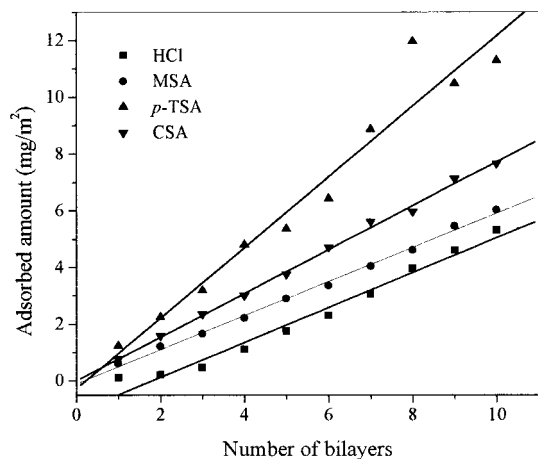

**Figure 1** Adsorption kinetics for the first layer of POEA deposited onto quartz for different dopants, as indicated, at pH 3.

**Table II Adsorption Parameters Calculated Using the Data from the Adsorption of the First Layer of POEA with Different Dopants, According to Figure 1 and Eq. (1): Maximum Amount of Material Adsorbed when Deposition Time Goes to Infinite ( $\Gamma_{\max}$ ) and Characteristic Time ( $\tau$ )**

Dopant Type	$\Gamma_{\max}$ (mg/m <sup>2</sup> )	$\tau$ (s)
HCl	2.76	63
MSA	1.79	60
TSA	3.28	70
CSA	3.87	129

has been demonstrated<sup>12,13</sup> that 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.<sup>12</sup> The Cl<sup>-</sup> ions, for instance, are more solvated than CS<sup>-</sup> ions, being less associated to the positive charges of the POEA, which then exhibits a higher hydrodynamic volume and further contributes to a more extended conformation due to the repulsion between the similarly charged POEA chain segments.<sup>12,13</sup> It has been demonstrated in a previous work<sup>10</sup> that the polymer arrangement and packing during adsorption is favored for a more compact molecular conformation leading to a greater amount of polymer deposited by the self-assembly technique.

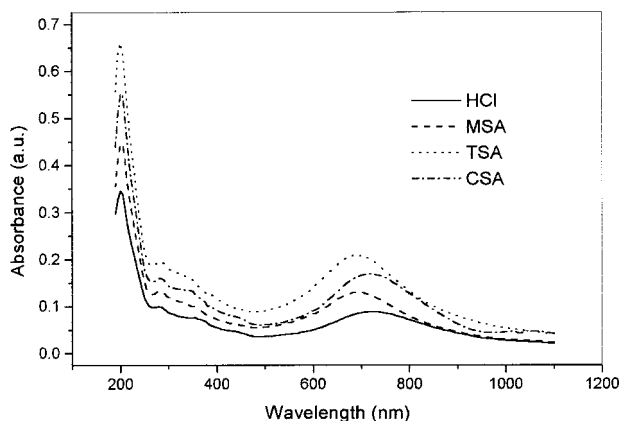
In the present study, it is suggested that the low mobility and low solvation of the bulkiest dopant counterions lead to a higher screening effect of the charges present in the POEA chains and therefore to a more compact conformation of the polymer, which results in a greater amount of material adsorbed (greater  $\Gamma_{\max}$ , e.g., TSA). On the other hand, when the charge screening is less effective, the charges in the polymer chains are more available and present a higher electrostatic attraction (driving force) to the substrate, resulting in a faster adsorption (shorter  $\tau$ , e.g., MSA), consistent with results presented here. Additionally, 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 total amount of material adsorbed.



**Figure 2** Amount of material deposited as a function of number of bilayers for POEA/SL prepared with different dopants, as indicated, at pH 3.

These results are consistent with other studies in the literature<sup>20</sup> 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 a polymeric solution is increased. They propose that the addition of salt to these polymer solutions promotes screening of the electrostatic charges on the polymer chains, causing the intra- and intermolecular 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.<sup>20</sup> A similar effect known as Donnan effect, has also been observed during the synthesis<sup>21</sup> and doping<sup>22</sup> 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.

