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Doping in poly(*o*-ethoxyaniline) nanostructured films studied with atomic force spectroscopy (AFS)

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ABSTRACT

The study of intermolecular interactions at interfaces is essential for a number of applications, in addition to the understanding of mechanisms involved in sensing and biosensing with liquid samples. There are, however, only a few methods to probe such interfacial phenomena, one of which is the atomic force spectroscopy (AFS) where the force between an atomic force microscope tip and the sample surface is measured. In this study, we used AFS to estimate adhesion forces for a nanostructured film of poly(*o*-ethoxyaniline) (POEA) doped with various acids, in measurements performed in air. The adhesion force was lower for POEA doped with inorganic acids, such as HCl and H₂SO₄, than with organic acids, because the counterions were screened by the ethoxy groups. Significantly, the morphology of POEA both in the film and in solution depends on the doping acid. Using small-angle X-ray scattering (SAXS) we observed that POEA dissolved in a mixture of dimethyl acetamide exhibits a more extended coil-like conformation, with smaller radius of gyration, than for POEA in water, as in the latter POEA solubility is lower. In AFS measurements in a liquid cell, the force curves for a POEA layer displayed an attractive region for pH ≥ 5 due to van der Waals interactions, with no contribution from a double-layer since POEA was dedoped. In contrast, for pH ≤ 3, POEA was doped and the repulsive double-layer force dominated. With AFS one is therefore able to correlate molecular-level interactions with doping and morphology of semiconducting polymers.

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1. Introduction

In recent years, molecular assemblies in the nanometer scale have been achieved mostly with the Langmuir–Blodgett (LB) (Gaffo et al., 2007; de Souza et al., 2007) and self-assembly or layer-by-layer (LbL) methods (Lvov et al., 1997; Xing et al., 2007). The LbL method, in particular, is experimentally very simple and versatile, which has made it possible to employ nanostructured films in sensors (Kim et al., 2008), biosensors (Liang et al., 2008), and in chemically modified surfaces (Yu et al., 2007). Though the method was originally conceived for polyelectrolytes, now a variety of materials are used, including semiconducting polymers such as

polyanilines (Kilmartin et al., 2008; Liu et al., 2008). These polymers exhibit significant overlap of delocalized π -electrons along the polymer chain, and may have electrical and optical properties varying considerably by doping (Suarez and Compton, 1999). The polymer may be reversibly switched from the insulating into the conducting states, a process accompanied by insertion or removal of dopant ions (Barisci et al., 2000).

In addition to the doping level and other features of the semiconducting polymer chains, the final film properties depend strongly on film morphology, especially in nanostructured films. Here, processibility of the polymers is essential, which has prompted many researchers to seek ways to improve solubility of polyanilines (Wei et al., 1990). Indeed, substituted polyanilines, such as poly(*o*-toluidine) (POT), poly(*o*-methoxyaniline) (POMA) and poly(*o*-ethoxyaniline) (POEA) (Kim et al., 2001; Horvat-Radosevic et al., 2006), normally maintain the electrical and optical properties of the parent polyaniline, with the added solubility in some organic solvents and even in aqueous media in special cases. Therefore, attempts to understand the mechanisms

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behind the usefulness of semiconducting polymers for the various applications must involve studies of intermolecular interactions (Guimard et al., 2007; Rahman et al., 2008). For the sensing ability in liquids, for instance, one has to investigate how minute changes in the liquid affect the film properties.

One method suitable for probing interactions at the molecular level is the atomic force spectroscopy (AFS) (Drelich and Mittal, 2005; Leite and Herrmann, 2005; Leite et al., 2005, 2008), in which an atomic force microscope is used to measure the force – for varying distances – between a tip and the sample surface. AFS was used for studying the doping degree, morphology and non-specific interactions of POEA (Leite et al., 2007a). Here we employ AFS to study properties of POEA in the form of a one-layer, nanostructured film, adsorbed using the concepts of the LbL method. Emphasis is placed on the dependence with the doping acid used to process POEA in the film fabrication procedure. Unique to this system, as we shall show, is the ability to control the degree of attractive and repulsive interactions through the selective doping or dedoping of the POEA film.

2. Materials and methods

POEA was chemically synthesized according to the method described by Mattoso et al. (1995). Polymeric solutions were prepared by dissolving 0.005 g of POEA dedoped (emeraldine base) in 10 mL of *N,N*-dimethylacetamide (DMAc), and then adding one of the following acids: *p*-toluenesulfonic (*p*-TSA), camphorsulfonic acid (CSA), sulfanilic acid (SAA), H₂SO₄, HNO₃ and HCl. After ensuring that there were no precipitates, 40 mL of ultrapure water were added and the pH adjusted to the desired value with the acid,

thus completing a final volume of 50 mL. Then, the final polymer concentration was $0.5 \times 10^{-3} \text{ mol L}^{-1}$ in a 1:4 (v/v) mixture of DMAc and ultrapure water. Using this solution one-layer LbL films were produced by immersion of the substrate into a POEA solution for several adsorption times, viz. 10, 30, 60 and 180 s for each layer.

