Macromolecules **1997,** *30,* 7237−7244

Ionic Effects of Sodium Chloride on the Templated Deposition of Polyelectrolytes Using Layer-by-Layer Ionic Assembly

Sarah L. Clark, Martha F. Montague, and Paula T. Hammond*

Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Received May 2, 1997; Revised Manuscript Received August 21, 1997[⊗]

ABSTRACT: A new method for the patterning of ionic layer-by-layer assembled films with micron-sized features is presented. Self-assembled monolayers (SAMs) were used as templates to direct the deposition of sulfonated polystyrene (SPS) and poly(diallyldimethylammonium chloride) (PDAC) multilayers onto a surface. Both polyelectrolytes were assembled electrostatically from dilute solutions (10 and 20 mM on a repeat unit basis) with varying amounts of sodium chloride. The ionic content was varied from 0 to 4 M NaCl. The optimal conditions for templating were found at moderate salt contents. At high salt contents ($\geq$1 M NaCl) the templating behavior of the chemically patterned SAM surface completely reversed due to electrostatic screening and dehydration of an oligo(ethylene glycol)surface, indicating that ionic strength can be used to dramatically alter polyion deposition behavior on the functionalized surface.

Introduction

Layer-by-layer assembly processes based on electrostatic or other intermolecular forces are techniques that present a new approach to the formation of supramolecular architectures.[1−10] The method, which involves the sequential adsorption of two or more polymeric or difunctional molecular species, does not require expensive equipment, elaborate materials design, or a clean room environment. This fabrication procedure has the added benefits of an environmentally benign process in a benchtop environment. The simplicity of layer-by-layer techniques, as well as the versatility of the approach, has resulted in a large increase in this area of research. A range of potential applications are currently being explored, from electroluminescent devices to biosensor arrays.[5,11,12] A greater understanding of the formation of continuous films has been pursued by several researchers. New challenges in this area are to present methods for containing the multilayers to discreet regions of the substrate's surface, adding new dimensions of organization to multilayer systems. In this work, we investigate the use of patterned self-assembled monolayers with micron-sized features as a means to direct the deposition of ionic multilayers.

Previous work in our group has established chemical patterning of SAMs as a viable method for templating the adsorption of ionic multilayers of various molecular weight polyelectrolytes.[13] This approach provides a means to spatially contain polyions to designated regions based on specific surface interactions. In an earlier paper, we examined the effects of molecular weight and found it had a significant effect on the selectivity of polyion deposition and the resolution of the three-dimensional multilayered structures. The use of an oligo(ethylene glycol)-functionalized SAM (EG) to resist polyion adsorption was most effective in samples of low molecular weight polymers. For higher molecular weight polyions, the driving force for adsorption was greater than the entropic repulsion of the EG, causing deposition on all regions of the patterned surface.[13] These effects were attributed to a decreased entropic penalty for adsorption on the hydrated EG resist as the polyion chain lengthened. It is thought that this lowered selectivity was exacerbated by the fact that the polyions adsorbed as long, extended chains in dilute solution, providing maximal opportunity for chain overlap in the lateral dimensions of the patterned film. In many cases, patterned edges exhibited lower edge resolution at the interface between the COOH and EG surfaces for the higher molecular weight polyions.

The present study extends this previous work by addressing the effects of ionic content on the selectivity of deposition for polyion adsorption on patterned surfaces for the first time. The presence of salt ions affects the conformation of adsorbing polyelectrolytes, altering the Debye length of electrostatic interaction and shielding the charge on the polyion repeat units. These changes, as well as the effects of ionic content on each of the two regions of the chemically patterned substrate, dictate the relative amounts of polymer that will adsorb on each chemical surface. These studies present the ability to control important parameters such as film thickness, roughness, patterned edge profile, and selectivity. As discussed below, we have demonstrated the ability to reverse the polyelectrolyte deposition on the SAM surfaces at very high salt concentrations, creating a negative to the original positive structure. This discovery could lead to opportunities for the fabrication of more complex structures involving two or more layer-by-layer systems on the same substrate.

Experimental Section

Substrate Preparation and Patterning. Gold substrates were prepared by thermally evaporating gold shot (99.99% purity, American Gold & Silver) onto n-type test grade silicon wafers (Silicon Sense). A 100 Å film of evaporated chromium served as the adhesive layer between the 1000 Å gold film and the silicon wafer. Typically, the surface roughness of the resulting substrate was 1.8 nm root mean square (rms) roughness in tapping mode AFM on a 10 μm^2 region of the surface.

Alkanethiols (R = COOH, $(OCH_2CH_2)_3OH$) were used to functionalize the gold surface using the microcontact printing process[14] pictured in Figure 1. The stamps were inked using the supernatant of a saturated solution of $HS(CH_2)_{15}COOH$ (COOH in this paper) in hexadecane. The second alkanethiol, $HS(CH_2)_{11}(OCH_2CH_2)_3OH$ (EG hereafter), was deposited on the surface from a 1 mM solution in absolute ethanol. Two poly(dimethylsiloxane) (PDMS) stamps were used in this study.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

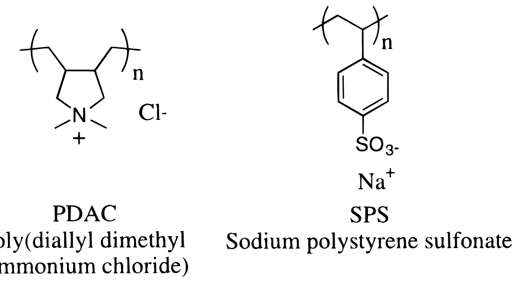


Figure 1. Chemical structures of the polyelectrolytes.

