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Counterions – A new approach to control the degree of ionization of polyelectrolytes in layer-by-layer films

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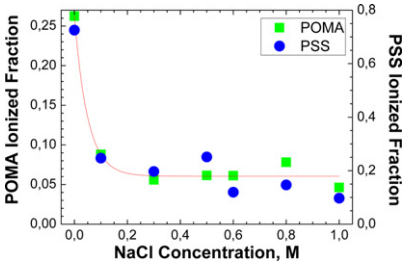
HIGHLIGHTS

- The degree of ionization in weak and strong polyelectrolytes is controlled by salt.
- The amount of counterions/co-ions in the films increases with NaCl concentration.
- Nanocrystals are being formed with ions which are not compensating the ionic groups.
- Some Cl atoms are being used in an extra chlorination chemical reaction with POMA.
- The water molecules retained in the films decrease with the salt concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

The atomic composition of layer-by-layer (LbL) films of the conductive polyelectrolyte poly(o-methoxyaniline) (POMA) alternated with the strong polyelectrolyte poly(styrene sulfonate) (PSS) was obtained from X-ray photoelectron spectroscopy (XPS), in order to study the influence of sodium chloride concentration of PSS aqueous solutions on the degree of ionization of polyelectrolytes in the film structure. The results revealed that the degree of ionization for both weak and strong polyelectrolytes decreases with NaCl concentration while the relative amount of counterions/co-ions increases. A larger number of ions, in comparison with the number of polylectrolytes ionic groups, indicate the formation of NaCl nanocrystals in the LbL film. However, results showed that some Cl atoms are being used in an extra chlorination chemical reaction with POMA. The number of water molecules retained in the films decreases with salt at a rate lower than that of the degree of ionization indicating that water molecules are close to salt ions. Moreover, the ratio water molecules per sodium assumes a value of 4 for films prepared without salt, which is the typical hydration number value for NaCl in solution, and decreases linearly with salt concentration pointing out to nanocrystals increase in size with salt concentration.

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1. Introduction

The buildup of layer-by-layer (LbL) films [1–8] and their properties are highly influenced by the degree of ionization of polyelectrolytes used for film preparation. This is because the driving force for polyelectrolyte adsorption from solution is mainly coming from the electrostatic interactions between polyelectrolytes

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opposite charged groups. However, once each layer in a LbL film results from adsorption onto the solid support from polyelectrolyte aqueous solutions, where the polyelectrolyte ionic groups are being compensated by counterions, some of these counterions may also be brought to the LbL film during polyelectrolyte adsorption. Therefore, film cohesion will depend, on the number of anchors established as a result of charge compensation between polyelectrolyte opposite charged groups. Thus the presence of counterions in the LbL film modifies the polyelectrolyte adsorbed amounts, the polyelectrolyte layer morphology and, consequently, the LbL film properties.

Concerning the role of both counterions and added salt to polyelectrolyte aqueous solutions in the formation of polyelectrolyte multilayers prepared by the LbL technique, several studies have been carried out with respect to the number of incorporated ions in the films and its influence in the morphology [9–13]. The relative amount of counterions near polyelectrolyte ionic groups in LbL films of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) has already been investigated in a previous work [14]. As a result, the presence of counterions has been attributed to the Manning condensation near the polyelectrolyte ionic groups, which gives rise to ionic networks through the formation of interpolyelectrolyte ionic bonds [14]. In addition, condensation was shown to lead to the formation of NaCl nanocrystallites in the LbL films, as confirmed by X-ray diffraction measurements [15]. The film drying procedure was also seen to influence the amount of counterions in the film: smaller amounts of counterions were observed in films dried after adsorption of each layer, when compared to those that were never dried during preparation. This behavior was attributed to the formation of NaCl nanocrystals during the drying process, which dissolved when the film was again immersed in the next polyelectrolyte solution. Another important issue to be remarked, concerns to the presence of water molecules in the LbL films and the role they play in the interaction processes with polyelectrolyte ionic groups. The presence of bound water molecules suggests that the counterions near the ionic groups are immersed in a water network [14]. It has also been proved that for wet samples, samples which were only dried when all layers had been adsorbed, the increase in salt concentration led to a decrease of the number of PAH ionized groups. This behavior is predicted in Muthukumar theory [16], which takes into consideration the counterion condensation on flexible polyelectrolytes. However, PAH is a weak polyelectrolyte and so far this behavior has not been shown experimentally for strong polyelectrolytes such as PSS.

