



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 cm^{-1} bands due to maleic anhydride carbonyl group. Further evidence of the completed functionalization ($\sim 98\%$) was obtained from ^{13}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 NaHCO_3 during ten days. The resulting solutions were ultrafiltered and finally lyophilized. Polyelectrolyte samples were coded as PC₂Ph, PC₄Ph, PC₂N, and PC₄N. 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/SiO₂ 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 N₂ [21]. All substrates were ca. $10 \times 10\text{ mm}^2$ in area.

2.2. Methods

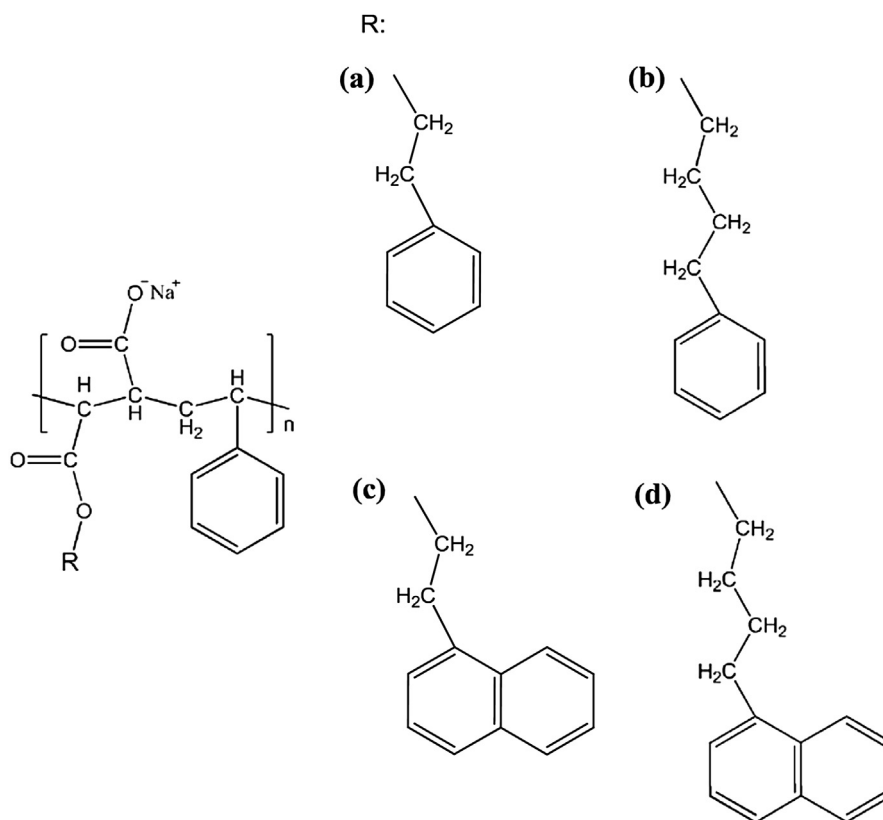
2.2.1. Atomic force microscopy

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 256×256 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



Scheme 1. Hydrophobically modified polyelectrolytes: (a) PC₂Ph, (b) PC₄Ph, (c) PC₂N and (d) PC₄N.

on silicon wafers modified with 3-aminopropyltrimethoxysilane (APS) [21]. The effect of the spacer group, the chemical nature of the side chain, molecular weight of polyelectrolyte, and ionic strength of solution on the amount of adsorbed polyelectrolyte was studied by ellipsometry. We found that the amount of adsorbed polyelectrolyte increased with increasing ionic strength, in agreement with the screening-enhanced adsorption regime described by Van de Steeg et al. [26]. Interactions between polymeric segments and silicon wafer surface modified with 3-aminopropyltrimethoxysilane are not predominantly electrostatic in nature, favoring van der Waals, H-bonding, cation- π and hydrophobic interactions. These interactions compete with electrostatic interaction between charged segments of polyelectrolytes and the surface. Moreover, at constant ionic strength, the adsorbed amount is slightly higher for polyelectrolytes with butyl spacer group and decrease with the hydrophobicity of aryl group. This effect was attributed to the increasing chain flexibility as the length of the spacer group increased. Thin films were also characterized by contact angle measurements as was reported in our previous work [21]. These results reflected a high chemical heterogeneity and a moderate hydrophobicity of polyelectrolyte films, indicating that the polymer chains are adsorbed on silicon wafer surfaces modified with APS with the hydrophobic groups of the main chain, carboxylates, and aryl-alkyl groups of side chain exposed to air. This gives to the polyelectrolyte films a combination of hydrophilic/hydrophobic character, namely, chemical heterogeneity reflected in the high hysteresis values reported [21].

