



## Thin films of amphiphilic polyelectrolytes. Soft materials characterized by Kelvin probe force microscopy



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### ABSTRACT

Hydrophobically modified amphiphilic polyelectrolyte films derived from poly (maleic anhydride-*alt*-styrene) containing hydrophobic aryl-alkyl type side chains such as phenyl-ethyl, phenyl-butyl, naphthyl-ethyl and naphthyl-butyl were studied by Kelvin probe force microscopy. These films were adsorbed from polyelectrolyte solutions at 0.001 mol/L and 0.1 mol/L NaCl onto silicon wafers modified with 3-aminopropyltrimethoxysilane. At high ionic strength, the work function was dependent on the hydrophobic character of the side chain. At low ionic strength this behavior was determined by the spacer group in the side chain. The fractal analysis of the films indicated self-affinity surfaces whereas the fractal dimensions of the surface topography follow a similar trend as the electronic work function with the ionic strength. This behavior can be explained by the increasing hydrophobic character of the side chain with naphthyl moieties. Relationship between the molecular structure and the fractal dimensions with the work function of the adsorbed polyelectrolytes was found.

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### 1. Introduction

The characterization of solid surfaces modified with polyelectrolytes and other macromolecules is relevant in order to understand how the chemical structure determines the film properties at molecular level. It is particularly interesting in different fields such as engineering and biology among others. Thus, the adsorbed hydrophobically modified polyelectrolytes onto solid substrates allows obtaining thin films with different functional groups that can be envisaged as a valuable tool to control the nature of the surface [1,2]. The presence of charged functional groups regulates the specificity of the modified solid substrate by means of electrostatic interactions. These functional characteristics and the surface properties are crucial for the designing of new advanced materials and technologies such as drug delivery systems, molecular containers, sensors, responsive materials, catalysts, miniaturized devices, lab-on-chip, micro fluidic technologies and surfaces and interfaces with antimicrobial activity [3–5].

Kelvin probe force microscopy, KPFM, is a very important technique that allows obtaining simultaneously at the nanoscale a surface morphology measure together with the electronic surface potential. It was introduced as a tool to measure the local contact potential difference between a conducting tip in the atomic force microscopy (AFM) and the sample, allowing mapping a work function or electronic surface potential of one sample with high spatial resolution [6]. Through KPFM, the electronic work functions of the surfaces can be observed at atomic or molecular scales relating many surface phenomena, including catalytic activity [7], surface reconstruction [8], doping and band-bending of semiconductors [9], charge trapping in dielectrics [10] and corrosion [11]. The map of the electronic work function produced by KPFM also gives information about the composition and electronic state of the local structures on the surface of a solid [12].

KPFM has been successfully employed to investigate various systems, including inorganic and organic thin films [13,14] as well as proteins [15] across multiple length scales from meso- to nanoscopic scale [16]. Recently, KPFM has also been used to study the electrical properties of biological materials [17]. The local electronic surface potential in a heterogeneous biomolecular film is a direct reflection of its molecular-level structure.

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High resolution, high sensitivity and performance in ambient conditions are required in order to study biologically relevant samples. Moores B. et al. [18] compared the resolution of frequency modulation (FM-KPFM), amplitude modulation (AM-KPFM), and lift modes KPFM for imaging the local electronic surface potential of complex biomolecular films demonstrating that FM-KPFM mode has superior resolution for biological applications. This method was illustrated on pulmonary-surfactant films, revealing nanometric spatial resolution and a potential sensitivity in the mV scale in air, allowing them to relate the structure and function of the biomolecular film *in vivo*. Recently, Finot E. et al. [17] studied by KPFM the changes in the electrical properties of the lipid-protein film of pulmonary surfactant (PS) produced by excess cholesterol. They found that the presence of nanometer-sized electrostatic domains affects the electrostatic interaction between the tip and PS film.

The influence of different experimental parameters on the interaction between the probe and the sample in KPFM measurements was studied by Liscio et al. [16]. They provided a precise and reproducible determination of the local electronic surface potential (SP) of clean macroscopic highly oriented pyrolytic graphite (HOPG) samples and of organic semiconducting nanostructures of an alkyl-substituted perylene-bis(dicarboximide) (PDI) self-assembled at surfaces. These authors also have applied a new model for the quantitative analysis of KPFM measurements of semiconducting nanofibers of poly(3-hexylthiophene) (P3HT) self-assembled on various flat substrates. They found that this model represents a useful tool to study with a high degree of precision the surface potential characteristics of nanowires paving the way towards their use as building blocks for the fabrication of electronic nanodevices with improved performance [19].

This kind of characterization opens new possibilities for the molecular characterization of surfaces modified with polyelectrolyte thin films. The fundamental principle of the surface modification with polyelectrolytes is the charge introduction onto surfaces. The characterization of polyelectrolyte thin films onto solid surface by Kelvin probe force microscopy has been scarcely used.

Guzman et al. [20] studied the influence of ionic strength on the growth of multilayers formed by the sodium salt of poly(4-styrenesulfonate), and poly(diallyldimethylammonium chloride). The charge inversion found in the multilayers was monitored by the electronic surface potential measured with a Kelvin probe, finding that the formation of the multilayers is driven by the overcompensation of charge at the multilayer surface. From a macroscopic point of view, the multilayer is electrically neutral which it can be achieved by two different mechanisms.