AFM images were obtained with a Topometrix TMX 2010 Discoverer, operating in the contact mode, being analyzed using WSxM (Nanotec Electronica S.L.) (Horcas et al., 2007). The cantilevers had a spring constant, $k = 0.08 \pm 0.02 \text{ N m}^{-1}$, and tip curvature radius $R = 38 \pm 3 \text{ nm}$. The tip and cantilever were made of silicon nitride (Si₃N₄). The low contact force was chosen to reduce deformation or indentation of the POEA surfaces. Before acquiring the images, the piezoscanner of the AFM system was calibrated, since its behavior may depart from linearity between the force and displacement. In order to check the accuracy of the measurements, subsidiary experiments were performed with a Topometrix standard grade silicon (Si) coated with quartz (average height: 24.0 μm and pitch: 15.0 μm). The errors in length measurements were lower than those expected for the standard grade (AFM Standard-B, P/N 10-10299, Topometrix. maximum deviation: average height = 8% and pitch = 2.5%), being 2.5% and 0.1% for average height and pitch, respectively. The scanner used in the experiments has maximum scan ranges of 70 μm in both *x* and *y* axes. Force curves were measured in solution with a cell developed by Topometrix consisting of a glass support with two orifices for the inlet and outlet of liquids and an O-ring for sealing it. The curves were also acquired in ambient conditions, at several points over the sample scanned area. The theoretical background and possible applications of AFS are given in the reviews (Cappella and Dietler, 1999; Leite and Herrmann, 2005).

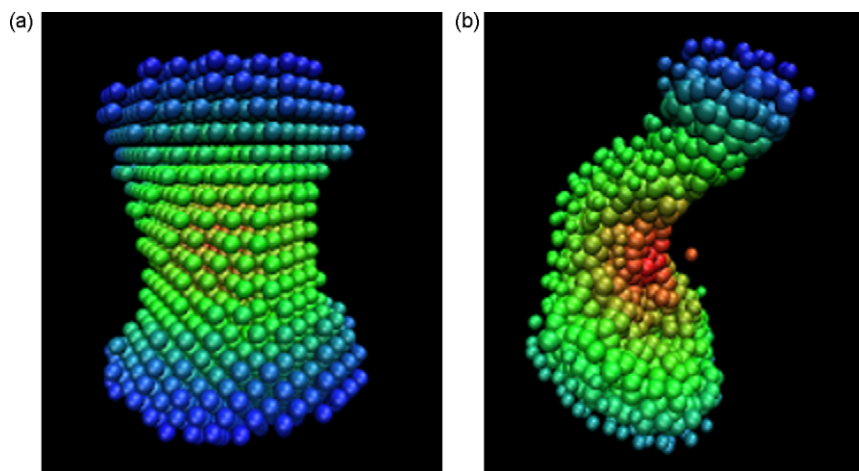


Fig. 1. Average dummy atom model (DAM) for POEA in (a) water and (b) DMAc/water (1:4, v/v).

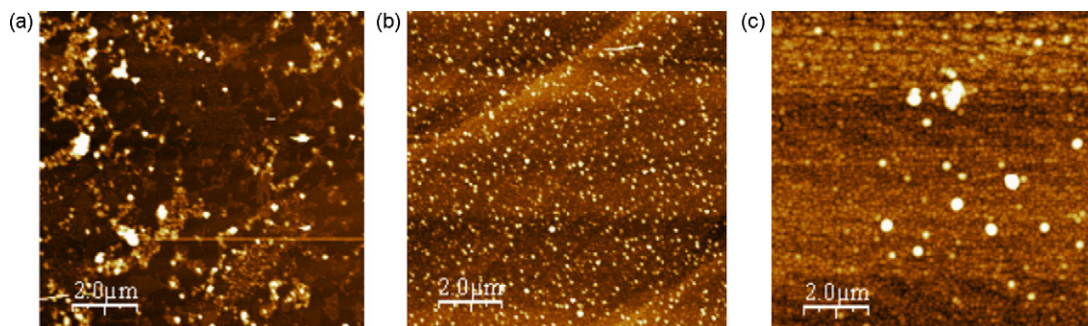


Fig. 2. AFM image of a POEA film doped with HCl (pH 3) for different immersion times on mica. (a) 10; (b) 60 and (c) 180 s.

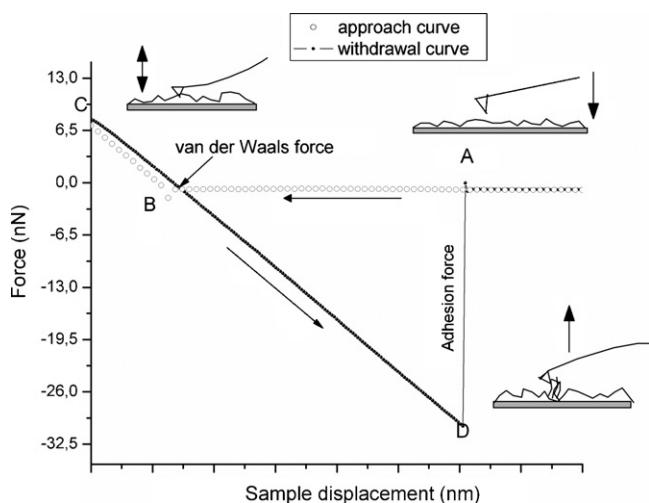


Fig. 3. Typical force curve obtained in air for a POEA film adsorbed on mica. This force curve was taken with a frequency of jump of $10^4 \mu\text{m/s}$. If the force curve were obtained with a frequency of jump $\leq 1 \mu\text{m/s}$, an attraction peak would appear due to stretching of POEA chains (adapted from Leite et al., 2007a).