The growth of multilayered films of POEA alternated with SL (Fig. 2) for the different dopants is consistent with these results, the greater amount of POEA being deposited for the bulkiest dopants. One should note a linear relationship between the number of bilayers and the amount of material adsorbed for all dopants, indicating that approximately the same amount of polymer is being adsorbed at each deposition step, which demonstrates the great reproducibility of the system. It can be observed that the POEA films obtained for the different dopants at pH 3 are all in a similarly doped state, as indicated by the presence of an adsorption band at about 700 nm, shown in Figure 3, and attributed to the excitonic transitions.<sup>17</sup>

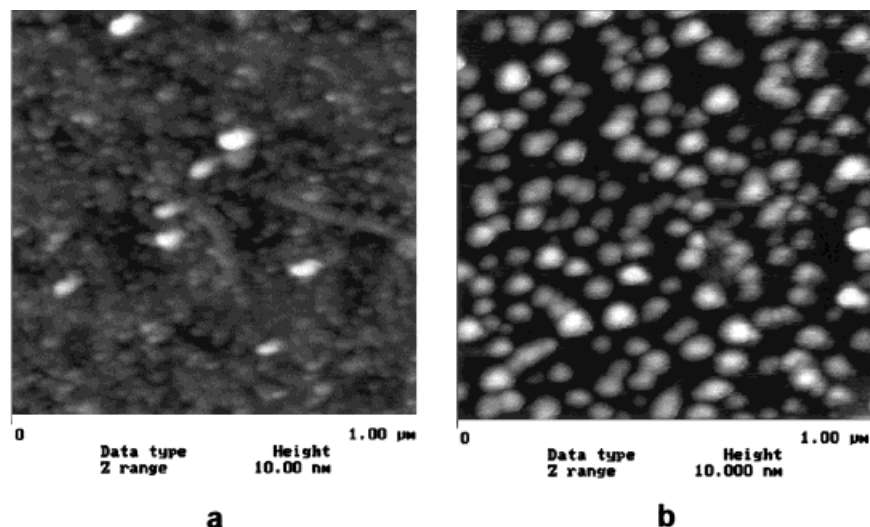


**Figure 3** UV-vis spectra of POEA/SL films (10 bilayers) prepared with different dopants, as indicated, at pH 3.

Analyzing the surface potential of the different POEA films (Table III) we observe that it increases from 100 to 240 mV, respectively for HCl and CSA, as the hydrodynamic volume of the dopant is increased. Such behavior is also consistent with the increase in the amount of POEA adsorbed since it leads to an increase in the amount of dipole moments, which therefore contributes positively to the surface potential values obtained.<sup>23</sup> Such values do not change considerably when the surface potential probe is scanned over the sample surface, which indicates the uniformity of the adsorbed films, at least at the macroscopic level. The surface potential of an adsorbed layer may arise from several contributions,<sup>23</sup> namely: (1) the vertical component of the molecular dipole moments; (2) charge injection from the metallic electrode into the film material, which gives a negative contribution that is practically independent of the material; (3) charge induction on the metallic substrate owing to charged molecules in the film. For POEA, it is known from Langmuir monolayer studies that their net dipole moment contributes positively to

**Table III** Surface Electrical Potential for Films Formed by One Layer of POEA for Different Dopants at pH 3

Dopant Type	Surface Potential (mV)
HCl	100 ± 10
MSA	160 ± 10
TSA	190 ± 10
CSA	240 ± 10

