Layered, Erasable, Ultrathin Polymer Films

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The fabrication of molecularly thin organic films that possess nanoscopic patterns in the direction normal or parallel to a solid surface constitutes an emerging theme of modern materials science.[1,2] New applications are proliferating, for example, in the fields of biosensors, light-emitting diodes, nonlinear optical devices, and perm-selective gas membranes.[1−8] Prior work has concerned films that are intended to be durable. Here we show that when molecules are deposited by layer-by-layer assembly that is guided by hydrogen bonding or complex formation, the resulting multilayers can be erased by environmental stimuli that introduce electrostatic charge into ionizable elements within them. These erasable polymer multilayers are envisioned to have new applications in areas ranging from medicine to pharmaceutics to materials science.

The scheme of intermolecular hydrogen bonding at a surface was as follows. First a poly-acid (or poly-base) was applied to the surface from solution, then on top of this a poly-base (poly-acid), and so forth sequentially. We have worked with several acid−base pairs: poly(ethylene oxide)/poly(acrylic acid), poly(ethylene oxide)/poly(methacrylic acid), and poly(vinylpyrrolidone)/(poly(methacrylic acid). These systems, and others that should work by the same principle, e.g., poly(carboxylic acid)/poly(vinyl alcohol) and synthetic nucleotides such as poly(adenylic acid)/poly(uridylic acid), are known to form tight complexes when mixed in bulk aqueous solution[9−11] and are expected to also do so at a surface. Various other polymer and copolymer pairs can be imagined by rational extension. Rubner and co-workers first showed that deposition is possible with polymers that form hydrogen-bonded pairs, but the system was thought to be unique and extension to destroying the multilayer was not made. The concept builds upon the large body of knowledge concerning the use of hydrogen bonds to induce supramolecular ordering in other polymeric systems.[13−16] It is critical to work with polymers rather than small molecules because the limited driving force from a single hydrogen-bonded pair needs amplification by polyvalency to produce an integral film.

The fidelity of layer-by-layer deposition of poly(methacrylic acid), PMAA, and poly(vinylpyrrolidone), PVPON, is illustrated in Figure 1 (the molecular structures are shown on an inset in Figure 2). These experiments concern films deposited on a macroscopic-sized germanium crystal support and characterized by Fourier transform infrared spectroscopy in attenuated total reflection, ATR-FTIR (see figure caption), which affords direct in situ measurement of ionization as well as of mass deposited. Control experiments by other characterization methods showed applicability of this buildup method to other polar substrates such as glass and mica, and also to nonpolar substrates such as Teflon and polyethylene. Following the recent example of Möhwald and colleagues as concerns electrostatic self-assembly,[3] the method was also found to apply to small micron-sized down to nano-sized particles, thereby affording a method to encapsulate small particles within these coatings.

In Figure 1, one observes that the same incremental mass was deposited, layer-by-layer, during a sequence of 10 steps of sequential assembly. The driving force for self-assembly evidently competed favorably with the known intramolecular association of carboxylic acid units within single PMAA molecules at low pH.[19] Ancillary ellipsometric measurements showed that the average dry layer thickness was 3.5 nm per layer (2.6 nm per PVPON layer, 4.4 nm per PMAA layer) and that the dry layer thickness could be manipulated by changing the solution concentration during the adsorption step. In extensions of this method these uncharged polymers could alternatively be deposited from nonaqueous solutions.

The unique aspect of this self-assembly method is reversibility: multilayers could be selectively destroyed after creation. Figure 2 illustrates the controlled destruction, by change of the environmental pH, of the same multilayers whose assembly was illustrated in Figure 1. One observes, in the top panel, that the multilayers were stable up to pH 6.9 but dissolved when the pH was raised above this point. The bottom panel points to the reason: the multilayers dissolved because negative electric charge, introduced into the multilayers by ionization of the carboxylic acid functionality in PMAA, produced an electrostatic repulsion at ≈14% ionization that could not be contained within an integral film. Practical applications are suggested because the pH range for this transition was so sharp.

In other investigations we found that this critical pH, at which hydrogen-bonded multilayers fell apart owing to internal ionization, could be controlled by choice of the hydrogen-bonded chemical system. It was pH 6.9 in the example just shown, but pH 4.6 in the poly(methacrylic acid)/poly(ethylene oxide) system, PMAA/PEO, and pH 3.6 in the poly(acrylic acid)/poly(ethylene oxide) system.

The different stability, according to the chemical system, was consistent with quantitative ATR-FTIR measurements of the extent of ionization that a film would tolerate while still remaining intact. The PMAA/PVPON complexes were strongest, ∼5−7 times stronger than those formed from the pairing of PMAA and PEO.

