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Factors Controlling the Growth of Polyelectrolyte Multilayers

Stephan T. Dubas and Joseph B. Schlenoff*

Department of Chemistry and Center for Materials Research and Technology (MARTECH),
Florida State University, Tallahassee, Florida 32306

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ABSTRACT: The dependence of polyelectrolyte multilayer thickness on salt concentration, salt type, solvent quality, deposition time, and polymer concentration is evaluated. Polymers are deposited on spinning silicon wafers. For the strong polycation/polyanion pair studied, film thickness is approximately proportional to the number of layers and the salt concentration. The irreversibility of overall molecule adsorption is indicated by the lack of exchange of surface (radiolabeled) for solution polymer. The hydrophobic nature of the driving force for polymer sorption is illustrated by the choice of salt counterion or solvent. Analyzed within the framework of ion exchange, the net energy of ion pair formation is not high, at most a few *kT*. Salt, competing with polymer segments for the surface, permits localized rearrangements. In the mechanism proposed, excess polymer is accommodated within several layers, rather than in one layer of loops and tails. Steric barriers coupled with slow conformational changes are responsible for long-term polymer adsorption. Considering the disorder and interpenetration, multilayer buildup has much in common with solution phase or coprecipitated polyelectrolyte complexes. Surface hydrophobicity can be enhanced using fluorinated surfactants as counterions.

Introduction

Uniform thin films of polyelectrolytes may be assembled on a variety of substrates by alternating exposure to solutions of polyanions and polycations.[1−5] Each exposure deposits a reproducible quantity of material and reverses the charge on the surface, leaving it primed for the next layer of polymer. Much of the recent work on these polyelectrolyte multilayers has focused on generalizing and expanding the technique to various combinations of charged components, including synthetic polyelectrolytes, biopolymers such as proteins,[6,7] clay minerals,[8] dendrimers,[9] metal colloids,[10] silica,[11] and other inorganic particles.[12,13] Applications have surfaced almost simultaneously and include conducting layers,[14] permselective membranes,[15,16] enzyme-active thin films,[17] sensors,[18] light-emitting thin films,[19] selective area patterning,[20] electrochromic films,[21,22] electrocatalysis,[21] and noncentrosymmetric films for nonlinear optics.[23]

Comparatively little attention has been paid to the structure of these novel films and to the mechanism of their formation. At first glance, the electrostatic nature of the assembly process would seem to be intuitive and somewhat trivial. However, it was shown quite quickly that the polymers are not stratified into well-defined layers but are dispersed and interpenetrating.[5,24] Thus, the anisotropy in physical properties cannot be as significant as they are in, for example, inorganic superlattices grown by molecular beam epitaxy.[25] Apart from the finding that intermixing occurs on a molecular level, a good microscopic picture of multilayer buildup and the impact of growth conditions has been lacking. Recent works have begun to address compositional and structural details. For example, we evaluated the way net charge neutrality is maintained and found that small ("salt") ions do not participate in charge balance within as-made multilayers.[26] Lowack and Helm,[27] using the surface forces apparatus, investigated steric and electrostatic interactions between multilayer-bearing surfaces and concluded that ion pairing causes attraction between oppositely charged polymers and an electrostatic barrier limits the amount adsorbed.

In exploring growth conditions, it is generally observed that salt has the strongest influence on the amount deposited ("layer" thickness) per cycle. Polymer concentration, molecular weight, and deposition time are known to be less important variables.[2,4,5] In this paper we present a coordinated study of growth conditions on polyelectrolyte deposition, including the effect of salt concentration, salt type, exposure time, polymer concentration, and solvent quality. In our studies we employ robotic deposition at a spinning disk, which ensures well-defined, efficient transport of material to the surface. We then present an analysis of the forces that drive and control multilayer formation.

