



Overshoots of adsorption kinetics during layer-by-layer polyelectrolyte film growth: Role of counterions



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ABSTRACT

Layer-by-layer adsorption of polycation poly(trimethylammonium ethyl methacrylate chloride) (MADQUAT) and polyanion poly(acrylic acid, sodium salt) (PAA) on silicon oxide substrates was studied in order to understand non-regular multilayer buildup. Indeed during MADQUAT adsorption, a special variation in the signal, called overshoots, was monitored with stagnation point adsorption reflectometry (SPAR). These overshoots were observed under different experimental conditions (pH, polymer concentration, salt concentration and molecular weight variations). A method called “substrate thickness method” was applied to determine the thickness, the refractive index and the adsorbed amount variation during the overshoot. Results clearly showed a decrease in the adsorbed amounts, but which does not necessarily indicate dissolution of the adsorbed multilayer. Therefore we also investigated layer-by-layer adsorption on colloidal silica particles (SiO₂) under the same conditions as those in reflectometry. Indeed the high specific surface area of particles allowed titration of chloride ions and unadsorbed polymer in the bulk during the adsorption process. An increase in chloride ions concentration with no increase in the polymer concentration was observed. Accordingly, overshoots in cases of MADQUAT/PAA multilayer are not due to desorption of cationic polyelectrolyte but to desorption of chloride ions from the adsorbed multilayer film.

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1. Introduction

Adsorption of polyelectrolyte is a major topic in academic research but also relevant to many industrial processes. Depending on the purpose, polyelectrolytes can either be deposited, forming either a monolayer or a multilayer film. In order to buildup a multilayer film, a simple, low-cost technique can be used. This method is based on a layer-by-layer (LbL) adsorption of oppositely charged polyelectrolytes driven by electrostatic attractions. Since Decher's research, [1] other studies have also shown the possibility of building a multilayer film using hydrogen bonding [2]. The alternate sequential adsorption is now extended to a wide range of compounds such as proteins [3–5], DNA [6,7], or inorganic particles [8–10].

To understand the mechanism involved in the growth of a polyelectrolyte film, many experimental techniques have been used. Among them, *in situ* techniques such as optical reflectometry (also called stagnation point adsorption reflectometry, SPAR), ellipsometry, surface plasmon resonance, optical waveguide light microscopy or quartz crystal microbalance with dissipation have been used to monitor the evolution of the adsorbed amount of each

polymer, the refractive index or the thickness of the deposited film. These parameters varied in duration from a few seconds up to several hours. Therefore numerous investigations have been carried out on the kinetic of polymer adsorption [11,12].

Under certain experimental conditions, specific evolution of the monitoring output appears at the beginning of adsorption. For example, in the study of adsorption kinetic by optical reflectometry, a phenomenon called overshoot was monitored on the reflectometer signal during polyelectrolyte adsorption. Indeed overshoot corresponds to a rapid increase in the reflectivity signal followed by a slow decrease. It not only has been observed during the adsorption of grafted copolymers poly(acrylamide)/poly(ethyleneoxide) [13], proteins [14] or cationic starch [15] but it has also appeared in multilayer films composed of cationic/anionic polyelectrolytes [16–18], cationic polyelectrolytes and colloidal silica (18 nm) [19], protein and polyelectrolyte [20], polypeptides [21] or proteins [22].

There is ongoing debate in the literature over possible explanations for overshoots observed in the polyelectrolyte multilayer buildup. Indeed Cohen Stuart and co-researchers have suggested a combined adsorption/desorption process of the polyelectrolytes [18,23]. They studied the effect of KCl, NaNO₃ and CaCl₂ salt concentration on the occurrence of the overshoot during polyelectrolyte adsorption. Using a stability diagram, they showed the

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possibility of the formation of a soluble complex composed of the introduced polyelectrolyte and the previously adsorbed polymer above a critical salt concentration. Another explanation is a conformational rearrangement of polymer molecules at the surface. Filippov and Filippova [24] have theoretically demonstrated that the overshoots are controlled by conformational kinetics of the adsorbed layer. Using experimental data, Wågberg and co-researchers have also proposed as an explanation for the overshoots, a rearrangement of the polyelectrolyte conformation in the adsorbed layer resulting in a change in the reflectometer signal [25]. However any conformational changes at a constant adsorbed amount (optical mass) cannot be detected using reflectometry [13].

In our previous studies, we also observed overshoots in the reflectometer signal during the growth of multilayer films with oppositely charged polyelectrolytes [26,27]. In view of these findings, the aim of the present work was to investigate the reason for the overshoots appearing during the buildup of a multilayer made of a strong cationic polyelectrolyte and a weak anionic polyelectrolyte with special attention given to the counterions of each polyelectrolyte. Using an optical reflectometer equipped with an impinging jet cell, several physico-chemical parameters (pH, ionic strength, monovalent and divalent ions, weak and strong polyelectrolytes with different molecular weights) were tested to observe their effect on the overshoots. The refractive index and thickness variations during an overshoot were determined using a method previously developed by our team (substrate thickness method) [28]. Adsorption of layer-by-layer films was also carried out onto colloidal silica particles which due to their large specific surface area allowed us to determine the amount of adsorbed polymer. Adsorption of each polyelectrolyte was recorded using the titration of the unadsorbed amount of polymer. Concentration of chloride ions was measured *in situ* during MADQUAT adsorption with an ion-selective electrode.

