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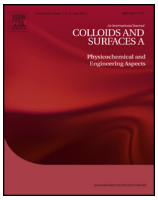

Influence of the formulation pathway on the growth of polyelectrolyte multilayer films

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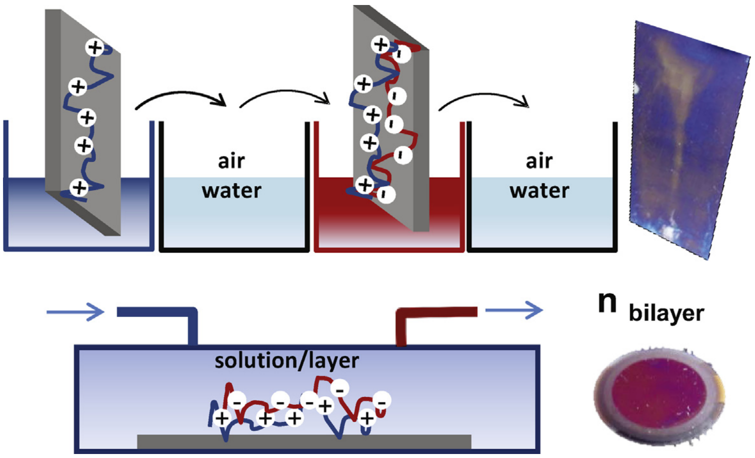
HIGHLIGHTS

- The way to adjust the pH of a PE solution can influence the morphology of the growing LbL film.
- Numerous transfers through the air/water interface during a LbL deposition can impact the multilayer morphology due to dewetting.
- Preliminary desalting transition tests performed on the studied PEs can avoid working at a ionic strength where the growth is reduced or inhibited.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the most important objectives in the fabrication of polyelectrolytes (PEs) multilayers is a fine control of the thickness and/or morphology of the resulting films intimately connected to the final properties. The formulation pathway should then be fully under control, a feature rarely studied in the literature. In this work, we put forward on the well-studied poly(acrylic)/poly(diallyldimethylammonium) system, that the formulation route followed during the multilayer fabrication is responsible for some of the observed inconsistencies. In particular, we show that (i) the way to adjust the pH of the different dispersions can influence the state of complexation/aggregation of the oppositely charged components, (ii) the numerous transfers through the air/water interface during a standard LbL sequential adsorption can influence the overall assembly process especially for hydrophobic PEs and more generally that (iii) working conditions close to the ionic strength of the bulk desalting transition of the polyelectrolyte pair can significantly alter the growth mechanism during the multilayer build-up.

1. Introduction

Over the past two decades, an extensive body of work has been devoted to the generation of smart functional surfaces. Vari-

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ous deposition techniques have been developed, among which the very popular Layer *by* Layer (L*b*L) sequential adsorption method. Originally put forward by Iler et al. [1] in the sixties to generate *all*-nanoparticle multilayers, it was then rediscovered and brought to fame by Decher et al. in the nineties [2–4]. Initially implemented on oppositely charged polyelectrolytes (PEs), it was later on extended to all types of inorganic materials such as nanoparticles, nanowires and nanotubes *etc*... Now-a-days, the L*b*L process is an efficient platform to develop organic/inorganic tunable functional coatings [5] as well as colloids or capsules [6] *via* the sequential deposition of oppositely charged components [7] driven by various interactions including electrostatic [8], entropic [9,10] hydrogen bonding [11,12], van der Waals [13] and hydrophobic ones [14,15]. Electrostatic L*b*L deposition is the most used and documented approach with a growth mechanism driven by the overcharging of the complementary charged functional groups [5,10,16]. Over the year, the oppositely charged polyelectrolyte multilayers have generated a very rich bibliography; with some contradictions and/or differences however that might appear if one compares some of the publications made by different teams around the world working on the same system.

In this work, we would like to put forward on the well-known and well-studied poly(acrylic) PAA/poly(diallyldimethyl-ammonium) PDADMAC pair, that the formulation pathway followed during the multilayer fabrication is responsible for some of the observed inconsistencies. Indeed, small differences in the growth conditions can lead to quite important changes in the thickness and/or morphology of the resulting films, ruining then the highlighted *fine control* of the multilayer final properties. In particular, (i) the way to adjust the pH of the different dispersions can influence the state of complexation/aggregation of the oppositely charged components, (ii) the numerous transfers through the air/water interface during a classical L*b*L sequential adsorption can impact the overall assembly and in some cases (iii) the proximity with the bulk desalting transition [17–19] (salt concentration beyond which oppositely charged polyelectrolytes are non-interacting/complexing anymore) can change/alter the growth mechanism during the multilayer build-up. The L*b*L formulation pathway should then be fully under control in our opinion, a feature that is rarely put forward or studied in the literature.

