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Weak versus Strong: A Weak Polyacid Embedded within a Multilayer of Strong Polyelectrolytes

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The goal of controlling molecular organization and orientation of organic films on a nanoscopic level has seen profound development using techniques based on the layer-by-layer deposition of polyelectrolytes.[1−5] Applications have burgeoned. Building on the original focus upon polyelectrolytes whose charge density is fixed, the use of weak polyelectrolytes (whose charge density depends on local electrostatic environment) opens a window for additional control.[6−12] Here, for the first time, we investigate local electrostatic interactions *within* a polyelectrolyte multilayer. The enabling strategy was to embed a weak polyacid whose charge density *responds* to changes of the local environment.

We used infrared spectroscopy in the mode of attenuated total reflection (FTIR-ATR) to quantify local surface effects on the ionization of carboxylic acid groups. Mass adsorbed and ionization of carboxylic acid groups were quantified in situ from the integrated absorbances of infrared peaks.[12] A detailed account of the methods and calibration is described elsewhere.[12] The experiments were performed at 25 °C in D_2O with phosphate buffers constructed from Na_2HPO_4 and $NaH_2PO_4{*}H_2O$ (General Storage, pure grade). We chose the working pH = 6.0 because it was within the window where the ionization of our polymer is sensitive to changes of chemical potential (its ionization in bulk solution rose from 0.15 to 0.8 as pH increased from 5 to 7). The procedure to build up multilayers was the following. First, a layer of cationic polymer (quaternized 1,4 polyvinylpyridine, QPVP) was deposited from dilute solution onto the initially bare surface of a Si ATR crystal carrying negative charge from dissociated silanol groups. This caused surface charge to switch from negative to positive.[13] The second layer was composed of a weak polyacid (poly(methacrylic acid), PMA). After the adsorption of PMA equilibrated, alternate layers of QPVP and of anionic polymer (poly(styrenesulfonate), PSS) were deposited sequentially from dilute solution. To eliminate the possibility of charge−charge complex formation in solution, solutions containing polyelectrolytes were rinsed away with pure buffer solution between successive adsorption steps. Details of the polymers used and their solution conditions are given in the caption of Figure 1. Figure 1 shows the infrared bands used to quantify the ionization of PMA and further shows the fidelity of layer-by-layer deposition.

The main finding of this communication is that ionization of the embedded polyacid oscillated with net charge of the electrostatic multilayer on top. Figure 2 illustrates this. In the top panel, the ionization of PMA is plotted against elapsed time, first during the deposition of the strong polycation (QPVP) on top, next during the deposition of the strong polyanion (PSS) on top. One sees at first enhanced negative charge on PMA but subsequent depression to less than for bulk solution. The bottom panel of Figure 2 shows that these changes were in nearly linear proportion to the amounts of polycation and polyanion deposited. Figure 3 shows that oscillations persisted up to the thickest films investigated (a further 10 layers of electrostatic multilayers on top of the embedded layer). Their minima showed no systematic dependence on layer number. Their maxima decayed slightly with increasing layer number. The magnitudes were large—the ionization level changed by a factor more than two, between ∼30 and 70%, as successive layers were added.