On the other hand, AFM images obtained in tapping mode show the presence of aggregates and a closed globular structure of polyelectrolyte adsorbed on the surface of silicon wafer modified with APS which agrees with a 3D growth mechanism [21].

In this study polymer thin film were characterized by Kelvin probe force microscopy (KPFM) in order to elucidate how the

chemical structure of polyelectrolyte adsorbed on these surfaces determines the properties of adsorbed polyelectrolytes thin films. This technique determines the electric surface potential and consequently the work function of the surfaces at atomic or molecular scale. Also the fractal dimensions are obtained from the surface morphology on a nanometer scale.

Fig. 1a and b shows the images of AFM topography of PC₂Ph films at ionic strength values of 0.001 mol/L and 0.1 mol/L NaCl. These results were obtained by the intermittent contact mode (tapping mode), where polyelectrolyte aggregates and free regions are observed. The influence of ionic strength on the size of the aggregates is notorious. In fact, aggregates are densely packed and distributed heterogeneously on the surface silicon wafer modified with 3-aminopropyltrimethoxysilane. PC₂Ph, PC₄Ph, PC₂N and PC₄N films show similar behavior.

Fig. 2 shows images of KPFM topography for PC₂Ph (2a), PC₄N (2c) and surface potential difference $\varphi_{\text{sample}} - \varphi_{\text{Tip}}$ for PC₂Ph (2b) and PC₄N (2d) films with NaCl 0.001 mol/L and Fig. 3 shows images of KPFM topography for PC₂Ph (3a) and PC₄N (3c) and surface potential difference $\varphi_{\text{sample}} - \varphi_{\text{Tip}}$ for PC₂Ph (3b) and PC₄N (3d) films with NaCl 0.1 mol/L adsorbed onto Si/SiO₂ substrates modified with 3-aminopropyltrimethoxysilane.

The images show that the adsorbed layers have a globular morphology, with an average aggregate sizes summarized in Table 1. The average aggregate size of the globules appearing in each image was determined by a threshold method included in the Gwyddion program. This method is an algorithm to define particles by means of a height threshold marking. After the topography points of the particles with height higher than 15 nm are marked, a statistical procedure allowed obtaining some parameters such as number of aggregates, mean aggregate area and mean aggregate size. The threshold value was arbitrarily selected as 15 nm in order to quantify as aggregates the regions with heights higher than this