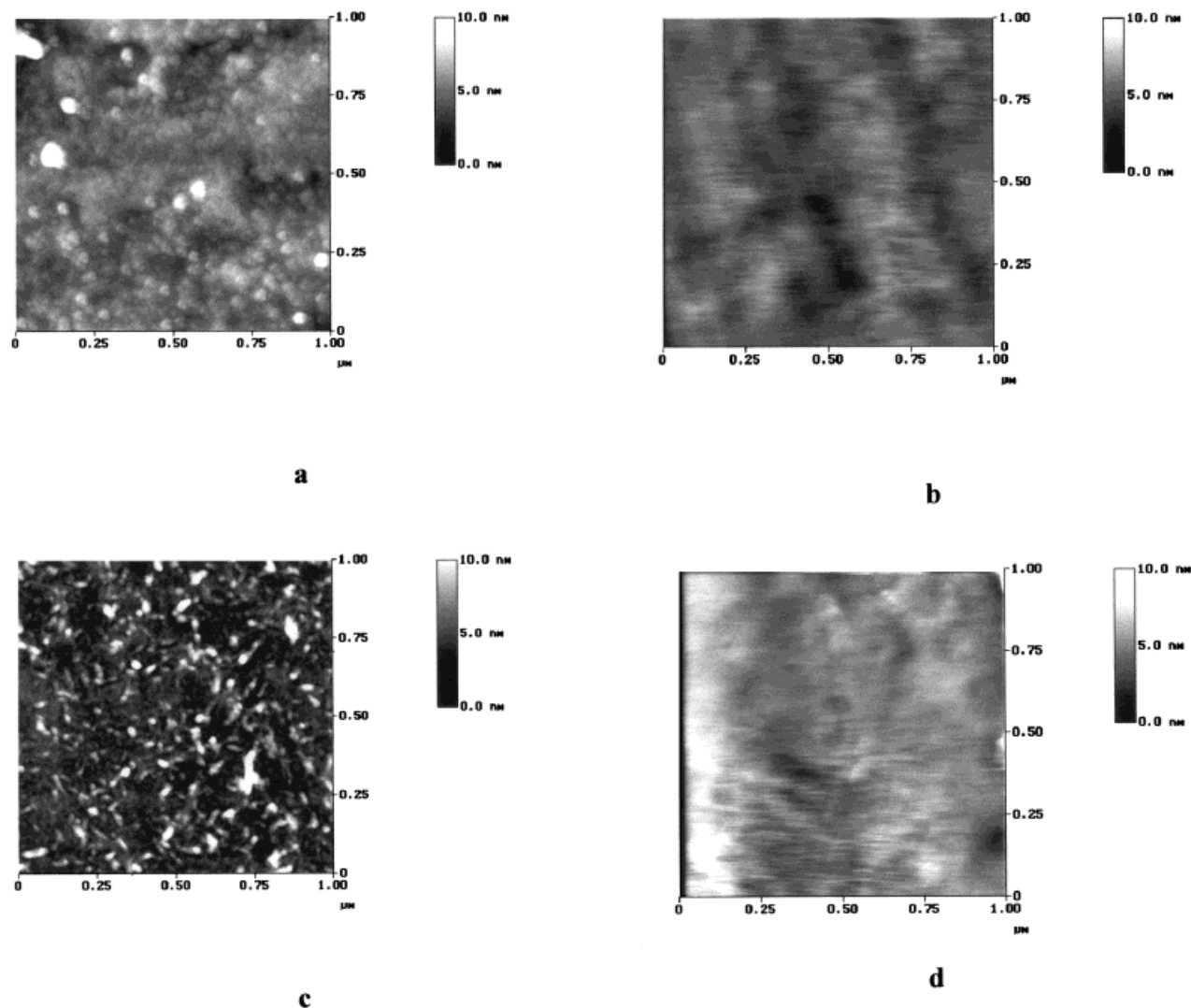


**Figure 4** AFM two-dimensional (2D) images for films containing one layer of POEA (a) as prepared and (b) doped with 1.0M aqueous HCl for 2 h. Images:  $1 \times 1 \mu\text{m}$ ; vertical z scale: 10 nm.

the surface potential.<sup>24</sup> Such positive contribution arises from charge induction, since POEA chains are positively charged. Although other hypothesis such as the chemical nature of the dopant can be also, in principle, affecting the results, no other correlation was so far noticed.

It is known in the literature<sup>25</sup> that the dopant can also greatly change the morphology of conducting polymers in different ways and to different extents depending on the preparation conditions. The effect of the dopant on the morphology of the POEA films were analyzed by atomic force microscopy as described below. Figure 4 shows the effect of doping with 1M HCl on the as-prepared film containing only one layer of POEA. One can observe that the grain size is significantly increased upon doping. A similar effect was also observed for other authors in films cast from solutions.<sup>25</sup> It has been suggested that polyaniline behaves as a granular conductor whose morphology is formed by conducting islands (in the form of grains) surrounded by an insulating matrix.<sup>26</sup> Therefore, it seems likely that as we increase the doping level a swelling effect occurs within the polymer grains due to an increase in the dopant and its counterion concentration. Furthermore, it has been suggested by Angelopoulos<sup>27</sup> an increase in the interchain distance in PANI films as a result of the intercalation of bulky counterions between the polymer chains, since a structural reordering needs to take place in order to accommodate the dopant counterions.