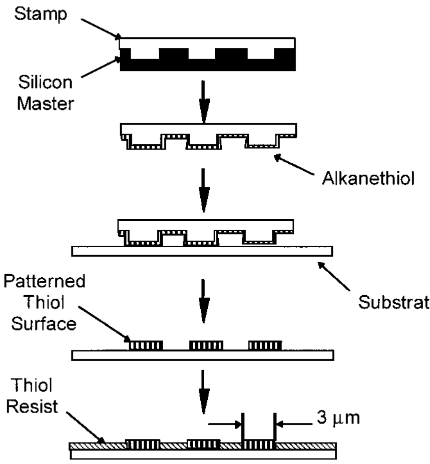


Figure 2. Schematic of the microcontact printing (μcp) method.

One printed straight lines of 3.5 μm with spaces of 2.5 μm between the lines and the second printed the negative of a two-dimensional array of 6 μm crosses.

A second set of substrates was prepared with continuous films of the alkanethiols. A cotton-tipped applicator was used to spread the solution of COOH thiol on half a substrate, and the remaining bare gold was covered by dipping the entire substrate in the solution of EG thiol. The surface was rinsed with absolute ethanol to remove excess alkanethiol and dried with nitrogen.

Aqueous polyelectrolyte solutions of poly(diallyldimethylammonium chloride) (PDAC) (~150 000 M_w, Aldrich, low molecular weight PDAC 20% solution in water) and sodium poly(styrene sulfonate) (SPS) (35 000 M_w, Polysciences, Inc., $M_w/M_n = 1.10$, molecular weight standard) were prepared using Milli-Q water (Millipore). All polymer concentrations reported are based on moles of repeat units. The structures of SPS and PDAC polyions are shown in Figure 2. Sodium chloride (99.3% purity, Mallinckrodt) was added without further treatment to the solutions. Solutions were filtered with 0.22 μm MILLEX-GS Filter Units (Millipore) to remove any particulates. SPS polyion concentrations of 10 and 20 mM were paired with 20 mM solutions of PDAC. The salt concentrations ranged from 0.001 to 4 M NaCl.

Polyion Multilayer Formation. Patterned surfaces were placed in a 20 mM solution of PDAC to form an initial PDAC monolayer on the ionized COOH surface. Next, the patterned substrate was placed in a dilute solution of the polyanion, SPS. Ionic multilayers of PDAC and SPS were thus alternately deposited onto the COOH-functionalized surface by dipping the patterned substrate in the solution of polyelectrolyte with a charge opposite the previous layer until the desired number of bilayers was formed. The substrates were soaked in the polyelectrolyte solutions for 20 min, rinsed with Milli-Q water and dried with a stream of nitrogen before soaking in the next solution. After each bilayer of PDAC and SPS was deposited, the sample was cleaned for 4−5 min in an ultrasonic cleaning bath (Bransonic).

Characterization of Samples. Ellipsometry was used to measure the film thickness of both the patterned and unpatterned films. Since the ellipsometer's spot size is approximately 1 mm by 3 mm, the data gathered for patterned films was an average film thickness over the patterned area covered by the laser spot.

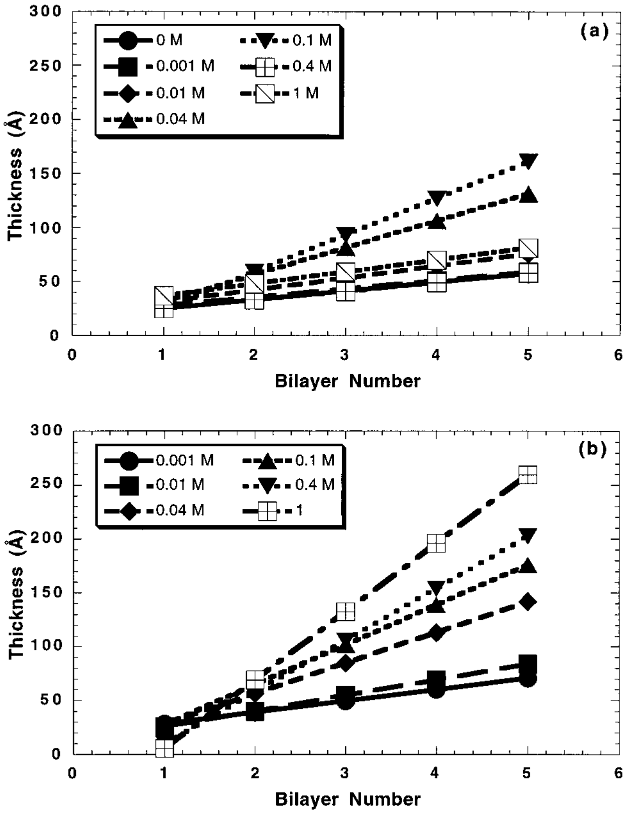


Figure 3. Plots of multilayer thickness on continuous COOH surfaces versus bilayer number with a drying step for (a) 10 mM SPS concentration and (b) 20 mM SPS concentration.

Atomic force microscopy (AFM) was used to collect data on the surface roughness, the height of the patterned features, and the overall appearance of the patterned surface. A Digital Instruments Dimension 3000 AFM was used in tapping mode with a standard etched silicon tip to study areas ranging from 1 μm square to 10 μm square. Data between the two techniques could be correlated by calculating the height of the patterned features from the averaged ellipsometry data.