In this context, the aim of this work was to characterize by KPFM measurements hydrophobically modified amphiphilic polyelectrolyte thin films derived from poly(maleic anhydride-*alt*-styrene), containing aryl-alkyl-type side chains, such as phenylethyl, phenylbutyl, naphthylethyl, and naphthylbutyl adsorbed on the surface of silicon wafers modified with 3-aminopropyltrimethoxysilane. The values of electronic work function of adsorbed polyelectrolyte thin films were analyzed in terms of the nature of aryl-alkyl group present in the side chain of polyelectrolyte and the ionic strength.

## 2. Experimental part

### 2.1. Materials

Poly(maleic anhydride-*alt*-styrene), P(MA-*alt*-St) was synthesized by free radical polymerization. These copolymers were functionalized with 2-phenyl-1-ethyl, 4-phenyl-1-butyl, 2-naphthyl-1-ethyl and 4-naphthyl-1-butyl groups, by refluxing with the respective aromatic alcohol in acetonitrile/THF (80/20)

using 4-dimethylaminopyridine (4DMAP) as a catalyst for the reaction. The functionalization of P(MA-*alt*-St) was considered completed when in the IR spectra of copolymer the absorption band at  $\sim 1650\text{ cm}^{-1}$  due to the ester carbonyl group appeared instead of 1854 and  $1779\text{ cm}^{-1}$  bands due to maleic anhydride carbonyl group. Further evidence of the completed functionalization ( $\sim 98\%$ ) was obtained from  $^{13}\text{C}$  NMR spectroscopy (400 MHz, DMSO). These spectra showed that signals at 172.0–173.1 ppm corresponding to carbon atom of maleic anhydride carbonyl group disappeared and the characteristic signal of the carboxylic acid group at 178.0 ppm and that of the carbon atom of the carbonyl ester appeared at 167 ppm [21].

The sodium salts were obtained by treating the functionalized copolymers with 10% w/v  $\text{NaHCO}_3$  during ten days. The resulting solutions were ultrafiltered and finally lyophilized. Polyelectrolyte samples were coded as PC<sub>2</sub>Ph, PC<sub>4</sub>Ph, PC<sub>2</sub>N, and PC<sub>4</sub>N. The corresponding chemical structures are shown in Scheme 1.

Samples were prepared by dissolving the polyelectrolyte in deionized water containing 0.001 mol/L or 0.1 mol/L NaCl at pH 4. The pH was adjusted by adding diluted HCl. The copolymer concentration was 1.0 g/L. Si/SiO<sub>2</sub> substrates, purchased from Silicon Quest, USA ([100], p-doped,  $R = 0.01\ \Omega\text{ cm}$ ) were cleaned by using a standard procedure [22]. The surfaces were functionalized with 3-aminopropyltrimethoxysilane (APS) (Aldrich), following a method described elsewhere [22]. Finally, the substrates were immersed in solutions of polyelectrolytes for 3 h, time in which the amount of adsorbed polyelectrolyte reaches a plateau, indicating the equilibrium conditions of the adsorption process and dried with N<sub>2</sub> [21]. All substrates were ca.  $10 \times 10\text{ mm}^2$  in area.

### 2.2. Methods

#### 2.2.1. Atomic force microscopy

Intermittent contact AFM topographical and KPFM images were simultaneously recorded by using a Dimension 3100 Nanoscope IV SPM system from Digital Instruments-Veeco-Bruker. The measurements were carried out under atmospheric conditions at room temperature with scan rates of 1.0 Hz line. Scan sizes spanning from 5.0 down to  $1.0\ \mu\text{m}^2$  were explored, with a resolution of  $256 \times 256$  pixels using Budget Sensors ElectriMulti-75 conductive silicon probes, Pt/Cr coated, with a spring constant of 3.0 N/m and with a tip curvature radius of lower than 25 nm. KPFM measurements were carried out in lift mode: each line was scanned twice, first to measure the topography in tapping mode and second to measure the electrostatic potential at a predefined lift height of 80 nm. Several values of lift-height were evaluated in the range from 10 to 100 nm, being 80 nm a safe height for avoiding the tip-sample contact in the lift mode. It is important to choose a lift height in which the cantilever can move freely during the lift cycle. Otherwise topographic feature will contribute to the surface potential image [23].

For KPFM measurements, an Au film was used as a reference sample and a thick film of TiN was used to clean the probe after each scanning on a polymeric film. To obtain the electronic work function value of each sample, the value of  $\varphi_{\text{Au}} = 5.3\text{ eV}$  for the electronic surface potential for Au was assumed [24] and the value of the electronic surface potential for the tip was calculated,  $\varphi_{\text{Tip}} = 5.4\text{ eV}$ . The value obtained for each sample corresponds to  $5.0 \times 5.0\ \mu\text{m}^2$  surface by using the Gwyddion program [25].

## 3. Results and discussion

We recently reported the adsorption of hydrophobically modified polyelectrolytes derived from poly(maleic anhydride-*alt*-styrene) (P(MA-*alt*-St)) containing aryl-alkyl groups in their side chain

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