The small angle X-ray scattering (SAXS) experiments were conducted at the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil, using a monochromatic X-ray beam ($\lambda = 1.488 \text{ \AA}$). To perform the SAXS measurement, the aqueous

solution was placed in a flat cell and sealed. The SAXS curves were normalized with respect to (i) the decreasing intensity of the coming synchrotron beam and (ii) the sample absorption. The SAXS intensity produced by the solvent (water and DMAc) was measured and subtracted from the total scattering intensity before the analysis. Since solutions containing particles of different sizes (polydisperse) show several linear regions in the Guinier plot, in order to generate low resolution models we considered only the SAXS curve from the last linear region (Leite et al., 2007b). This was performed as an attempt to include the information due to the smallest particles in solution as if the system were monodisperse (three-dimensional models).

3. Results and discussion

The properties of polymer films produced with the layer-by-layer (LbL) technique depend on a number of experimental parameters, including the solvent for preparing the solutions and the time of adsorption of each layer. Fig. 1 shows the low-resolution particle shape for POEA molecules in solution, determined from the SAXS data using the *ab initio* procedure (Semenyuk and Svergun, 1991). A less-packed, coiled structure is observed for POEA dissolved in DMAc/water (Fig. 1b), while for POEA dissolved in water blobs are formed (Fig. 1a). The values of radii of gyration, R_g , for POEA dissolved in water and water/DMAc are 64 and 32 Å, respectively. The larger radius for POEA in water may be caused by larger aggregates arising from the rod-like

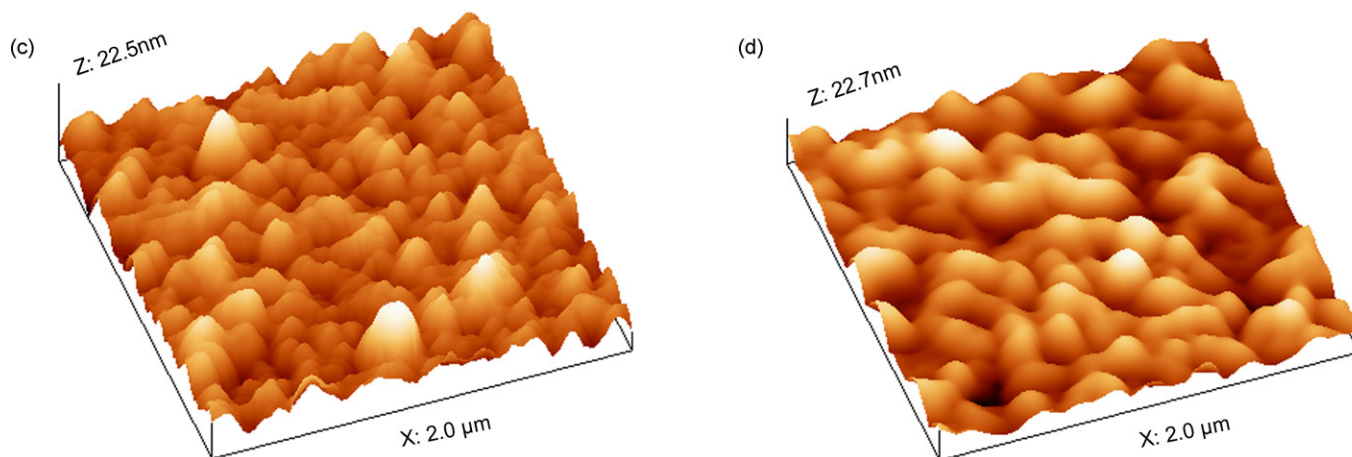
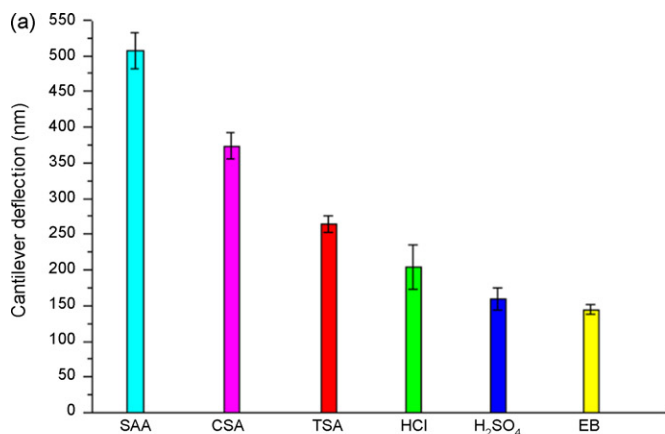
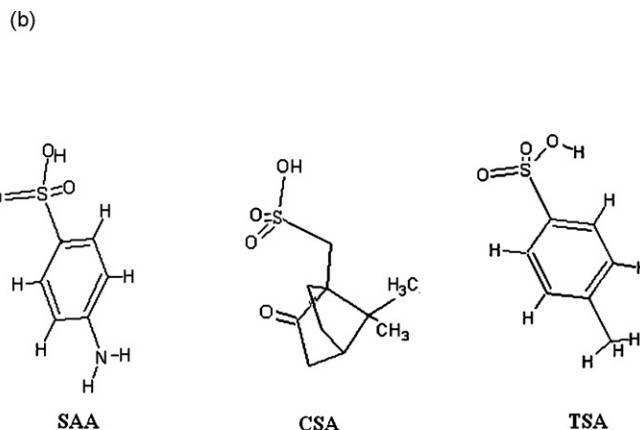