The morphology of the POEA films is also greatly affected by the type of dopant used as shown in Figure 5. The use of different types of protonic acids to dope polyanilines has been successfully used in the literature since it allows the preparation of materials with a variety of selected properties. Although the dopant species are protons in all cases, the nature of the dopant counterion plays a key role in determining other very important properties of the system such as solubility and conductivity. Therefore, it is extremely important to evaluate how the counterion can affect the morphology of the films produced. It can be observed in Figure 5 that the morphology obtained is different for each dopant used to prepare the POEA films. Furthermore, the bulkiest dopant counterions present the roughest morphology as confirmed by the roughness analysis presented in Table IV. The increase in the average roughness can reach ca. 100% on going from HCl to CSA. These results are in agreement with the work of Xie,<sup>15</sup> who observed a roughening effect on the surface of PANI films cast from NMP upon doping with HCl and TSA. The highest roughness was observed for PANI films doped with TSA due to a rearrangement of the polymer structure promoted by the diffusion of a bulky dopant counterion into and along the chain network. They also observed that the grain structure appeared more pronounced upon doping and it was accompanied by a general bulging and thickening of the surface.



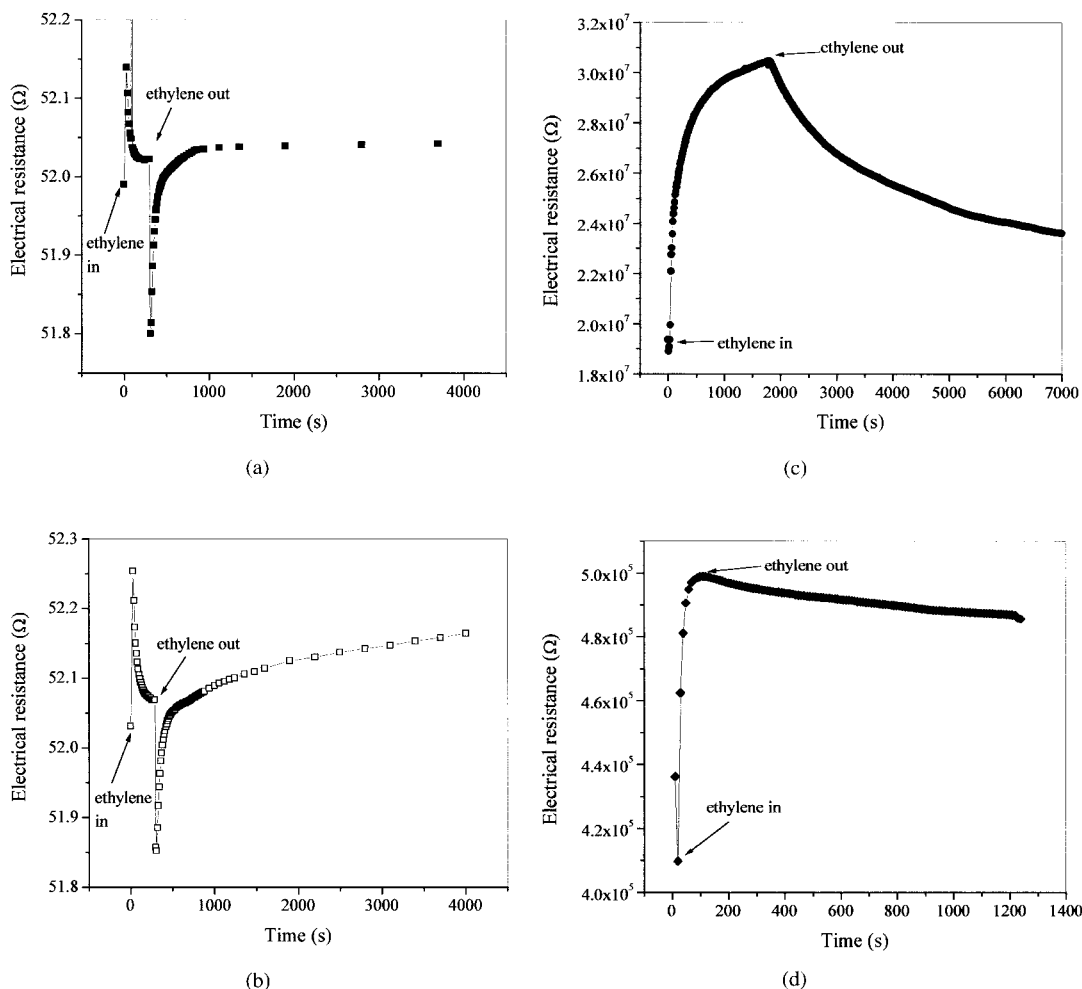
**Figure 5** AFM 2D images for films containing one layer of POEA prepared with different dopants at pH 3: (a) HCl, (b) MSA, (c) TSA, (d) CSA. Images:  $1 \times 1 \mu\text{m}$ ; vertical z scale: 10 nm.