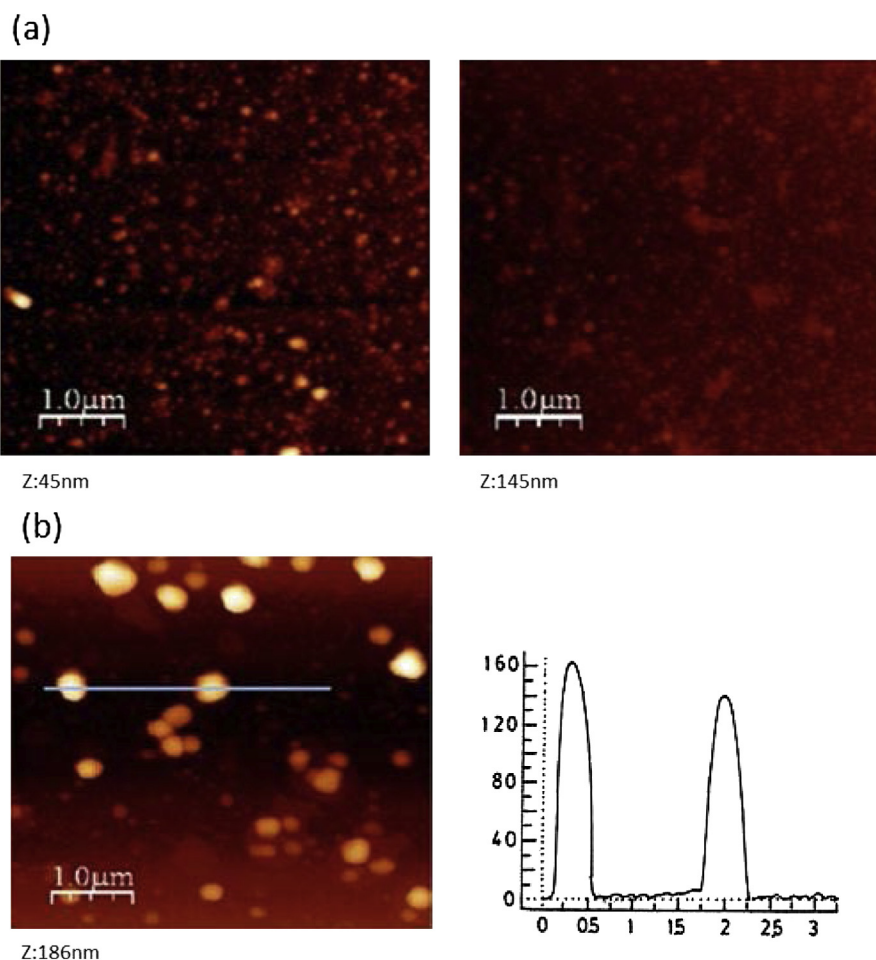


Fig. 1. Images of AFM topography for PC₂Ph films for NaCl concentration of (a) 0.001 mol/L and (b) 0.1 mol/L.

value, considering the surface free of aggregates has topography lower than 15 nm.

Considering the error associated, the average aggregate sizes are practically constant as the NaCl concentration is increased from 0.001 mol/L to 0.1 mol/L. For PC₂Ph and PC₄N samples the aggregate size values are smaller than 100 nm, but the error increases from about 10% to values greater than 20% compared with the average values. It can be observed that the increase of NaCl concentration introduces topographic disorder, where large aggregates are formed on the surface. Thus, in this case, the surface induces the aggregation process at high ionic strength. These polyelectrolytes form aggregates in aqueous solution, which are in equilibrium with free chains. At high ionic strength, the adsorption of chains in loop and tail is favored. The ionic strength not only screens the charged segments of the polyelectrolyte but also the surface charged sites, favoring intra- and inter-molecular hydrophobic interactions. Therefore, the first layer of polyelectrolyte would attract other free polyelectrolytes chains, followed by a cooperative process, generating nucleation sites on the surface for the aggregates growth or for the adsorption of aggregates formed in the solution.

On the other hand, it is well known that the adsorption process is determined by a balance between enthalpy and entropy of the system. The enthalpy of the adsorption process involves some water desolvation of the “icelike” water structure around the polyelectrolyte non-polar moieties. This process is endothermic involving small values of enthalpy. The adsorption of polyelectrolytes, in turn, is an exothermic process where hydrophobic

interactions predominate with low enthalpy values. Therefore, the total enthalpy of the process is very small or nearly zero. Thus, the adsorption process should be determined by the entropy. As stated, water desolvation of the non-polar polyelectrolyte residues occurs in solution, resulting in entropy increase. Consequently, the adsorption of a disordered polyelectrolyte at the surface, as compared with their ordered conformation in solution, results also in a gain of entropy for the adsorption process.

Fig. 4 shows the images of AFM topography for PC₂N films obtained at ionic strength value of 0.1 mol/L NaCl. In Fig. 4a the straight line is related with the profile curve in Fig. 4b, where the 15 nm height threshold used for calculating the aggregate size is shown as a horizontal line in Fig. 4b. The average roughness is obtained from the root mean square, rms, of the topography height of the samples and their values are shown in Table 2.