Fig. 4. (a) Cantilever deflection (representing adhesion force) for POEA films doped with various acids (pH 3) and non-doped POEA-EB. In all cases, the films were adsorbed on mica with 3 min of immersion. Also shown are the structural formulas of the organic acids (b); AFM images for (c) POEA doped with HCl and (d) POEA doped with TSA. Measurements performed in air.

conformation of the polymer chains. For POEA in water/DMAc, the chains assume a more extended coil-like conformation due to the higher solubility. It is known that aggregates formed already in solution affect film morphology (Leite et al., 2005); in particular at early stages of adsorption film morphology appears entirely governed by the chain conformation in solution and adsorption of aggregates (Leite et al., 2007b). A careful investigation of the Guinier plots revealed a larger size of chain aggregates for POEA dissolved in water; the size of the aggregates decreased with increasing amount of DMAc in the solution. In fact, the best tradeoff between solubility and aggregation is attained in a 1:4 (v/v) mixture of DMAc and water.

The influence from the time of adsorption on the film properties was investigated by adsorbing POEA molecules on mica within short time periods. If full coverage of the substrate by a POEA layer is desired, one has to use adsorption times above 180 s. In AFM experiments, we observed that non-covered areas were apparent when shorter adsorption times were employed, as depicted in the images of Fig. 2. For 10 s of immersion time, for instance, most of the substrate area appears to be uncoated. For 60 s, granular structures characteristic of POEA films become apparent, which only occupy the whole area for the 3rd image obtained with 180 s of adsorption (Fig. 2c).

Fig. 3 shows typical force curves for POEA in air, in which the adhesion force was 30 ± 5 nN, whereas the van der Waals was 1.3 ± 0.6 nN, for measurements performed in five distinct regions. The total downward force in air comprises several contributions, including the van der Waals and bridge forces, with the adhesion

force between the tip and the sample surface being the sum of them all. On the other hand, when force curve measurements are performed in solution, electrostatic and hydration forces may appear between the tip and sample. The interaction forces most relevant to the present work are contact, van der Waals, capillary and electrostatic forces. van der Waals forces are significant for smooth contacts and in solution but are expected to be small compared to other forces involving relatively rough surfaces in air. Liquid bridges provide the dominant adhesion forces only above $\sim 40\%$ of relative humidity (Xu et al., 1998). It should be mentioned that for a POEA film, the force curves obtained in air may vary depending on the spot chosen for the measurement due to the intrinsic film roughness. Furthermore, the force may depend on how many times that spot has been used in previous measurements as the area of contact varies with consecutive measurements because polymer chains may be adsorbed (desorbed) onto the tip. Generally, the adhesion force is lower in the first 3 measurements, especially in a liquid cell. This occurs because the tip is at least partially covered with the polymer after a series of measurements, giving rise to the so-called bridge forces between tip and sample (Leite et al., 2007a). The bridge forces depend on the frequency in the tapping mode, because at high frequencies the relaxation time of the polymer may be exceeded (Biggs and Proud, 1997).

The type of acid used to dope POEA affects the interaction with the AFM tip, most probably due to the different chemical nature of the dopant counterion and also because of distinct 'chain conformations' on the substrate. Fig. 4a shows the cantilever deflection due to the adhesion force between the AFM tip and POEA

