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Step-by-Step Assembly of Self-Patterning Polyelectrolyte Films Violating (Almost) All Rules of Layer-by-Layer Deposition

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The deposition of polymer-based films via layer-by-layer (LBL) assembly has become a popular surface functionalization method because of its versatility and the fact that it can be applied not only to oppositely charged polyelectrolytes[1] but to many types of polymers carrying mutually complementary functionalities (e.g., hydrogen-bond donors and acceptors).[2,3] Consequently, such hybrid films offer a wealth of potential applications in materials science.[4] Of course, a detailed understanding of the relationship between the molar mass and architecture of the polymers, the film deposition parameters (e.g., ionic strength,[5] the nature of the supporting electrolyte,[6] and temperature[7]) and the resulting film properties would be desirable, but this is often not the case. It is for instance well-known that the permeability and the mechanical properties of a film depend strongly on its growth regime, which can be linear (occurring preferentially at low temperature and low ionic strength[7]) or superlinear (occurring preferentially at higher ionic strength[8] or higher temperature[7]). The superlinear regime is often exponential as a result of the fact that at least one of the polyelectrolytes can diffuse freely throughout the whole film.[9] Independent of their dynamic properties, polyelectrolyte multilayer (PEM) films can be rationalized by a three-zone model [Scheme 1 in the Supporting Information (SI)][10] arising from interfacial effects of the substrate and the surrounding medium (e.g., air). However, not all LBL films fall into simple categories: there are cases in which the growth cannot be described by either a linear or a supralinear growth regime.[11,12] In a few systems, the growth is best described by a succession of two linear regimes (the first one influenced by the surface and the second one corresponding to "free" growth).[13] Unfortunately, the fact that most investigations have been performed with standard polyelectrolytes has prevented the discovery of more exotic cases and limited the investigations of polyelectrolyte complexation at interfaces to a small subset of systems. Here we report on the highly unusual film-forming behavior of a short polyanion, poly(sodium phosphate) (PSP), and a much longer polycation, poly(allylamine hydrochloride) (PAH). PSP is an interesting water-soluble, inorganic polyelectrolyte with some unique properties concerning its interactions with charged species.[14] We produced deposits made of PAH and PSP according to the LBL spray deposition method[15] (see the SI), with the main variable being the concentration of the two polyanions, which varied between 10^{-5} and 10^{-2} M (with respect to monomer repeat units). All of the experiments were performed at pH 6.7 in 0.15 M NaCl.

It appears that the growth regime depends strongly on the concentration of PSP and PAH (Figure 1-SI): the growth *seems* to be linear at the lowest concentrations (10^{-5} and 10^{-4} M) and can be fitted by an exponential growth at 10^{-3} M; the combination of an exponential growth followed by a linear one is mandatory at 10^{-2} M. This difference in growth regime with concentration is not related to insufficient spraying times at the lower concentrations (Figure 2-SI). Despite of the appearance of optical interference colors (Figure 1a), atomic force microscopy (AFM) topographies show that the deposits obtained at 10^{-4} M are islandlike and that the islands increase in size up to a layer number (m) of at least 150 (Figure 1b-e).

On the other hand, at 10^{-3} M, the deposits have the morphology of smooth films (data not shown). Analysis of the root-mean-square (RMS) roughness of the deposits as a function of the number of deposition steps showed a markedly different behavior. While the roughness decreased from $\sim$5 to $\sim$1 nm at 10^{-3} M, it increased from $\sim$5 to $\sim$75 nm at 10^{-4} M (Figure 1f).

Another unusual observation is related to the ζ potential, whose sign is normally expected to correspond to the sign of the charge of the polyelectrolyte adsorbed as the last layer.[10,16] However, when the deposition was carried out with 10^{-4} M solutions, *the ζ potential did not alternate between positive and negative values upon the deposition of the polycation and polyanion* (Figure 2). As long as the ζ potential was positive (i.e., for $m \lesssim 75$), the ζ potential continuously decreased with increasing m. When the ζ potential approached zero, an instability occurred with respect to the previously regular film growth. Some samples temporarily showed slightly sublinear growth while others temporarily showed slightly superlinear growth (Figure 2). After ζ reached a plateau value of about -20 mV after 150−200 deposition steps, the film growth continued with approximately the same slope as observed at small layer numbers. It should be noted that the spray deposition of poly(styrene sulfonate) and PAH under identical conditions led as expected to an alternation of the ζ potential between positive and negative values (data not shown). Even exponentially growing films, which exhibited islandlike growth for very small layer numbers ($m < 15$) showed an alternating ζ potential.[17]

Hence, we have an interesting example of a film growth process in which the nanoscale roughness increases linearly with the film thickness while the macroscopic film homogeneity is remarkable, as observed by optical interference colors (Figure 1). It is highly surprising that chains of the polycation PAH can adsorb onto a surface with a macroscopically positive ζ potential and that the polyelectrolyte complex formation at the interface leads to the development of islands