Results and Discussion

Bilayer and Multilayer Formation. PDAC and SPS bilayers were adsorbed onto the patterned surface from dilute polymer solutions containing 0.001 to 4 M NaCl. Within the salt and polyion concentration ranges used, all polyion solutions containing added salt were below or close to the critical concentration c^* for polyelectrolytes, for which the macromolecules may be treated as isolated molecules in solution. Ellipsometry indicated the multilayer films grew linearly with sequential deposition of the polyions over the range of salt concentrations studied. The amount of polymer adsorbed per bilayer, based on ellipsometric film thickness measurements, grew with increasing electrolyte concentration, as shown in Figure 3a,b for continuous films of the two different SPS concentrations. The increase of bilayer thickness with increasing salt concentration has been observed by other researchers,[2,15] and it is attributed to changes in the chain conformation and molecular shape of the polyions in dilute aqueous solutions. As salt is added to a dilute aqueous polyelectrolyte solution, the charges on the polyion become shielded, and the conformation of the polyelectrolyte chain changes from an extended, rodlike molecule to a

Table 1. Thickness per Bilayer for Continuous, Five Bilayer Films of SPS/PDAC Deposited from Solutions with Different Ionic Contents onto a COOH Surface with and without a Drying Step

	film thickness, Å	
ionic content, M	10 mM SPS, drying step	10 mM SPS, no drying step
0	8	7
1.0×10^{-3}	8	14
1.0×10^{-2}	11	16
4.0×10^{-2}	25	26
1.0×10^{-1}	34	28
4.0×10^{-1}	44	48
1.0	11	21
2.0		0

three-dimensional random coil. The expanded molecular shape results in increased layer thicknesses, which correspond to the expected increase in molecular dimensions upon salt addition. We had previously reported the observation of nonlinear growth of these films on patterned surfaces at high (1 M) salt concentrations.[13] We now attribute this phenomenon to nonuniformities across the patterned surface, as well as the loss of accuracy of ellipsometry due to diffraction of the laser on the patterned films as the films become thicker.

We have observed that with all of our continuous film samples, the increase in film thickness per layer is proportional to the square root of the ionic content of the adsorption solution, as predicted for polyelectrolyte adsorption on neutral surfaces and charged surfaces in the case of screening enhanced adsorption.[16] The square root dependence of film thickness on ionic strength is derived from theoretical predictions of the radius of gyration of a polyelectrolyte in aqueous solution.[17] Our observations are also consistent with previous experimental studies of ionic layer-by-layer films[18] but are counter to observations made by Decher[19] on similar multilayered films, in which thickness was proportional to the square of ionic content. It is also worth noting that we observe significant increases in layer thickness at salt concentrations ranging from 0.01 M and higher, whereas Decher[19] and others have observed or predicted little or no effect in systems until 0.1 M ionic content was reached.[16,20]

A summary of the bilayer thicknesses for 10 mM SPS samples appears in Table 1. Data for samples that were dried between each step and data from a similar set of nondried 10 mM SPS samples are given for comparison. The numbers shown represent the average bilayer thickness derived from the data for each set. Both sets of data show a characteristic increase in the bilayer thickness as the ionic content increases from 0 to 0.4 M. After 0.4 M, the thickness decreases, until at 2.0 M, there is no evidence of bilayer growth on the COOH region at all. This effect is discussed in detail in patterned films in the following section.

Selectivity Dependence on NaCl Concentration: Results with a Drying Step. One series of