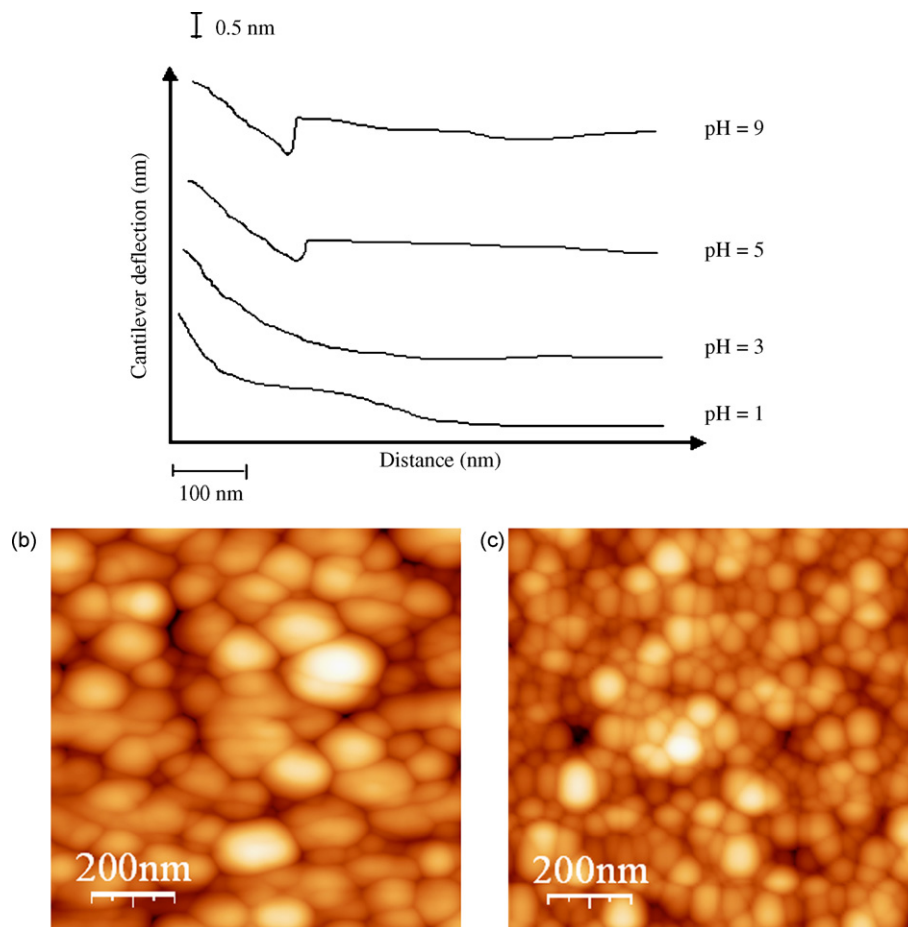


Fig. 5. (a) Force curves (pull-on forces) for a POEA film deposited on mica in solutions of various pH values (HCl); (b) AFM image of POEA (pH 3) and (c) AFM image of POEA (pH 9). The curves have been shifted vertically to facilitate visualization. Only the approach curves were included.

films doped with various acids, with the measurements performed in air. The pull-off force measured is higher for POEA films doped with organic acids, such as *p*-toluenesulfonic (*p*-TSA), camphor-sulfonic (CSA) and sulfanilic (SAA) acids, whose structures are shown in Fig. 4b. The smaller adhesion for inorganic acids may be due to the polymer steric protection, *i.e.* the counterions (SO_4^{2-} and Cl^-) are screened by ethoxy groups of POEA, being less attracted by the AFM tip. This is why the forces for POEA doped with HCl and H_2SO_4 are close to that measured with dedoped POEA (emeraldine base (EB)), as shown in Fig. 4a.

For the comparison of adhesion forces in POEA doped with organic acids, one notes that the sample doped with SAA has more polar groups on the surface due to the presence of amine groups (NH_2 -polar). Therefore, interaction with the tip may occur via H-bonding between the oxygen from the oxidized silicon nitride tip and the hydrogen from the amines, in addition to van der Waals forces. This additional interaction increases adhesion. The POEA film doped with CSA has methyl groups (CH_3 -apolar) and oxygen atoms bonded to sulfur and carbon, which imparts polarity to the polymer chains. From AFM images it was possible to infer that the film doped with TSA has hydrophobic groups on the surface, leading to a distinct chain conformation on the surface, *i.e.* fibrillar morphology (Fig. 4d), while the film doped with HCl has globular morphology (Fig. 4c). These conformations are affected by the doping degree and acid used. A more extended structure is obtained by increasing the doping level. Indeed, POEA molecules in solution have a less-packed coiled structure for pH 3.0 while at pH 10.0 blobs are formed. POEA solutions doped with TSA at pH 3.0 showed a cylindrical-like conformation (Leite et al., 2007a,b), which gives origin to the fibrilles observed in AFM images of Fig. 4d. These distinct conformations may lead to different pull-off forces, since the contact area between the AFM tip and the sample varies.

In force curves obtained in a liquid cell, the interaction between two surfaces depends on several factors, including surface charge density and conformation of the polymer chains at the interface. Also important is the possible aggregation of particles. We investigated first bare substrates and adsorbed POEA in contact with pure water. For a mica substrate immersed in water, there is no interaction down to a separation of 6.7 ± 0.7 nm between the tip and the mica surface. Some dispersion is observed when measurements are carried out in different regions of a sample (Leite et al., 2003). The force at all regions is attractive, approximately 0.7 nN. For POEA adsorbed onto the mica, an attractive force of 3.2 nN appears for the tip-surface distance of 12.0 ± 0.8 nm. In both cases, bare mica and POEA film, the forces occur for almost neutral or hydrophobic surfaces, since the attractive van der Waals forces will operate at distances smaller than 5 nm. The long-range interactions responsible for the force measured are hydrophobic, which arise from repulsion of water. This induces hydrophobic particles to aggregate.

The force curves in solution are also affected by the level of POEA doping, which may be studied by measuring forces with POEA in liquid cells at different pHs. Fig. 5a shows force curves for POEA adsorbed onto mica in contact with aqueous solutions of various pHs. For $\text{pH} \geq 5.0$, the attractive force ranged from 0.6 to 1 nN. POEA is expected to be non-protonated, and therefore there is no double-layer, the attractive force being entirely due to van der Waals forces. For pHs between 4 and 5 POEA becomes doped and the repulsive force from the double-layer counterbalances the van der Waals forces. For pH 3, where POEA is almost completely charged, the double-layer contribution dominates and leads to a repulsive force, which is even more evident for the curve at pH 1. It is recalled that the tip becomes charged because in aqueous solutions the surface of silicon tips comprises amphoteric silanol

and basic silylamine (secondary (silazane, $-\text{Si}_2\text{NH}_2$) and possibly primary (silylamine, $-\text{SiNH}_3$) amines though the latter are rapidly hydrolyzed) surface groups (Drummond and Senden, 1994). The commercial silicon nitride tip surface has been found to be almost electrically neutral over a wide pH range, from at least pH 6–8.5, thus indicating equal densities of silanol and silylamine surface groups (Borato et al., 2006). For Si_3N_4 tip on mica, the total tip-sample force changes from attractive for $\text{pH} \leq 6$ to repulsive at $\text{pH} \sim 8$, because mica is negatively charged at any pH value, while the isoelectric point for Si_3N_4 tip is ca. pH 6.3 (de Souza et al., 2001).