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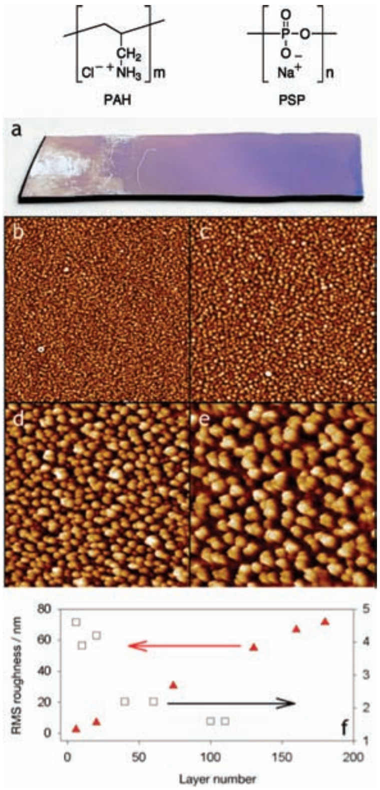

Figure 1. (top) Chemical structures of PAH and PSP. (a) Photographic image of a deposit obtained after 150 deposition steps (the marks on the left side of the sample are due to handling). (b−e) Representative surface topographies (2 μm × 2 μm) of deposits prepared by spray deposition (10 s spraying time per step) of PSP and PAH (each at 10^{-4} M in the presence of 0.15 M NaCl at pH 6.7), with a number of layers (*m*) of (b) 6, (c) 20, (d) 60, and (e) 110, illustrating the increase in roughness with the number of deposition steps. (f) Evolution of the RMS roughness (determined from the AFM topographies) with *m*: (▲, left-hand axis) 10^{-4} M; (□, right-hand axis) 10^{-3} M.

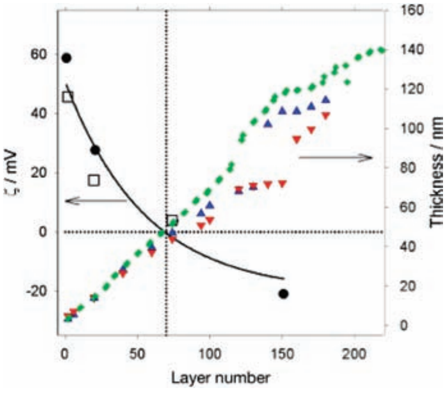

Figure 2. (left-hand scale) Evolution of the macroscopic ζ potential (the error bars correspond to one standard deviation over five measurements and are smaller than the symbols) of deposits obtained by alternatingly spraying PSP and PAH at 10^{-4} M onto PEI-coated glass slides as a function of *m*: (□) even values of *m* (the last sprayed layer was anionic PSP); (●) odd values of *m* (the last sprayed layer was cationic PAH). The dotted horizontal line corresponds to $\zeta = 0$ mV and the vertical one to $m = 75$. (right-hand scale) Evolution of the average film thickness as a function of *m*. Different symbols correspond to different experiments.

with a rather small polydispersity that then grow to sizes of more than 300 nm without coalescing into a continuous film. Possible explanations for this phenomenon include unusually strong hydrogen bonding and/or nanoscale heterogeneities in the ζ potential. Such heterogeneities could for example arise from the growth of negatively charged islands on the initial layer of cationic poly(ethylene imine). This would suggest that the unusual growth process at 10^{-4} M may be substrate-dominated and thus restricted to zone I in the three-zone model for multilayer growth,[10] whereas at higher concentrations a more regular film growth is observed. However, the fact that at 10^{-4} M the ζ potential does not alternate is puzzling, as it requires that polymers adsorb onto a surface of the same charge, independent of whether the ζ potential is positive (at small *m*) or negative (at large *m*). The adsorption of a polyelectrolyte onto a surface of the same sign is exotic but has been observed previously.[18,19] This indicates that interactions other than electrostatic ones contribute to the buildup of the multilayer deposit[20] and/or that dynamic structural changes occur in the polyelectrolyte complexes on the surface. The complex formation between PAH and PSP in bulk is indeed dynamic,[14] and a detailed study comparing the phenomena of polyelectrolyte complexation of PSP and PAH in the bulk and at interfaces will be the issue of a forthcoming manuscript.

A practical consequence of this highly unusual behavior is that (PSP/PAH)$_n$ films can be used for the creation of precise and adjustable nanoscale patterns on large surface areas ("self-patterning surfaces") by simple spray deposition from aqueous solutions. On the other hand, some of the "obvious" rules of polyelectrolyte multilayer formation will obviously need to be revised.[21]

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Supporting Information Available: Experimental details, a scheme displaying the three-zone model for polyelectrolyte multilayer films, deposition experiments followed by ellipsometry as a function of the polymer concentration, and thickness of deposits obtained by spray deposition of PSP and PAH (both at 10^{-4} M in the presence of 0.15 M NaCl at pH 6.7) as a function of *m* at two different spraying times. This material is available free of charge via the Internet at http://pubs.acs.org.

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