One of the physical properties which are related with the degree of ionization is the electrical conductivity of polyanilines. Their conductivity is known to decrease as the degree of ionization decreases which is usually associated to pH increase. One of the polyanilines, poly(o-methoxyaniline) (POMA) is a water soluble polyaniline that can be found either in the emeraldine salt conductive form or emeraldine base, Fig. 1a and b. In the emeraldine salt form, POMA presents counterions, usually chloride ions, close to the nitrogen ionic groups. Under these conditions POMA is in the doped/conductive form, thence, with localized bounding states stabilized by the presence of counterions [17,18], and can be easily processed in thin film form via the LbL technique to build molecular heterostructures [19,20], with composition and consequently featured properties dependent on the polyelectrolyte solutions preparation conditions. POMA solubility decreases when the solution ionic strength increases, meaning that the presence of ions is influencing its molecular structure and morphology and, consequently, its physical properties, namely, electrical conductivity. For example, the morphologic structure of a POMA layer adsorbed onto a PSS polyelectrolyte cushion prepared with salt was characterized by neutron reflectivity technique, revealing that the POMA layer thickness is about 1.5 nm while the surface roughness in aqueous media is 3.6 nm which is similar to the roughness of PSS cushion [21]. A rough stratified layer gives from external point of view the general idea of interpenetration which is in accordance with Guzmán et al. results [22], but it is not expected that both POMA and PSS polyelectrolytes are homogenously mixed. In addition, it has been also demonstrated that POMA/PSS LbL films conductivity is dependent of the salt of PSS aqueous solutions used in the preparation of LbL films being this dependence associated to disorder created by an increase of roughness due to presence of salt ions [23].

In this work, the atomic composition of POMA/PSS LbL films prepared from PSS aqueous solutions with different salt concentrations was analysed by X-ray photoelectron spectroscopy (XPS) in order to study the influence of the PSS aqueous solutions salt concentration on POMA and PSS electrical charge degrees, relative amount of counterions and relative number of water molecules retained in these films under high vacuum conditions.

2. Materials and methods

LbL films of poly(o-methoxyaniline) (POMA) and poly(styrene sulfonate) (PSS), chemical structures shown in Fig. 1, were prepared from polyelectrolyte aqueous solutions with the PSS solutions having different ionic strengths. This is so, because POMA is only soluble in acidic aqueous solutions without salt. The films were adsorbed onto aluminium substrates for XPS measurements. POMA was synthesized using o-anisidine monomer from Aldrich, in accordance with the methodology described in Ref. [19]. Aqueous solutions were obtained by dissolving POMA in acetonitrile and subsequently in pure water (acetonitrile/water-1/49 (v/v)). Aqueous solutions (10^{-2} M) of the opposite charged polyelectrolyte PSS, obtained from Aldrich, were prepared by dissolving it in deionized water with a resistivity of 18.2 MΩ cm (Milli-Q, Millipore GmbH). Sodium chloride salt was added to PSS solutions to achieve solutions with different salt concentrations. For the sake of simplification, from now on, when salt concentration is mentioned, it refers to the PSS solutions salt concentration. The final pH of POMA and PSS aqueous solutions was adjusted to 3 by adding a 1.0 M HCl solution. The pH measurements were performed with Eco Scan pH 516 mV Meter Eutech Instruments. The LbL films were built according to the following procedure: (a) the substrate was immersed in the cationic polyelectrolyte solution for 3 min, for a layer of POMA to be adsorbed, this adsorption period of time was chosen in accordance with POMA adsorption onto LbL films kinetic curves obtained in [19]; (b) the substrate was rinsed with a HCl aqueous solution with pH 3; (c) the substrate was immersed in the PSS anionic polyelectrolyte for 3 min [24]; and (d) the substrate was rinsed in a pH 3 HCl aqueous solution. This procedure was repeated the number of times required to obtain the intended number of bilayers: eight times for XPS measurements and twenty for profilometry thickness measurements. Films were maintained always wet during the preparation procedure and were dried only after the adsorption of all bilayers with nitrogen flux. This procedure was used in order to obtain a high amount of salt ions retained in the LbL film, according the conclusions drawn in Ref. [14]. Following the nomenclature of [14], the films prepared here can be designated as “wet” films.

The composition of POMA LbL films was analyzed in an X-ray photoelectron spectrometer XSAM800 (Kratos) operating in the fixed analyzer transmission (FAT) mode [25], with a pass energy of 10 eV, a power of 130 W and the non-monochromatized MgKα X-ray ($h\nu$ = 1253.7 eV). All the samples were analyzed on the central part of the sample, i.e., over a $1 \times 3\ mm^2$ spot area at 0° angle relative to the sample surface normal, using the High Magnification mode. The sample prepared without salt was analyzed at two different ejection angles: 0° and 60° relative to the surface normal (see

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