Erasability was also controllable by changing the ionic strength. For example, in the PMAA/PEO system, the multilayers were stable only up to pH 4.6 in the environment of 10 mM ions (this was owing to the buffer solution to control pH) but stable to higher pH, up to pH 5.15, when 0.4 M NaCl was added. The reason is that free ions reduce the intensity of electrostatic repulsion between a given number of ionized groups within a multilayer assembly. Similarly, an external electric field is known to shift

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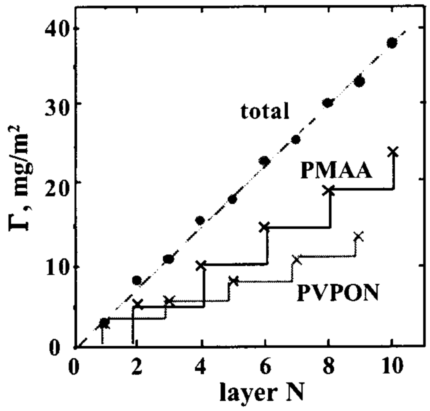

Figure 1. Illustration of layer-by-layer deposition of 10 layers in the PMAA/PVPON system. The mass deposited, measured in situ by FTIR-ATR, is plotted against the layer number for PMAA (crosses), PVPON (stars), and for the total mass deposited (circles). The experimental setup was described previously.[17] The spectra were taken in D_2O at 25 °C. The deposited amounts were calculated from the integrated intensities of infrared peaks at 1702 (CO stretch) and 1647 cm^{-1} (CON stretch) for the two polymers, respectively. The procedure to calibrate the mass deposited was described elsewhere.[17,18] The poly(methacrylic acid), PMAA, with weight-average molecular weight M_w = 327 000 g mol^{-1} and the ratio of weight-average to number-average molecular weights M_w/M_n = 1.03, was received from Polymer Standards Service (Germany). The poly(vinylpyrrolidone) (PVPON) with average molecular weight ~1 300 000 g mol^{-1} was purchased from Aldrich. First, to prime the surface for subsequent layer-by-layer deposition, 98% quaternized poly-4-vinylpyridine, QPVP, was allowed to adsorb from 0.2 mg mL^{-1} solution to the surface of the Ge crystal at pH 9.2. This solution was replaced by pure buffer and then PMAA was allowed to adsorb from 1 mg mL^{-1} solutions at pH 9.2. Before this primer layer was used for multilayer deposition, a buffer solution containing 0.01 M DCl was injected into the liquid cell. Subsequent layers were allowed to adsorb at pH 2. Solutions were rinsed with pure buffer between these adsorption steps.

the equilibrium between an acid's neutral and charged states.[20] In direct experimental tests (not shown) we applied external electric fields and confirmed the usefulness of this strategy for controlling the stability of multilayers when other conditions were otherwise constant.

Although this work is still a long way from practical application, the concept can be used to design the deliberate release of foreign elements that have been included within these layers. We have confirmed this expectation by studying release of Rhodamine 6G, a dye molecule. Release of the imbibed element, such as a dye or a drug, occurs when the multilayer films are exposed to environmental conditions that erase them.

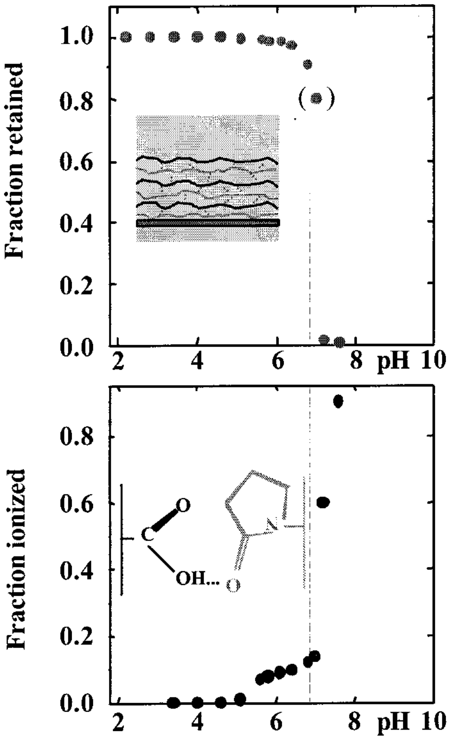

Figure 2. An illustration of the erasibility of the same multilayers whose self-assembly at low pH is shown in Figure 1. As a function of pH, the relative mass adsorbed is plotted (top panel) and the percentage of ionized carboxylic acids within PMAA layers is plotted (bottom panel). The inset in the top panel shows a schematic diagram of the multilayer hydrogen-bonded assembly. The inset in the bottom panel shows the molecular structure of the PMAA and PVPON repeat units. Note the sharpness of the erasure (denoted by the vertical dashed line) when pH was raised above a critical level. Datum in parentheses signifies that mass was being lost slowly even after 30 min of equilibration at this pH.

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