The morphology for POEA is globular, with the size of the globules increasing with pH. At pH 3, the interactions between doped chains and with the surface are less significant, favoring a less condensed packing of polymer chains (Fig. 5b). These results are consistent with the literature (Leite et al., 2007b), according to which charged polyelectrolytes form thin films as the charged molecules adsorbed create a potential barrier that prevents more molecules from adsorbing. For undoped POEA, the repulsive forces are minimized, leading to denser packing of molecules in solution or at the surface (Fig. 5c). Indeed, the potential barrier does not exist for undoped POEA, which can adsorb *via* hydrogen bonds. The measurements performed in pH 1 showed a larger double-layer force than for pH 3. However, in pH 1 the interaction map is more inhomogeneous, with several repulsive regions seen in Fig. 6.

A further possible control of film properties may be imparted if surfactant acids are used. This is the case of dodecylbenzene sulfonic acid (DBSA), which may help form the so-called hairy rod polymers, which are rigid polymers with a dense set of flexible side

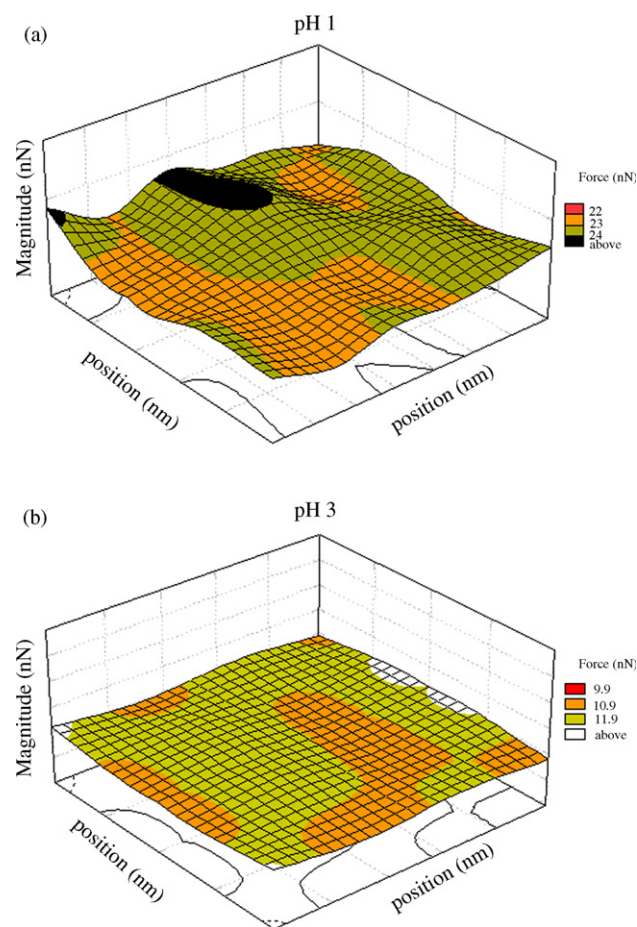


Fig. 6. Interaction maps ($20 \mu\text{m} \times 20 \mu\text{m}$) for (a) POEA-ES ($\text{pH} \approx 3.0$) and (b) POEA-ES ($\text{pH} \approx 1.0$).

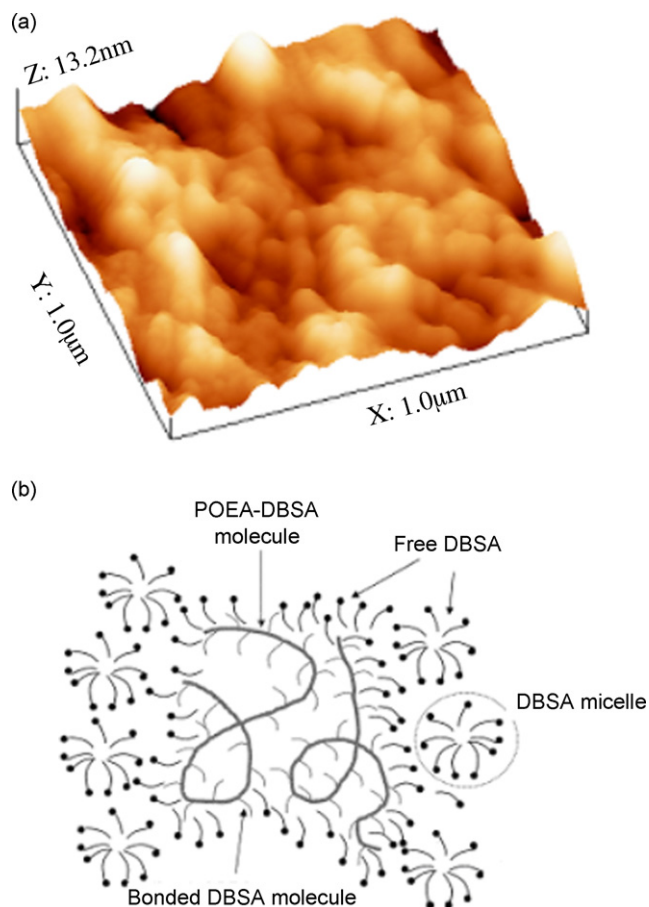


Fig. 7. (a) AFM image of POEA doped with DBSA (pH 3 and 5 layer) and (b) a schematic model of aqueous dispersions of POEA with DBSA (adapted from Levon et al., 1995).