2. Materials and methods

2.1. Chemicals and solutions

Quaternized polydimethylaminoethyl methacrylate chloride (MADQUAT) and poly(acrylic acid, sodium salt) (PAA) were synthesized by COATEX (Genay, France). MADQUAT (207 g per molar unit) with different molecular weights was used as a strong cationic polyelectrolyte. PAA (94 g per molar unit) has an average molecular weight of 10 kDa. PAA has frequently been used as a weak anionic polyelectrolyte for adsorption studies [29,30] and has an intrinsic ionization pK of 5 in 10^{-3} M NaCl solution and a half ionization pK around 6.8 [31]. Poly(4-styrenesulfonate, sodium salt) (PSS) with an average molecular weight of 70 kDa was purchased from Alfa Aesar. PSS is a strong anionic polyelectrolyte which was totally ionized across the whole range of pH used in this study [32]. The chemical structures of the polyelectrolytes are presented in Fig. 1.

Polymers were dissolved in ultrapure water having a resistivity above $18 \text{ M}\Omega \text{ cm}$ (Milli-Q Plus, Millipore). The solution pH was adjusted with HCl (Aldrich) or NaOH (Aldrich) and the appropriate amount of analytical grade NaCl (Aldrich) was added to set the ionic strength. Polyelectrolyte solutions were prepared just before each experiment.

Colloidal silica particles were synthesized using the Stöber method in ethanol [33]. After several washing/centrifugation cycles, particle size was measured in water using dynamic light scattering (Zetasizer 3000HS, Malvern). Monodispersed particles of 258 nm in diameter with a polydispersity index of 0.082 were obtained.

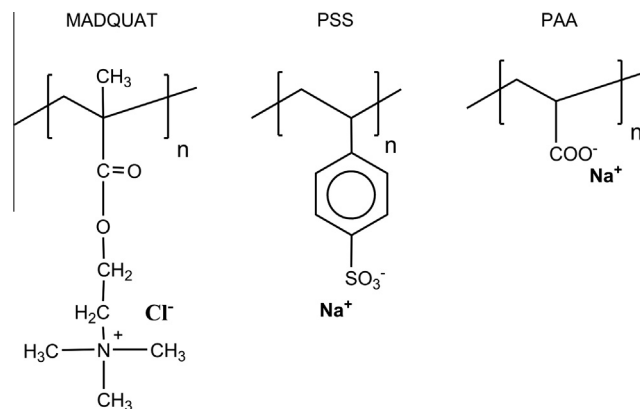


Fig. 1. Chemical structures of the polyelectrolytes used in this study.

2.2. Optical reflectometry

An impinging jet cell was mounted on the reflectometer, which created a stagnation point in the center of the cell where the solution was introduced through a cylindrical channel drilled into the glass prism [34]. A linearly polarized He-Ne laser beam entered the cell through one side of the prism. The beam was reflected on the stagnation point, then emerged from the cell, and was split into its parallel (p) and perpendicular (s) components (with respect to the plane of incidence) by using a beam splitter cube. Photodiodes were used to detect the beams. The resulting electric intensities, I_p and I_s , were then converted into electric tension and finally recorded. A two-way valve was used to switch between solutions with or without polyelectrolyte. Signals recorded during the injection of the polyelectrolyte free solution and polyelectrolyte solution were respectively denoted by S_0 and S . Finally $(S - S_0)/S_0$ represents, at least semi-quantitatively, the changes in adsorbed amount [18].

Silicon wafers coated with a silicon oxide (SiO_2) layer were used as the substrate. Prior to each experiment, wafers were cleaned with piranha solution (one part of hydrogen peroxide (30%) in three parts of sulfuric acid (98%)), then rinsed and finally stored in ultrapure water until use.

All experiments followed the same experimental procedure. In order to obtain a stable baseline of the reflectometer signal, a polymer free solution of the same pH and salt concentration as the subsequent polymer solutions was introduced into the cell for 5 min. Since the silicon oxide carried a negative surface charge under experimental conditions of pH 5.5 [35], MADQUAT was then introduced into the cell. In most cases in this study, ten layers of alternate polycation and polyanion (five bilayers) were deposited by switching the injection of the solution every 10 min. If not mentioned in the text, no rinsing step was done between each injection. For each of the experiments the solution flow rate was maintained at a constant rate. The experiments were repeated successfully three times with reproducibility of the order of 5%.

In order to determine the mean refractive index and thickness of the adsorbed layer during the overshoots, a method called substrate thickness method was used. Briefly, the principle of the analytical procedure is based on a comparison between the experimental and calculated reflectivities ratio R_p/R_s for the same adsorption experiment carried out with at least two substrates of different thicknesses. Reflectometer output S is linked to the reflectivities ratio by an apparatus transmission factor f . For a more complete description of the procedure, please refer to our previous paper [28]. In the present work, silicon wafers with a silicon oxide layer of $115 \pm 2 \text{ nm}$ or $298 \pm 1 \text{ nm}$ were purchased from ACM (France) and were used to apply the method. Thicknesses of SiO_2

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