Table 2 shows the rms values, work function, fractal dimensions and hysteresis of polyelectrolyte thin films studied. The electronic work function (φ) values of the polyelectrolyte films follow the decreasing sequence PC₂Ph > PC₄Ph > PC₄N > PC₂N at 0.001 mol/L of NaCl concentration. The sequence found for the values of work function for each polyelectrolyte at low ionic strength is determined by increasing the hydrophobic character of naphthyl-alkyl group in the side chain. This behavior can be explained in terms of greater steric hindrance of the naphthyl group, resulting in a surface modified with a macromolecule densely packed. This agrees with the lowest rms values obtained at low ionic strength compared with values at high ionic strength.

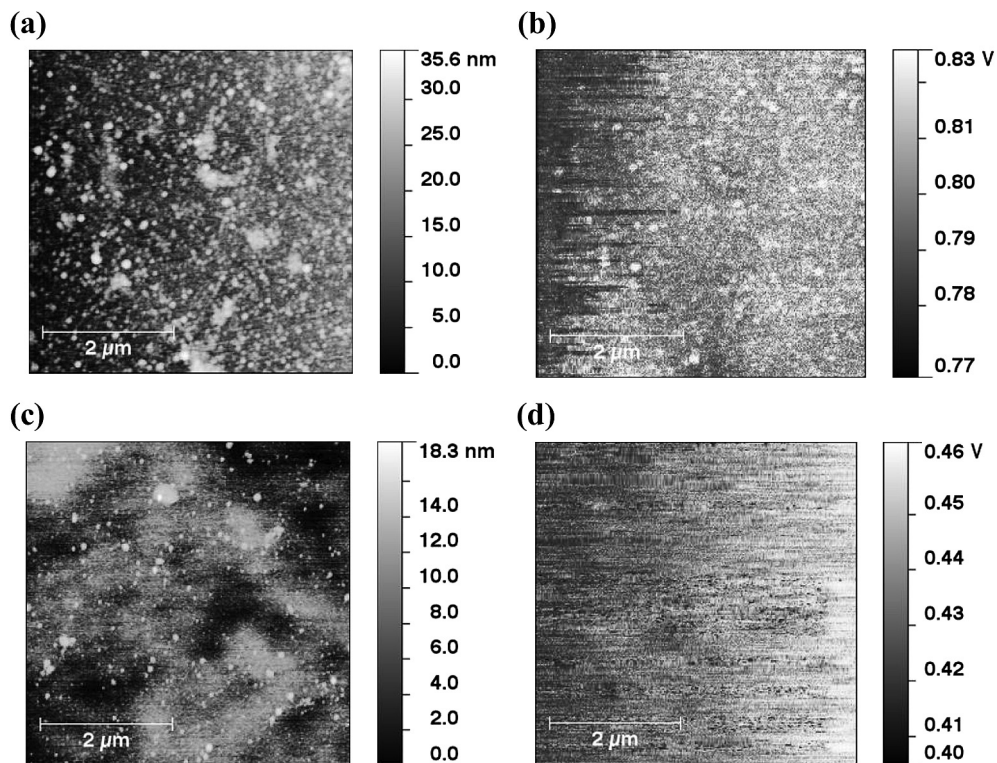


Fig. 2. Images of AFM topography for (a) PC₂Ph and (c) PC₄N and surface potential difference $\varphi_{\text{sample}} - \varphi_{\text{Tip}}$ for (b) PC₂Ph and (d) PC₄N films with NaCl 0.001 mol/L.

On the other hand, for the same deposited polyelectrolytes from an aqueous solution at high ionic strength (0.1 mol/L of NaCl), the order of the films, considering the work function values, is PC₂N > PC₂Ph > PC₄N > PC₄Ph. This behavior is determined by the

spacer group of the side chain of the polyelectrolyte. The flexibility of the side chain groups increases by increasing the length of the spacer group, facilitating molecular rearrangement on the surface. This is in agreement with the rms values found for polyelectrolyte