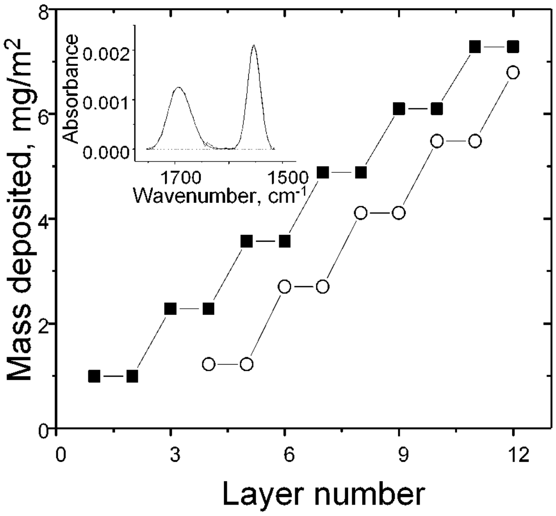

Figure 1. Illustration of layer-by-layer deposition, on top of an embedded layer of weak polyacid, PMA, of alternate layers of polycation and polyanion, QPVP and PSS. Mass deposited, measured in situ by FTIR-ATR, is plotted against layer number for QPVP (filled symbols) and PSS (open symbols). The deposited amounts were calculated from the integrated intensities of infrared peaks at 1643 cm^{-1} (vibrations of pyridine ring) and 1600 cm^{-1} (vibrations of aromatic ring), respectively. The PMA, M_w = 40 000 g-mol^{-1} and M_w/M_n = 1.02 was purchased from Polymer Standards Service, Mainz, Germany. The QPVP, 98% was quaternized in our laboratory from an anionically synthesized poly-4-vinyl pyridine with weight-average molecular weight M_w = 34 200 g-mol^{-1}, M_w/M_n = 1.23 (purchased from Polymer Source, Quebec, Canada) as described previously.[12] The PSS with M_w = 35 000 g-mol^{-1} and M_w/M_n = 1.1 was purchased from Polymer Laboratories, U.K. First, to prime the surface for subsequent layer-by-layer deposition, QPVP was allowed to adsorb from 0.01 mg-mL^{-1} to the surface of the oxidized Si crystal in 5 mM buffer at pH = 6.0. PMA was allowed to adsorb on top, and then alternate layers of QPVP and PSS, always from 0.01 mg-mL^{-1} solution. Solutions were rinsed with pure buffer between these adsorption steps. (Inset) Absorbance plotted against wavenumber for peaks associated with the symmetric $C{=}O$ stretch of the carbonyl group and the asymmetric COO^- stretch of the carboxylate moieties of PMA. The calibrated ratio of their integrated intensities gave the fractional ionization of PMA.

The slow decay of ionization oscillations is surprisingly larger than a traditional estimate[15] of electrostatic decay length. The local ionic strength within the multilayer was on the order of moles per liter, and thus the screening length of mobile charges should be expected to be tiny (Å), whereas the dry (ellipsometric) thickness of these films was 0.8 nm per layer. As Johnson and

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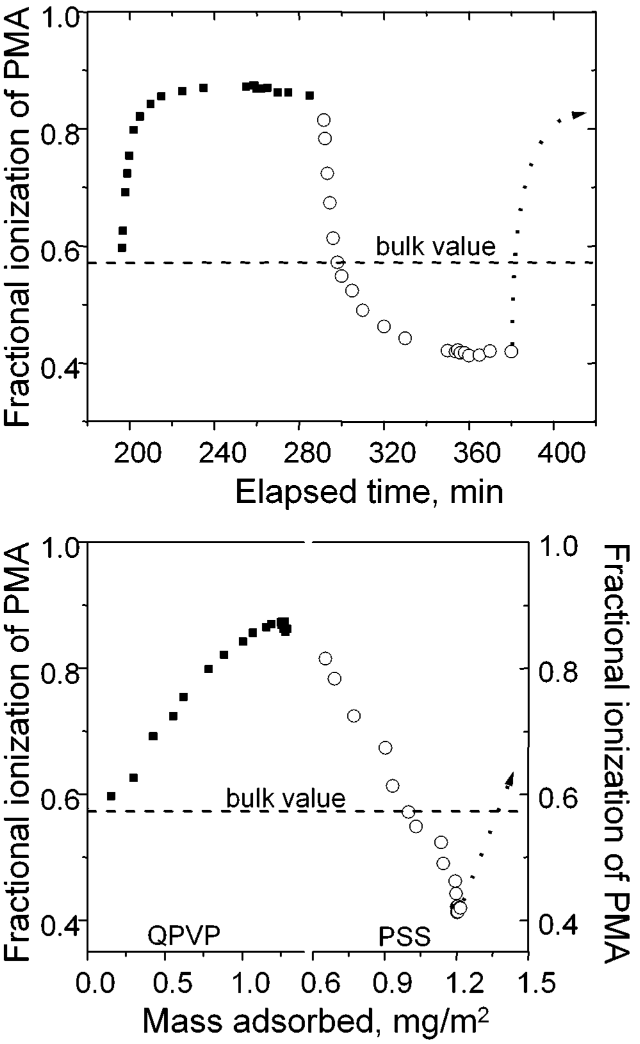