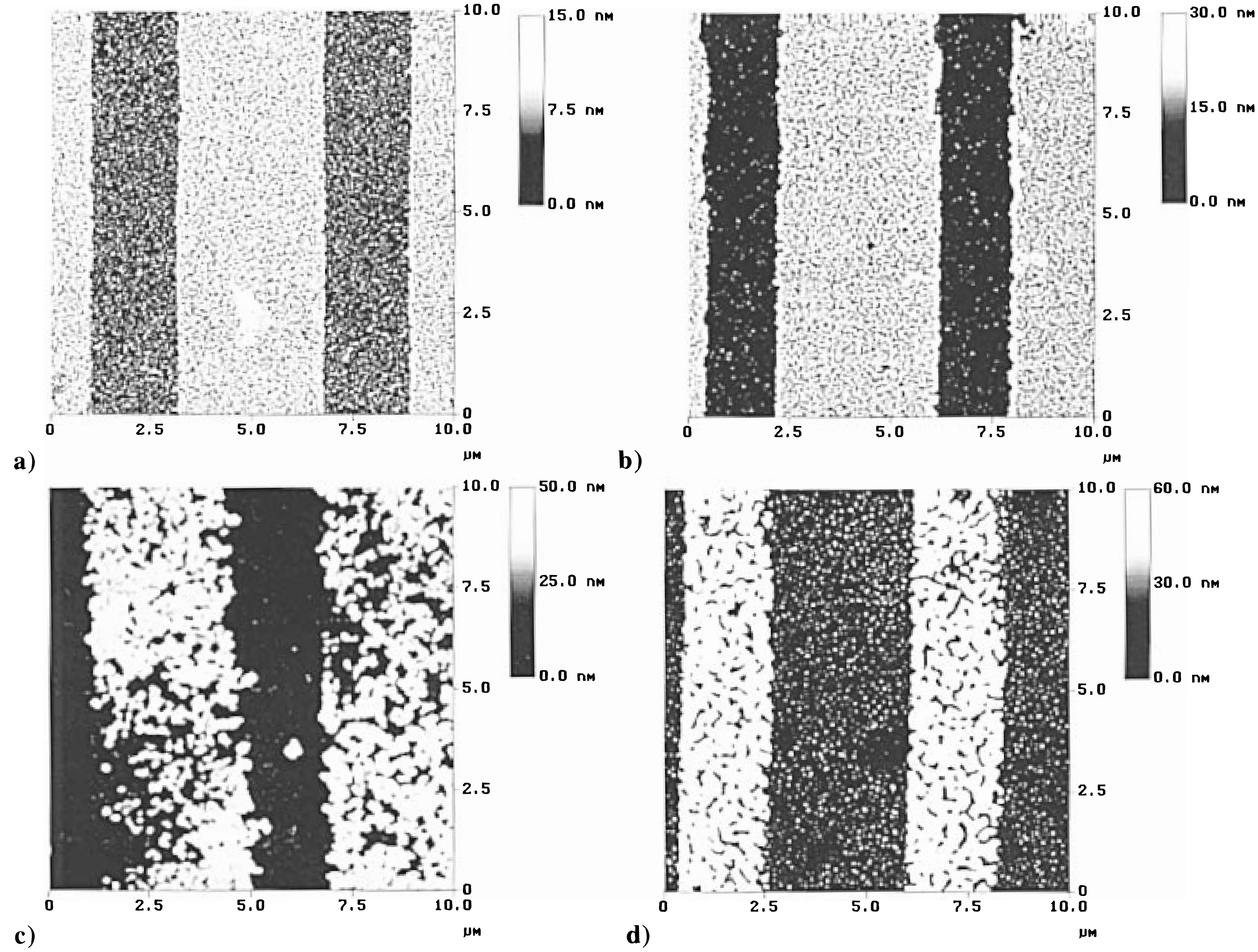


Figure 4. AFM tapping mode micrographs of patterned multilayer structures for different NaCl concentrations fabricated with a drying step and 10 mM SPS: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M; (d) 1.0 M. Wider 3.0 μm stripes are the COOH surfaces.

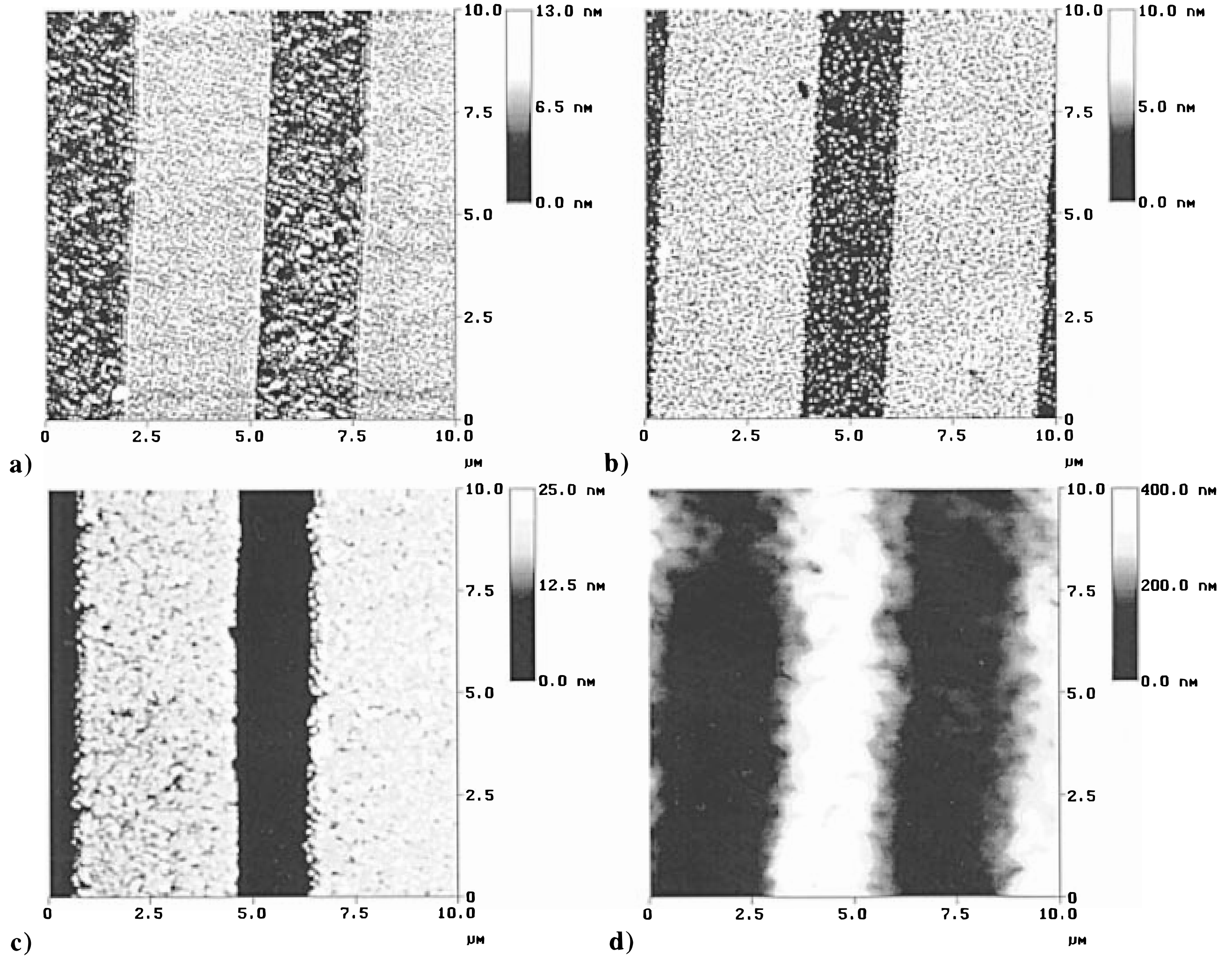
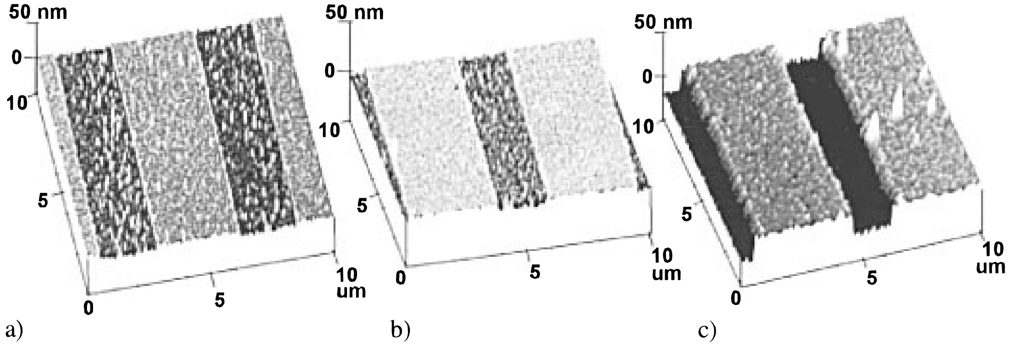