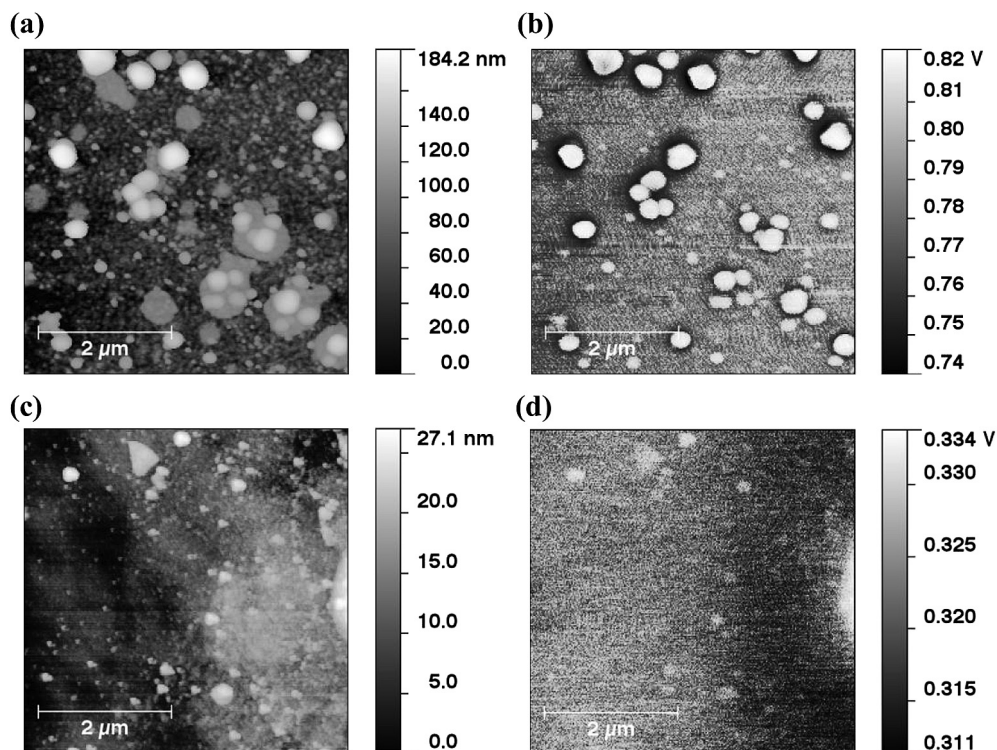


Fig. 3. Images of AFM topography for (a) PC₂Ph and (c) PC₄N and surface potential difference $\varphi_{\text{sample}} - \varphi_{\text{Tip}}$ for (b) PC₂Ph and (d) PC₄N films with NaCl 0.1 mol/L.

Table 1
Average aggregate size of the studied samples.

Polyelectrolytes	Average aggregate size (nm)	
	0.001 mol/L NaCl	0.1 mol/L NaCl
PC ₂ Ph	57 ± 6	72 ± 17
PC ₄ Ph	135 ± 21	112 ± 30
PC ₂ N	113 ± 37	180 ± 102
PC ₄ N	42 ± 3	51 ± 11

Table 2

Root mean square of the topography height (rms), electronic work functions (ϕ), fractal dimension (D_f) and hysteresis in the contact angle ($\Delta\theta$) for the studied samples. The resonance frequency of the probes was in the range from 65.69 to 66.15 kHz.

NaCl (mol/L)	Polyelectrolytes	rms (nm)	ϕ (eV)	D_f	$\Delta\theta^a$ (°)
0.001	PC ₂ Ph	3.00 ± 0.3	6.28 ± 0.02	2.38 ± 0.04	27 ± 3
	PC ₄ Ph	13.1 ± 0.9	6.00 ± 0.01	2.29 ± 0.03	30 ± 4
	PC ₂ N	2.50 ± 0.3	5.58 ± 0.04	2.20 ± 0.04	28 ± 3
	PC ₄ N	1.40 ± 0.2	5.75 ± 0.01	2.21 ± 0.02	28 ± 3
0.1	PC ₂ Ph	36.4 ± 3.2	5.77 ± 0.05	2.20 ± 0.03	31 ± 3
	PC ₄ Ph	27.3 ± 2.4	5.60 ± 0.01	2.20 ± 0.03	27 ± 3
	PC ₂ N	3.20 ± 0.3	6.10 ± 0.02	2.30 ± 0.02	25 ± 3
	PC ₄ N	18.2 ± 1.8	5.73 ± 0.01	2.20 ± 0.02	25 ± 4