chains (such as alkyl tails) covalently bonded to the backbone (Ballauff, 1989). The repulsion between alkyl tails and the rigid backbone controls self-organized structures. In conjugated polymers, lamellar self-organization in polypyrrole-alkyl, sulfates (Wernet et al., 1984) and polyaniline-dodecylbenzenesulfonates (Zheng et al., 1995) has been observed. Fig. 7a shows the morphology of POEA doped with dodecylbenzene sulfonic acid (POEA-DBSA), whose structure differs from those of POEA films doped with the acids mentioned above with regard to the size of the globules and roughness. The excess DBSA forms micellar structures that also act as a surfactant, as depicted in Fig. 7b. The hydrophobic tails of free and bonded DBSA molecules are so arranged as to turn to the aqueous phase, since the molecular conformation of POEA-DBSA chains is affected both by intermolecular interactions and interactions with the aqueous medium (Levon et al., 1995).

4. Conclusions

The AFS technique was used to study physicochemical properties of nanostructured films of the semiconducting poly(*o*-ethoxyaniline) (POEA) and interactions between the film and an AFM tip. Various effects could be identified since the polymer used, POEA, has a variable degree of doping, which depends on the acid used to process the polymer and on the pH. The structure and size of the acid counterions are important for the interaction forces because of steric effects. Force curves were obtained for POEA films displaying attractive regions due to van der Waals interactions and

repulsive interactions owing to double-layer contributions. When a liquid cell was used, the AFS measurements served to investigate specific interactions and the doping degree of POEA, which can be useful in the study of electronic properties of thin films. Also investigated was the influence of the solvent for the formation of aggregates, from which we concluded that the best tradeoff between solubility and aggregation is attained in a 1:4 (v/v) mixture of DMAc and water.

The interaction forces measured with AFS, especially in liquid cells, may help understand the mechanisms behind the high sensitivity of taste sensors, which has been attributed to interfacial phenomena between the liquid under analysis and the film-forming molecules of the sensing unit (Borato et al., 2006).

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References

- Ballauff, M., 1989. Stiff-chain polymers—structure, phase-behavior and properties. *Angew. Chem. Int. Ed. Engl.* 28, 253–267.
- Barisci, J.N., Stella, R., Spinks, G.M., Wallace, G.G., 2000. Characterization of the topography and surface potential of electrodeposited conducting polymer films using atomic force and electric force microscopies. *Electrochim. Acta* 46, 519–531.
- Biggs, S., Proud, A.D., 1997. Forces between silica surfaces in aqueous solutions of a weak polyelectrolyte. *Langmuir* 13, 7202–7210.
- Borato, C.E., Leite, F.L., Oliveira Jr., O.N., Mattoso, L.H.C., 2006. Efficient taste sensors made of bare metal electrodes. *Sensor Lett.* 4, 155–159.
- Cappella, B., Dietler, G., 1999. Force-distance curves by atomic force microscopy. *Surf. Sci. Rep.* 34, 1–104.
- Drelich, J., Mittal, K.L., 2005. Atomic Force Microscopy in Adhesion Studies. VSP—An Imprint of BRILL, Netherlands.
- de Souza, E.F., Ceotto, G., Teschke, O., 2001. Dielectric Constant measurements of interfacial aqueous solutions using atomic force microscopy. *J. Mol. Catal. A* 167, 235–243.
- de Souza, N.C., Ferreira, M., Wohnrath, K., Silva, J.R., Oliveira Jr., O.N., Giacometti, J.A., 2007. Morphological characterization of Langmuir-Blodgett films from polyaniline and a ruthenium complex (Rupy): influence of the relative concentration of Rupy. *Nanotechnology* 18, 075713-1–075713-7.
- Drummond, C.J., Senden, T.J., 1994. Examination of the geometry of long-range tip sample interaction in atomic force microscopy. *Colloids Surf. A* 87, 217–234.
- Gaffo, L., Zucolotto, V., Cordeiro, M.R., Moreira, W.C., Oliveira Jr., O.N., Cerdeira, F., Brasil, M.J.S.P., 2007. Structural aspects of Langmuir-Blodgett and cast films of zinc phthalocyanine and zinc hexadecafluorophthalocyanine. *Thin Solid Films* 515, 7307–7312.
- Guimard, N.K., Gomez, N., Schmidt, C.E., 2007. Conducting polymers in biomedical engineering. *Prog. Polym. Sci.* 32, 876–921.
- Horcas, I., Fernández, R., Gómez-Rodríguez, J.M., Colchero, J., Gómez-Herrero, J., Baro, A.M., 2007. WSXM: a software for scanning probe microscopy and a tool for nanotechnology. *Rev. Sci. Instrum.* 78, 013705-1–013705-8.
- Horvat-Radosevic, V., Kvastek, K., Kraljic-Rokovic, M., 2006. Impedance spectroscopy of oxidized polyanilines and poly(*o*-ethoxyaniline) thin film modified Pt electrodes. *Electrochim. Acta* 51, 3417–3428.
- Kilmartin, P.A., Martinez, A., Barlett, P.N., 2008. Polyaniline-based microelectrodes for sensing ascorbic acid in beverages. *Curr. Appl. Phys.* 8, 320–323.
- Kim, K., Lee, H.S., Yu, H.D., Park, H.K., Kim, N.H., 2008. A facile route to stabilize SERS-marker molecules on μ Ag particles: layer-by-layer deposition of polyelectrolytes. *Colloids Surf. A* 316, 1–7.
- Kim, J.W., Jang, W.H., Choi, H.J., Joo, J., 2001. Synthesis and electrorheological characteristics of polyanilines derivatives with different substituents. *Synth. Met.* 119, 173–174.
- Leite, F.L., Riul, A., Herrmann, P.S.P., 2003. Mapping of adhesion forces on soil minerals in air and water by atomic force spectroscopy (AFS). *J. Adhesion Sci. Technol.* 17, 2141–2156.
- Leite, F.L., Herrmann, P.S.P., 2005. Application of atomic force spectroscopy (AFS) to studies of adhesion phenomena: a review. *J. Adhesion Sci. Technol.* 19, 365–405.
- Leite, F.L., Paterno, L.G., Borato, C.E., Herrmann, P.S.P., Oliveira Jr., O.N., Mattoso, L.H.C., 2005. Study on the adsorption of poly(*o*-ethoxyaniline) nanostructured films using atomic force microscopy. *Polymer* 46, 12503–12510.
- Leite, F.L., Borato, C.E., da Silva, W.T.L., Herrmann, P.S.P., Oliveira Jr., O.N., Mattoso, L.H.C., 2007a. Atomic force spectroscopy on poly(*o*-ethoxyaniline) nanostructured films: sensing nonspecific interactions. *Microsc. Microanal.* 13, 304–312.
- Leite, F.L., Oliveira Neto, M., Paterno, L.G., Ballester, M.R.M., Polikarpov, I., Mascarenhas, Y.P., Herrmann, P.S.P., Mattoso, L.H.C., Oliveira Jr., O.N., 2007b. Nanoscale