Figure 5. AFM tapping mode micrographs of patterned multilayer structures at different NaCl concentrations fabricated with a drying step and 20 mM SPS: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M; (d) 1.0 M. Wider 3.0 μm stripes are the COOH surfaces.



a) b) c)

Figure 6. Side view of same samples in Figure 5 (20 mM SPS and a drying step) showing increased film thickness as the NaCl concentration increases: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M.

samples included a nitrogen drying step after the aqueous rinse step of each dipping cycle. Figures 4 and 5 contain AFM micrographs taken of 13 bilayer patterned films prepared from solutions of increasing ionic content with 10 and 20 mM SPS concentrations, respectively. In these micrographs, the lighter regions of the surface indicate regions of polyion film adsorption. Figure 6 presents a side view of the AFM micrographs depicted in Figure 5a–c to give an indication of edge resolution and relative film thicknesses. The patterned samples exhibited improved selectivity as the salt concentration rose from 0.01 to 0.1 M, as indicated in Figures 4 a,b and 5a–c. Polyion deposition on the EG resist region appears as spots or flecks of white material on the otherwise dark resist regions. The selectivity improvement is seen as a decrease in the adventitious polyion adsorption on the EG resist with increasing salt concentration and is particularly marked for the 20 mM sample in Figure 5c. Clearly, the degree of polymer deposition on the EG resist region decreases on addition of small to moderate amounts of NaCl. The height of the multilayers formed on COOH increases almost 6-fold from 6 nm at 0.001 M NaCl to 34 nm at 0.4 M NaCl with respect to the height of the resist regions.

The edge effects seen in the samples made from solutions of low or no salt concentration are lessened at moderate salt concentrations. Molecular conformation also appears to affect the roughness of the films.

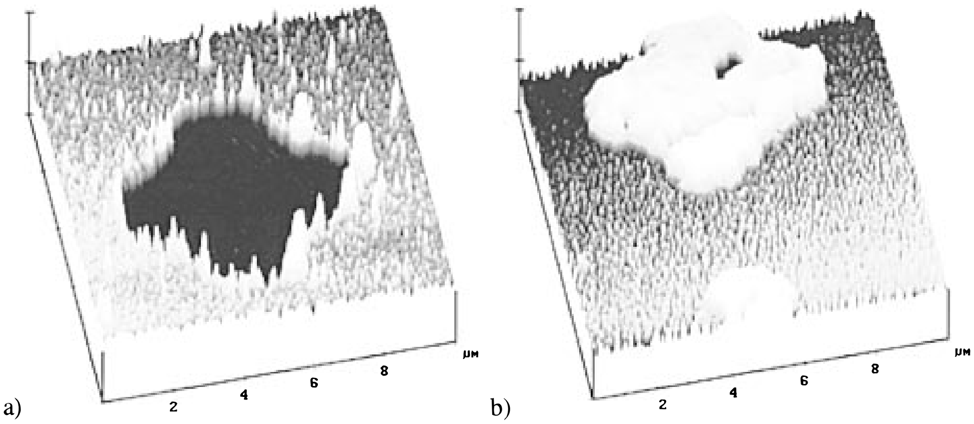


Figure 7. Two AFM tapping mode micrographs depicting reverse deposition: (a) 20 mM SPS concentration, 0.1 M NaCl, and no drying step; (b) 10 mM SPS concentration, 1.0 M NaCl, and a drying step. Crosses are EG surface.

Extended rods make smooth, thin layers (2 nm rms roughness), while random coils create thicker, rougher layers (6−12 nm rms roughness). These effects may be due in part to the more globular shape of the adsorbed molecules, as well as a more uneven adsorption on the COOH surface due to competitive adsorption with small ions, and some degree of desorption at much higher salt contents.