^a Ref. [21].

containing phenyl group, but not for that containing naphthyl group. In this case there would be a competition between flexibility and steric hindrance of the macromolecule in the adsorption process. Each polyelectrolyte film shows a different behavior for the electronic work function and roughness as the NaCl concentration increases. There is not a correlation between electronic work function and surface topography represented by the roughness. This could be a consequence of the surface chemical heterogeneity found for each adsorbed polyelectrolyte film, as shown by the hysteresis values determined from contact angle measurements (Table 2). Regarding the correlation between ϕ and D_f , it is observed that these values show the same tendency at low ionic strength. However, at high ionic strength ϕ values show variations, whereas the corresponding values of D_f are similar. This can be explained in terms of the shielding effect of the salt on the charged groups of the polyelectrolyte adsorbed on the surface. Therefore, from a microscopic point of view the modified surface is electrically neutral [20].

Considering the disorder of the surfaces, several authors have given attention to the AFM topography images. It is often assumed that AFM topography images exhibit fractal properties. Fractal analysis has proved to be useful to extract much information from measured textures respect to the conventional AFM analysis, so that this technique is very useful in order to describe surface characteristics of thin films. Several studies have indicated that the complexity of thin film morphology are fractal in nature and can be characterized quantitatively by the fractal dimensions [27,28]. Some methods have been used to characterize fractals, which can be classified as physical, chemical and electrochemical [29]. Concepts such as self-similarity and self-affinity are used in describing rough surfaces. Self-similarity refers to fractal objects that are exactly or approximately magnified in all directions. Self-affinity is a fractal concept where the pieces are scaled by different amounts in all directions of the surface.

The scaling properties of rough surfaces have been studied extensively, including surface growth simulations by means of continuum equations. The simulations for self-affinity surfaces

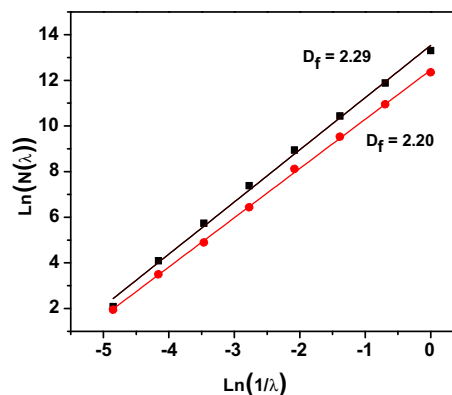


Fig. 5. Plots of $\ln(N(\lambda))$ vs. $\ln(1/\lambda)$ obtained by the fractal analysis method called the cubic counting method. AFM images of PC₄Ph film for two NaCl concentrations: (■) 0.001 mol/L and (●) 0.1 mol/L. The slope of the linear fitting corresponds to the fractal dimension (D_f).

have fractal dimension values in the range from 2 to 3 units. Surfaces of thin films prepared by different procedures can be measured by AFM and classified by fractal analysis [30,31]. Several methods have been developed to perform the fractal analysis including: cube counting method [32], triangulation method [33], variance method and power spectrum method [34]. With the purpose of obtaining a fractal analysis of the AFM topographic measurements, we applied the cube counting method by using the facilities given by the Gwyddion program. This method was derived directly from a definition of box-counting fractal dimension, and is