Preliminary studies have demonstrated that these self-assembled films present changes in the electrical resistance when deposited on the sur-

**Table IV** Roughness Values [Power Spectral Density (RMS) and Average Roughness (Ra)] for Films Formed by One Layer of POEA for Different Dopants at pH 3

Dopant Type	Ra (nm)	RMS (nm)
HCl	0.59	0.80
MSA	0.64	0.84
TSA	0.73	1.19
CSA	1.25	1.72

face of interdigitated microelectrodes and exposed to ethylene, as shown in Figure 6. One can observe that the behavior of the electrical resistance as a function of exposition time is dependent on the type of dopant used, leading to different shapes of curves from Figure 6. Moreover, the scale of time needed for the response to the gas used and the percentage of variation on resistance is also quite significant. For instance, the resistance variations were 22 and 60% respectively for CSA and TSA. As we have demonstrated in the present work, films doped with TSA and CSA present the highest values of surface roughness and amount of polymer adsorbed, which lead to a higher surface area available on the sensor



**Figure 6** Electrical resistance response as a function of time of exposition to ethylene, for POEA films prepared with different dopants: (a) HCl, (b) MSA, (c) TSA, (d) CSA.

unit for interaction with the gas and therefore to a greater electrical response. Nevertheless, several other factors—such as chemical nature of the dopant, and different polymer density and microstructure—promoted by the dopants<sup>14</sup> can also contribute for these different electrical responses and are currently being investigated in our group.

Additionally, we have also cycled the gas exposition for the TSA-POEA unit and the electrical behavior appeared to be quite reversible for the conditions used [10 s of exposition, 25°C, 60% relative humidity (RH)]. These results indicate that self-assembled films from polyaniline derivatives seems to be promising materials for ethylene gas sensor. Moreover, that different responses in resistance were obtained for each dopant used is also important, since each of these films could be used as a sensor unit that presents a particular response to compose a sensing instru-

ment which would give a pattern characteristic of the specific gas. Ongoing experiments are being taken to investigate the best setup for an ethylene gas sensor based on this first study.

## CONCLUSION

Self-assembled films of poly(*o*-ethoxyaniline) alternated with sulfonated lignin were successfully produced using different dopants (hydrochloric acid, methanesulfonic acid, *p*-toluenesulfonic acid, and camphorsulfonic acid). The bulkiest dopants lead to a greater time for the polymer deposition and greater amount of material adsorbed. This can be explained by the lower mobility and lower solvation of the bulkiest dopant counterions, which lead to a higher screening effect of the charges present in the POEA chains and there-

fore to a more compact molecular conformation. The morphology of the POEA films were greatly affected by the type of dopant used, being rougher for the bulkiest dopants, due to a rearrangement of the polymer structure promoted by the diffusion of a bulky dopant counterion into and along the chain network. The type of dopant used also affected the surface potential of the polymer films investigated. Furthermore, POEA films exhibited different electrical responses upon ethylene exposure depending on the dopant, indicating a promising use for gas sensor applications.

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