When the salt concentration is increased from 0.1 to 1.0 M NaCl, the deposition of polyion on the COOH is greatly decreased until only a small amount of patchy film is formed on the COOH ink regions. On the other hand, high salt concentrations for these samples appear to induce the adsorption of very thick polyion layers onto the narrower EG resist regions. In short, the deposition of the polyions is literally reversed at high salt concentrations. This phenomenon is illustrated in Figures 4d and 5d for the 10 and 20 mM SPS systems in which the rinse step was accompanied by a drying step. A more persuasive demonstration of the reversed deposition is shown in Figure 7 as the cross-stamped surface more clearly delineates the SAM regions. As can be seen, the COOH region changes from the area on which polyions selectively deposit to a region of poor polyion adsorption. In the meantime, the EG regions, which resisted adsorption of polyion at low and moderate salt content, become favorable sites for adsorption at high salt concentrations. A major difference between the 10 and the 20 mM samples is the concentration at which the bilayers begin to break up on the COOH region and reverse deposition begins. This point is reached at a lower salt concentration for the 10 mM SPS sample series, as seen by comparing Figures 4c and 5c. The polyelectrolyte adsorbed on the EG resist at 1 M NaCl is much thicker for the 20 mM SPS system in Figures 4d and 5d. The nature of the deposition onto the resist regions under these conditions appears to be a macroscopic adsorption rather than a monolayer adsorption process.

Selectivity Dependence on NaCl Concentration: Results without a Drying Step. To better understand how deposition selectivity is affected by drying the bilayer samples, a series of samples was prepared with the drying step eliminated from the overall procedure. Results from AFM studies of these samples are shown in Figure 8a−e. At low to moderate salt concentrations (Figure 8a−c) these patterned samples showed a result similar to what was observed in samples prepared with a drying step; the height of ionic multilayers deposited on the COOH regions grew and roughness increased until about 0.1 M NaCl, as indicated by the AFM. The bilayer thickness increased with salt concentration for both patterned (10 bilayers) and unpatterned multilayers (5 bilayers). The maximum height was reached at a NaCl concentration of 0.4 M. Under these conditions, the features of the patterned multilayers were 4 times the height of a patterned sample without added salt.

Unlike the samples prepared with a drying step, no reversal of the deposition was observed at higher salt concentrations (see Figure 8d,e). The COOH regions adsorbed less polyion at high NaCl, but the EG layer did not adsorb noticeable amounts of polymer. At very high salt concentrations (greater than 1 M NaCl), no pattern was visible as both EG and COOH became poor adsorption sites for the polyion. The drying step appears critical to the reversal of adsorption for the EG surface but is not significant to the reversed adsorption on the COOH surface.

In general, when comparing dried, patterned samples to samples prepared without a drying step, we observed that the EG resist appears to be much cleaner, with less adsorbed polyion, for any given salt concentration below 1 M. The drying step decreases the overall effectiveness of the EG resist, presumably by gradually decreasing the degree of hydration of the resist surface.

Model for Adsorption on Patterned Surfaces. Figure 9 contains plots of the total film thickness of continuous five bilayer films as a function of NaCl concentration. Above 0.4 M NaCl, deposition dropped off significantly until close to no material was adsorbed on the COOH surface. This sort of behavior has been described by van De Steeg[21] and others[16] as "screening-reduced adsorption". This phenomenon occurs when ions screen electrostatic interactions between the polyelectrolytes and the surface and more effectively compensate for the surface charge. At high enough concentrations, it is proposed that the ions will displace polyions that are already electrostatically adsorbed to the charged surface.

We therefore propose a model of selective polyion deposition which can be represented by the schematic in Figure 10. At low NaCl concentration, the initial polycation layer adsorbs preferentially onto the ionizable COOH surface, forming the basis for sequential deposition of SPS/PDAC bilayers. The polyion takes on a chain-extended conformation and adsorbs as a two-dimensional chain, resulting in thin bilayer thicknesses of 5−15 Å. The EG surface is hydrated and provides an entropic barrier to deposition, thus minimizing