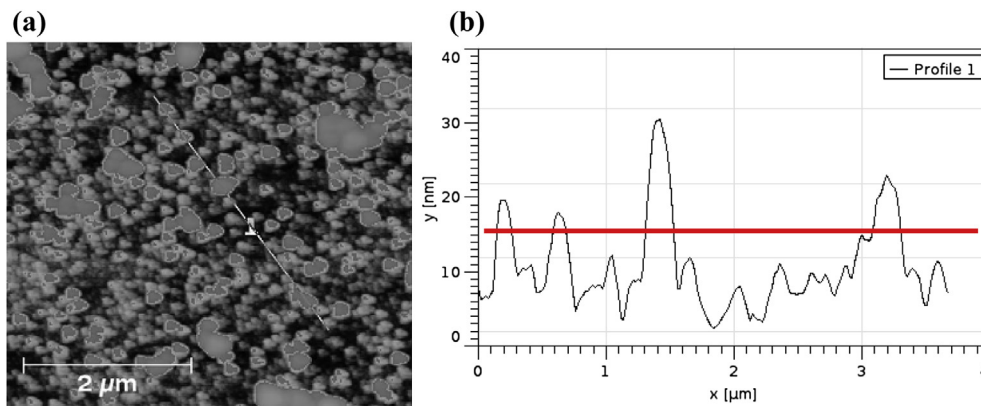


Fig. 4. (a) Images of AFM topography for PC₂N films with 0.1 mol/L NaCl. (b) The line is related with the profile curve.

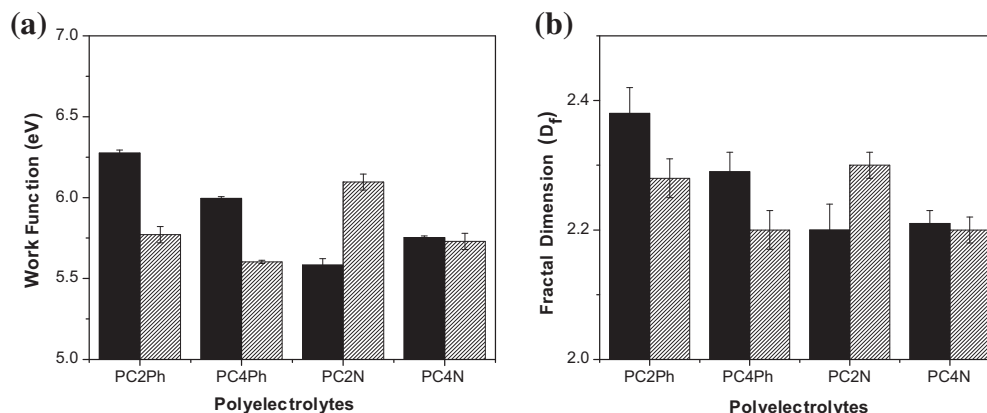


Fig. 6. Plots of average values of (a) work function and (b) fractal dimension (D_f) for 0.001 mol/L NaCl (■) and 0.1 mol/L NaCl (▨) concentration for PC₂Ph, PC₄Ph, PC₂N and PC₄N.

described in the manual of Gwyddion program [25]. The slope of a plot of $\ln(N(\lambda))$ versus $\ln(1/\lambda)$ gives the fractal dimension D_f directly, where $N(\lambda)$ is the number of all cubes that contain at least one pixel of the image and λ is the size of the cube or lattice constant. The value of λ is reduced stepwise by factor of 2 and the process repeated until λ is equal to the distance between two adjacent pixels. A fractal analysis of the AFM topographic images is shown in Fig. 5, where plots of $\ln(N(\lambda))$ vs. $\ln(1/\lambda)$ were obtained by the cubic counting method for PC₄Ph film at two NaCl concentrations of 0.001 mol/L and 0.1 mol/L. In this image the slope of the linear fitting corresponds to the fractal dimension D_f . The D_f values obtained for PC₂Ph, PC₄Ph, PC₂N and PC₄N films with NaCl 0.001 mol/L and 0.1 mol/L are listed in Table 2. The values of D_f are in the range from 2 to 3 unit, which indicates a fractal behavior of the films as self-affinity surfaces. These results also agree with a 3D growth mechanism proposed [21]. These features are in agreement with the scaling theory proposed by Dobrynin and Rubinstein [35].