Figure 2. Fractional ionization of PMA plotted against time elapsed during subsequent deposition of a QPVP and then a PSS layer on top (top panel) and, equivalently, against mass adsorbed during this process (bottom panel). Dashed lines show ionization in bulk solution. Squares denote QPVP, circles PSS. The dotted horizontal line denotes the value characteristic of the bulk solution at this pH and ionic strength.

Finkenstadt suggest,[14] the giant observed decay length probably signifies that electrostatic complexes between polycations and polyanions are fixed in space—not mobile as is normally supposed in a colloid analysis of electrostatic screening. In this respect they resemble ionic solids. Hydrophobicity within the multilayer (to lower the local dielectric constant), may also contribute. The same effect (nearly quantitatively so) was observed for buffer ionic strength 5 and 100 mM.

Previous related work concerned dried films in the solid state. Shiratori and Rubner reported that the degree of ionization of a weak polyacid outermost layer increased by about 10% when a polycation layer was deposited.[9] On the other hand, the degree of ionization of a polyacid in a multilayer thin film of weak polyelectrolytes remained unchanged even after the films were conditioned in solutions of low pH, until a pH of about 2.5 was reached.[10] Those results suggest that beyond the expected surface titration effect, once the films are dried, the degree of ionization of *dried* films remains essentially fixed. This is expected because a dry film must be electrically neutral. Polyelectrolyte multilayers in aqueous media may be slightly overcharged or undercharged, however, which explains the difference.

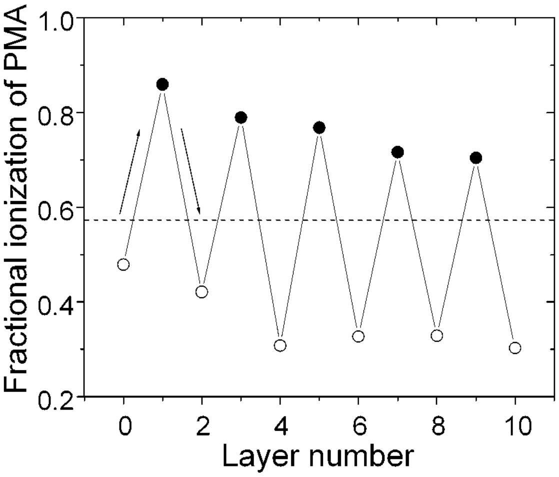

Figure 3. Fractional ionization of embedded PMA plotted against number of layers of strong polyelectrolyte (PSS and QPVP) deposited on top. The minima of the oscillations show no systematic dependence on layer number. The maxima decayed with a extraordinarily slow decay length of ~20 layers. The dashed line shows the ionization of PMA in the bulk solution at this pH.

The significance of these findings is 2-fold. First, it follows that charge within these polyelectrolyte multilayers is not a simple matter of counting the charges introduced by each successive layer. Instead, when dealing with a weak acid (or base), the layer becomes *responsive* and has the chemical capacity to adjust its charge in the direction of maintaining neutrality. There is long-range coupling—between ionization within the embedded weak polyacid and charge deposited on the outermost layer of strong polyelectrolyte, far removed from it in space. Conversely, when charges are added to the outermost layer by depositing other polyions on top, electrostatic changes are *induced* far away within the interior. A second significant conclusion falls on the practical side. The approach of embedding a weak polyelectrolyte within a multilayer of strong polyelectrolyte may allow one to sense changes in external environmental conditions that act upon the outside of the multilayer assembly. For example, we have verified that ionization responds, in the same way shown in this communication, to the adsorption of spermine (charge +3) and also to the adsorption of a charged protein (bovine serum albumin). This may find application in the design of surface sensors for adsorbed ions and polyions.

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