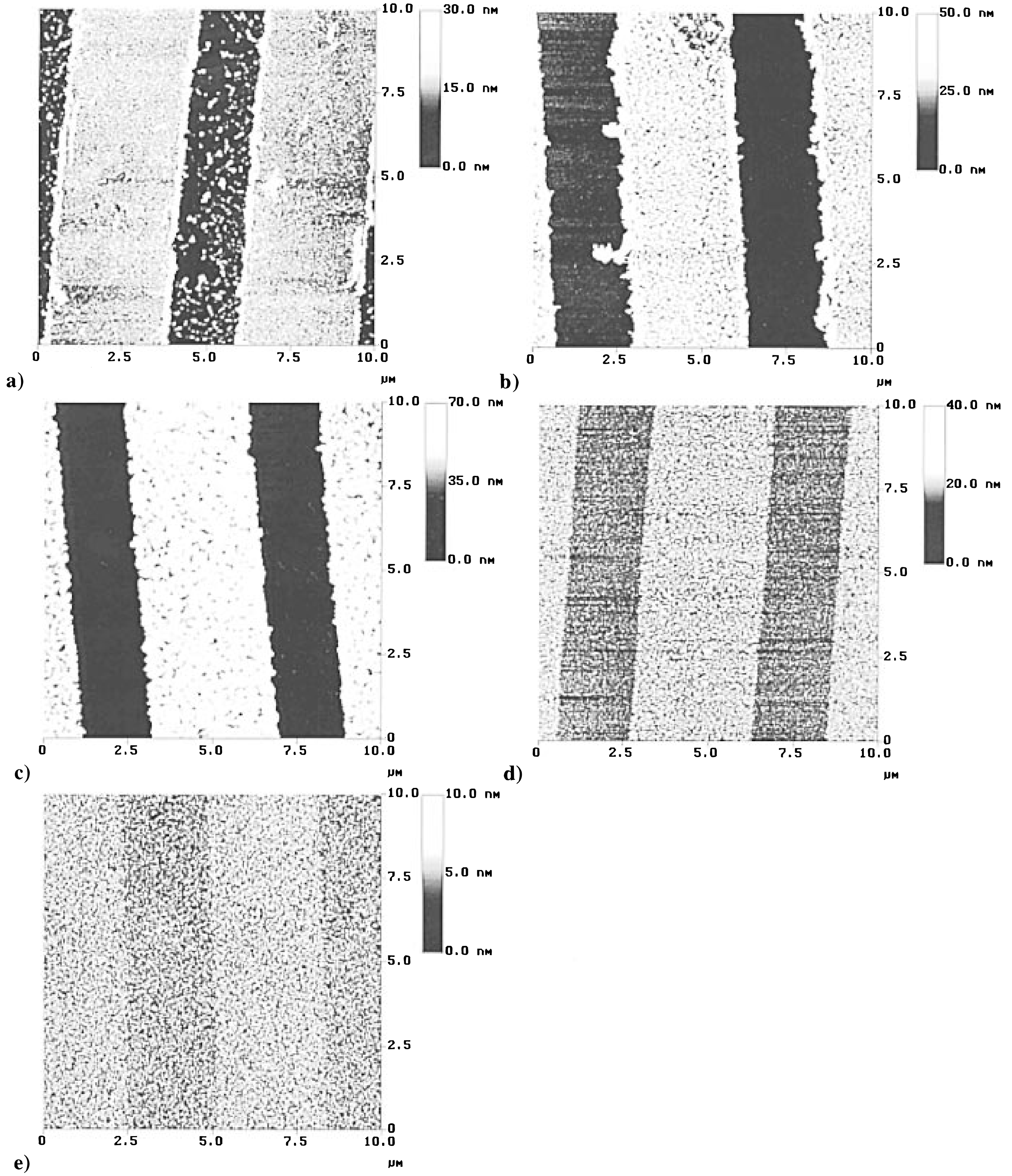


Figure 8. AFM tapping mode micrographs of patterned multilayers deposited from 10 mM SPS solutions with increasing NaCl concentrations: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M; (d) 1.0 M; (e) 4.0 M. Wider 3.0 μm stripes are the COOH surfaces.

polyelectrolyte deposition; this hydrated layer may exist as a brushlike entity or as a hydrated shell. Grunze et al.[22] have found spectroscopic evidence for the formation of an ordered helix of oligo(ethylene glycol) in the presence of water for similar SAMs using grazing angle FTIR. This hydrated layer prevents the unfavorable adsorption of most polymer, though it is most effective for the lower molecular weight polyions.[13]

At moderate NaCl concentrations, the first polycation layer is able to adsorb effectively on the COOH surface, allowing the formation of bilayers. The polyion becomes partially shielded, and the polymer chain takes on a more random coil or globular shape, leading to thicker layers. At intermediate NaCl concentrations, it is probable that the Na^+ ions complex with the EG resist due to an affinity of the ions for the EG functional group.[23,24] The presence of small ions at the surface stabilizes the hydrated layer and provides an additional barrier to the adsorption of polyion on EG, making it a more effective resist.

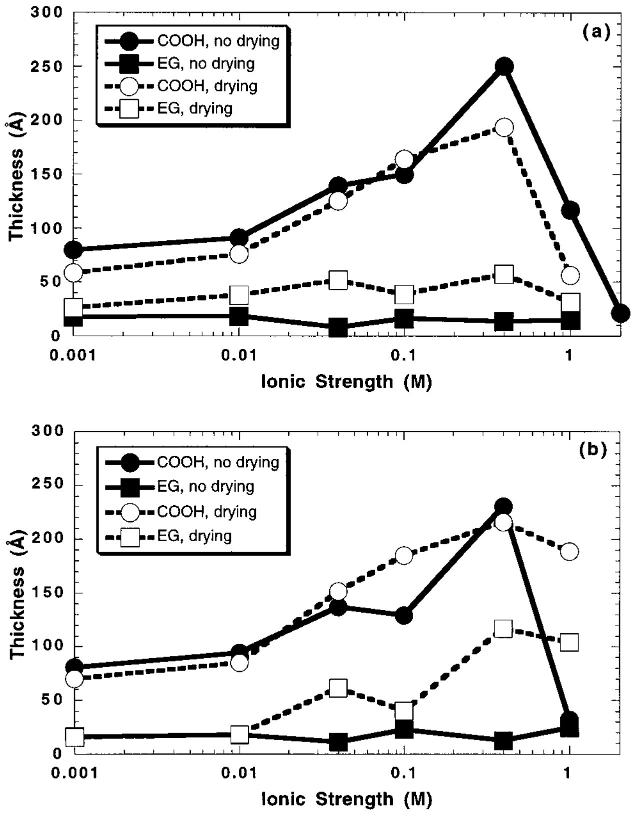


Figure 9. Plots showing the thickness of continuous five bilayer films on COOH (circles) and EG (squares), with (broken line) and without (solid line) a drying step: (a) 10 mM SPS; (b) 20 mM SPS.

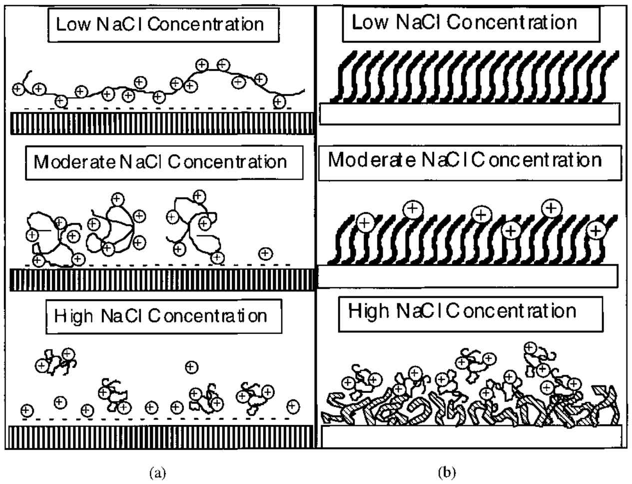


Figure 10. Cartoons of (a) screening reduced adsorption on the COOH surface and (b) dehydrating the EG surface to promote polyelectrolyte adsorption.