Fig. 6 shows plots of average values of (a) electronic work function and (b) fractal dimension (D_f) for 0.001 mol/L and 0.1 mol/L NaCl for all the polyelectrolytes studied. It can be observed that the fractal behavior of the surfaces of the polyelectrolyte films show correlation with the behavior of the respective electronic work

function. Thus, for PC₂Ph and PC₄Ph film their work function and fractal dimension decrease when the NaCl concentration increases from 0.001 mol/L to 0.1 mol/L. While for PC₂N film the work function and fractal dimension increase and for PC₄N film there is no change of values. In fact, as the ionic strength increases the fractal dimensions and the work function decreases for the polyelectrolyte containing phenyl moiety indicating that the spacer group is responsible for the flexibility of the main polymer chain and at the same time affects the fractal dimension and the work function. On the other hand, for the polyelectrolytes with naphthyl moiety, the behavior is determined by their higher hydrophobic nature.

A coarse linear correlation between fractal dimension (D_f) and the work function of the polyelectrolytes is shown in Fig. 7.

This plot indicates that the electronic work function (ϕ) increases with fractal dimension (D_f), independent of NaCl concentration. Moreover, the plot reveals that there exists a relationship between the molecular structure and the fractal dimensions with the work function of the adsorbed polyelectrolytes. Therefore, this dependence can be attributed to an increasing hydrophobic character of the side chain, mainly with the naphthyl moieties.

4. Conclusions

The value of the work function at low salt concentration depends mainly on the nature of the spacer group, ethyl or butyl, in the side chain of the polyelectrolyte while at high salt concentration, the electronic work function of the PC₂Ph, PC₄Ph, PC₂N and PC₄N films were dependent on the hydrophobic character of the aryl group; phenyl or naphthyl. The value of the work function decreases slightly as the ionic strength of the polyelectrolyte solution increases. On the other hand, the roughness, determined by the formation of aggregates, shows values higher than 3.5 nm for most of the samples. PC₄Ph and PC₄N show higher roughness with an increase in the fraction of the aggregate areas as the ionic strength increases.

The results show no correlation between the values of the work function and roughness of the studied films due to their complex morphology and the fractal nature of the surface determined by the chemical heterogeneity and their high hysteresis values.

The fractal analysis of the films indicated a behavior of self-affinity surfaces and the fractal dimensions of the surface topography follow a similar trend for the electronic work functions with the ionic strength. This dependence can be attributed to an increasing hydrophobic character of the side chain, mainly with the

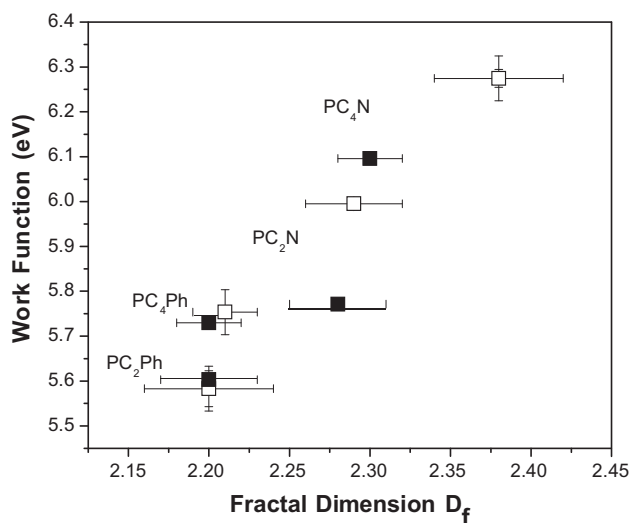


Fig. 7. Correlation between work function and fractal dimension (D_f) for PC₂Ph, PC₄Ph, PC₂N and PC₄N polyelectrolytes with (□) 0.001 mol/L and (■) 0.1 mol/L NaCl concentration.

naphthyl moieties. Therefore, there exists a relationship between the molecular structure and the fractal dimensions with the work function of the adsorbed polyelectrolytes as thin films on solid surfaces.

We can conclude that the electronic work function measured by KPFM is a useful property in order to detect structural modifications of surfaces modified by polyelectrolytes. The determination of fractal dimension of the surface topography is a good method of analysis of adsorbed polyelectrolyte thin films, particularly when the roughness does not give clear evidence of the observed surface morphology.

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