Before focusing on the very rich bibliography generated by the PAA/PDADMAC pair over the years, it is worth reviewing briefly the main features ruling the formation of multilayers comprising any weak/strong PEs pair; thanks to the comprehensive survey published recently by Lindhout and Cohen Stuart [20]. Depending on the charge density of the weak PE (tunable with the pH) and the ionic strength of the solution, different growth regimes can be observed. At low ionic strength and with a charge density above 75% for the weak PE, the pair behaves as two strong PEs. Both types of charged polymers adsorb flat due to a stretched conformation generated by the repulsion between the charged groups borne by the chains. A linear growth is observed resulting in thin glassy multilayers with thicknesses in the range of few Å per bilayer only. In contrast, when the charge density of the weak PE is very low or the ionic strength relatively high, charge reversal cannot occur and the multilayers will only form in the presence of secondary interactions (hydrophobic, hydrogen bonding or van de Waals). For intermediate charge densities or ionic strengths, thicker multilayers are formed because more weak PE chains are needed to compensate the strong PE charge; with chains adsorbing in that case as loops and tails. Exponential growth is then observed due to the vertical diffusion of one of the component resulting in liquid-like multilayers in competition with water soluble weak polyelectrolyte complexes (WPECs) and sensitive to the ionic strength. It should be noted that in this case, the multilayer stability depends on the PE molecular weight as well [21]. In the case of small M_w, the PEs present in solution will strip their oppositely charged partners from the surface to build-up soluble WPECs in order to minimize the entropic loss due to adsorption (/complexation).

The exponential growth and good swelling properties of the PAA/PDADMAC system were originally used to incorporate NPs in order to create new functional materials. The Kotov group [22] in particular used these features to incorporate negatively charged thioglycolic acid-capped CdTe quantum dots. These highly swollen films made from 45 or 100 bilayers were fabricated without salt by a robotic sequential dip coating process and loaded with NPs by a simple dipping during few hours. The sequential adsorption was made at pH 2.9 where PAA chains are uncharged suggesting that secondary forces (hydrophobic) where at play generating relatively thick films. Indeed, Choi and Rubner [23] have shown that the PAA/PDADMAC pair exhibit a dramatic change from thin (fully charged PAA at high pH) to much thicker films when the ionization degree falls below the critical value of 75% (at pH 6.2). Dubas and Schlenoff [24] studied the growth and deconstruction of the system at pH 5 and 11 as a function of the salt concentration and PAA molecular weight. The PE multilayer (PEMs) thickness was shown to reach a maximum and then decrease until its complete deconstruction when the salt concentration was raised beyond 0.6 M. This feature was exploited [21] to delaminate the membrane of a PSS/PDADMAC multilayer deposited on a PAA/PDADMAC assembly. After immersion in 1 M NaCl, the PAA/PDADMAC film dissolved immediately releasing the PSS/PDADMAC stratum (stable up to 3.5 M) used as a freestanding membrane [25]. It turned out that reducing the solution pH to minimize electrostatic interactions is not effective to delaminate the PAA/PDADMAC pair (where secondary hydrophobic forces hold the multilayer even in the neutralized state) [25]. On the other hand, lowering the pH from 11 to 5 generated a film 8 times thicker. The hyperswelling of PAA/PDADMAC films obtained by the spin assisted L*b*L method was also studied by Dubas and Schlenoff [26]. After drying, the film was first immersed in pure water, and then sequentially exposed to solutions containing an increasing amount of salt up to 0.3 M (beyond which the films dissociated) resulting in a final 400% swelling.

More recently, Alonso et al. [27] have studied the L*b*L assembly of the PAA/PDADMAC pair as a function of pH. For a 5,000 g mol^{-1} PAA at pH $\geq$ 6 in the presence of 0.5 M NaCl the multilayer growth was inhibited after the first few bilayers obtained due to interaction with the substrate. Thicker films were only generated at low pH (3) where secondary hydrophobic forces operate likely allowing the film to growth; authors did not comment.

From a careful analysis of the data presented above, it emerges that the way the multilayer is fabricated can directly impact its final properties. The work presented here confirms and completes some of the previous studies and highlights the importance of a controlled fabrication pathway. It also suggests some processing routes leading to reproducible morphologies. Finally, we recommend to systematically perform bulk desalting tests with the building-blocs under investigation to clearly asses the conditions at which electrostatic interaction is at play or not.

2. Materials and methods

PDADMAC 20%/w in water M_w = 100–200,000 g mol^{-1}, PAA M_w = 2,000 g mol^{-1} and 250,000 g mol^{-1} and ammonium chloride (NH_4Cl) were purchased from Sigma Aldrich whereas Polystyrene (PS) M_w = 250,000 g mol^{-1} was obtained from Acros. Sodium chloride (NaCl) was bought from Merck. MilliQ water (18 MΩ cm) and used for all experiments. Cerium oxide (ceria) nanoparticle (NP) dispersions (10%/w, pH 1.5) were kindly supplied by the Rhodia-Solvay chemical company (Belgium). The NPs of average diameter ~8 nm (from dynamic light scattering) were coated with PAA_{2k}