Finally, at very high salt concentrations, the Na^+ ions begin to compete with (now highly shielded) polycations for adsorption on the COOH surface, and the amount of adsorption of the initial polycation layer on the surface is greatly decreased, thus eliminating the possibility of building bilayers on this surface. On the other hand, the EG resist, when exposed to high salt concentrations and subsequently dried, becomes dehydrated. This phenomenon is possibly related to the phenomenon of "salting out" PEO at high salt concentrations due to changes in the degree of hydration of the polymer in the presence of additional ions. The "salted out" EG layer becomes a hydrophobic adsorption site on which highly shielded polyion molecules can readily adsorb to form thick layers. The result is the reverse deposition observed in this patterned multilayer system.

Implications and Conclusions

We conclude that varying ionic content not only changes the attributes of the multilayers but also varies the ability of the chemically patterned surface to template adsorption. Salt changes the conformation in polyelectrolytes and alters the thickness and roughness of patterned ionic multilayers.

Maximal selectivity and film thickness are achieved at a salt concentration of 0.1/0.4 M NaCl, with no drying step, and with a 10 mM concentration of SPS. At low salt concentrations the ability of the COOH region to adsorb layers of polyelectrolyte is not hindered. As the small electrolytes become more concentrated, the surface charges and the polyelectrolyte charges are screened, decreasing the driving force for polyion adsorption on the COOH surface. At the highest NaCl concentrations (>1 M NaCl), this driving force has completely disappeared.

We have observed an unexpected reversal of the adsorption behavior of polyelectrolytes on SAM surfaces in the presence of high salt concentrations. Higher ionic content (1 M) coupled with a drying step produced "reverse deposition"; the SAM regions that previously promoted polyelectrolyte adsorption prevented it and areas designed to discourage adsorption promoted it. High salt concentrations (≥ 1 M NaCl) screened the electrostatic attraction between the ionized surface and the polyelectrolytes, while the high salt concentration coupled with drying dehydrated the EG resist, promoting adsorption.

These observations may provide the basis for the patterning of complex three-dimensional superstructures. For example, it is conceivable that a first system of patterned bilayers may be put down on a surface, followed by a second step to reverse the adsorption behavior of the EG surface. Then a new series of bilayers may be used to cover or blanket the original patterned polymer film, forming a layered system appropriate to a simple optical or electrical device. By manipulating adsorption conditions such as ionic content and pH, there is the potential to further control adsorption on patterned surfaces to achieve more complex microstructures and advance research in the chemical design of adsorption templates.

Acknowledgment. The authors gratefully acknowledge the Office of Naval Research, grant number N00014-96-1-0789, for support of this work. Services for this work were also supported in part by the MRSEC program of the National Science Foundation, DMR-9400334.

References and Notes

(1) Decher, G.; Hong, J.-D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321–327.
(2) Decher, G.; Hong, J.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430–1434.
(3) Cheung, J. H.; Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2712.
(4) Ferreira, M.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107.
(5) Fou, A. C.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7115.
(6) Dressick, W. J.; Calvert, J. M. *Jpn. J. Appl. Phys., Part 1* **1993**, *32*, 5829.
(7) Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817.
(8) Kleinfeld, E. R.; Ferguson, G. S. *Science* **1994**, *265*, 370.
(9) Service, R. F. *Science* **1994**, *265*, 316.

(10) Lee, H.; Kepley, L. J.; Hong, H.-G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2597.

(11) Cheung, J. H.; Fou, A. F.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 985−989.

(12) Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485−1487.

(13) Clark, S. L.; Montague, M.; Hammond, P. T. *Supramol. Sci.* **1997**, *4*, 141−146.

(14) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498−1511.

(15) Lvov, Y.; Decher, G.; Mohwald, H. *Langmuir* **1993**, *9*, 481−486.

(16) Böhmer, M. R.; Evers, O. A.; Scheutjens, J. M. H. M. *Macromolecules* **1990**, *23*, 2288−2301.

(17) Nordmeier, E. In *Polyelectrolytes (Special Properties in Solution)*; Nordmeier, E., Ed.; CRC Press Inc.: Boca Raton, FL, 1995; Vol. 7, p 5816.

(18) Baur, J. W. Fabrication and Structural Studies of Sequentially Adsorbed Polyelectrolyte Multilayers. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1997.

(19) Lvov, Y. M.; Decher, G. *Crystallogr. Rep.* **1994**, *39*, 628.

(20) Böhmer, M. R.; Cohen-Stuart, M. A.; Fleer, G. J. *Macromolecules* **1990**, *23*, 2301−2309.

(21) van de Steeg, H. G. M.; Cohen Stuart, M. A.; de Keizer, A.; Bijsterbosch, B. H. *Langmuir* **1992**, *8*, 2538−2546.

(22) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B*, submitted for publication.

(23) Bailey, F. E.; Koleske, J. V. *Poly(ethylene oxide)*; Academic Press: New York, 1976.

(24) Dennison, K. A. Radiation Crosslinked Poly(ethylene oxide) Hydrogel Membranes. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1986.MA970610S

MA970610S