- conformational ordering in polyanilines investigated by SAXS and AFM. *J. Colloid Interface Sci.* 316, 376–387.
- Leite, F.L., Alves, W.F., Mir, M., Mascarenhas, Y.P., Herrmann, P.S.P., Mattoso, L.H. C., Oliveira Jr., O.N., 2008. TEM, XRD and AFM study of poly(*o*-ethoxyaniline) films: new evidence for the formation of conducting islands. *Appl. Phys. A* 93, 537–542.
- Levon, K., Ho, K.-H., Zheng, W.-Y., Laakso, J., Kärnä, T., Taka, T., Österholm, J.-E., 1995. Thermal doping of polyaniline with dodecylbenzene sulfonic acid without auxiliary solvents. *Polymer* 36, 2733–2738.
- Liang, M., Jia, S., Zhu, S., Guo, L.-H., 2008. Photoelectrochemical sensor for the rapid detection of in situ DNA damage induced by enzyme-catalyzed fenton reaction. *Environ. Sci. Technol.* 42, 635–639.
- Liu, H., Agarwal, M., Varahramyan, K., Berney, E.S., Hodo, W.D., 2008. Polymer-based microsensor for soil moisture measurement. *Sens. Actuators B* 129, 599–604.
- Lvov, Y.M., Yamada, S., Kunitake, T., 1997. Non-linear optical effects in layer-by-layer alternate films of polycations and an azobenzene-containing polyanion. *Thin Solid Films* 300, 107–112.
- Mattoso, L.H.C., Manohar, S.K., MacDiarmid, A.G., Epstein, A.J., 1995. Studies on the chemical syntheses and on the characteristics of polyaniline derivatives. *J. Polym. Sci. Part A: Polym. Chem.* 33, 1227–1234.
- Rahman, M.A., Kumar, P., Park, D.S., Shim, Y.B., 2008. Electrochemical sensors based on organic conjugated polymers. *Sensors* 8, 118–141.
- Semenyuk, A.V., Svergun, D.I., 1991. Gnom—a program package for small-angle scattering data-processing. *J. Appl. Cryst.* 24, 537–540.
- Suarez, M.F., Compton, R.G., 1999. In situ atomic force microscopy study of polypyrrole synthesis and the volume changes induced by oxidation and reduction of the polymer. *J. Electroanal. Chem.* 462, 211–221.
- Xing, Q., Eadula, S.R., Lvov, Y.M., 2007. Cellulose fiber-enzyme composites fabricated through layer-by-layer nanoassembly. *Biomacromolecules* 8, 1987–1991.
- Xu, L., Lio, A., Hu, J., Ogletree, D.F., Salmeron, M., 1998. Wetting and capillary phenomena of water on mica. *J. Phys. Chem. B* 102, 540–548.
- Zheng, W.-Y., Wang, R.-H., Levon, K., Rong, Z.Y., Taka, T., Pan, W., 1995. Self-assembly of the electroactive complexes of polyaniline and surfactant. *Macromol. Chem. Phys.* 196, 2443–2462.
- Yu, D.-G., Lin, W.C., Yang, M.C., 2007. Surface modification of poly(L-lactic acid) membrane via layer-by-layer assembly of silver nanoparticle-embedded polyelectrolyte multilayer. *Bioconjugate Chem.* 18, 1521–1529.
- Wei, Y., Hariharan, R., Patel, S.A., 1990. Chemical and electrochemical copolymerization of aniline with alkyl ring-substituted anilines. *Macromolecules* 23, 758–764.
- Wernet, W., Monkenbush, M., Wegner, G., 1984. A new series of conducting polymers with layered structure—polypyrrole normal-alkylsulfates and normal-alkylsulfonates. *Makromol. Chem. - Rapid. Commun.* 5, 157–164.