Experimental Section

Silicon wafers (Si⟨100⟩, 0.5 mm thick, 1 in. diameter, undoped, polished on one side, Topsil Inc.) were cleaned in 70% H_2SO_4(concentrated)/30% $H_2O_{2(aq)}$ ("piranha": *caution*, piranha is a strong oxidizer and should not be stored in closed containers) and then in hot H_2O_2/ammonia/water, 1:1:7 vol/vol, rinsed in water, and blown dry with a stream of N_2. Polystyrenesulfonate, PSS (sodium salt, molecular weight, MW, 5×10^5, Scientific Polymer Products), and poly(diallyldimethylammonium chloride), PDADMAC (MW 300 000−400 000, Aldrich), were dialyzed extensively against distilled water using 3500 molecular-weight-cutoff dialysis tubing. Radiolabeled poly(*N*-methyl-2-vinylpyridinum chloride), PM2VP, MW 133×10^3, was prepared as described previously.[26] Distilled water was passed through a Millipore deionizer before use. All polymer solution concentrations are quoted with respect to the monomer repeat unit. Salts (from Fisher or Aldrich) were either dried at 110 °C for 18 h (LiCl, KCl, NaCl, NaBr, NaI) or obtained as the anhydrous grade in sealed ampules (NaF, CsCl, RbCl).

The Si substrates were affixed to a stainless steel shaft with a small spot of melted high-vacuum wax (Apiezon) applied to

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* Corresponding author.

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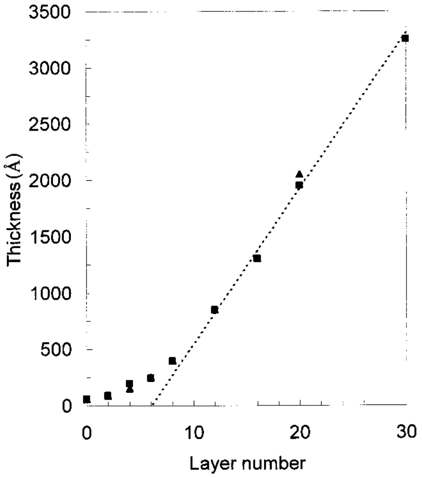


Figure 1. Thickness as a function of the number of layers for a PSS/PDADMAC multilayer deposited on silicon wafer from 1.0 M $NaCl_{(aq)}$. Odd layers are from PDADMAC and even layers from PSS. Hydrodynamic deposition at 600 rpm; polymer concentration 1 mM; 5 min deposition time with three water rinses between layers. Sample was either dried between layers (squares) or left in contact with solution (triangles). The latter condition was employed for subsequent experiments. Many points are superimposed.

the back (unpolished) side of the wafer. The shaft was rotated at speeds from 50 to 2000 rpm by a small dc motor containing an integral tachometer. A home-built robotic platform, accommodating eight 100 mL beakers, was programmed to expose the wafer alternately to two polymer solutions with three rinses of fresh water in between. Rinse and polymer solution volumes were approximately 50 mL each.

Thicknesses were determined using a Gaertner Scientific L116B Autogain ellipsometer with 632.8 nm radiation at 70° incident angle. The differences in ellipsometric thickness between measurements in ambient and in dry N_2 were less than 5%. Thus, while there is certainly water within the multilayers, thickness measurements made in ambient were judged to be adequate for comparison purposes. Uniformity of films was better than 2%, and reproducibility of film thickness between samples was ±5%. Some of the wafers were coated with aminopropyltrimethoxysilane (APT) according to a published procedure.[28] This produced an additional 40 Å of positively charged layer. Thicknesses of films using this procedure for surface modification were similar to those whose substrate treatment terminated with peroxide/ammonia. Multilayers coated with APT adhered better to the substrate. For example, they did not detach in the presence of surfactants.

The effect of cross-contamination was checked by mixing 1% of the oppositely charged counterpart into the polyelectrolyte solutions. At strongly nonstoichiometric ratios water-soluble polyelectrolyte complexes would be formed.[29] Multilayers made from these solutions had the same thicknesses as those from uncontaminated reagents.

Water/multilayer contact angles were measured under ambient conditions with a Rame-Hart contact angle goniometer. In this work, "layer" refers to the amount deposited after exposure to one of the polyelectrolyte solutions, and "layer pair" is used to describe a negative/positive polymer "bilayer".

Results and Discussion

Thickness vs Salt Concentration. The trends in films thickness on these rotating substrates are similar to those for static dip-cycled multilayers.[1-5] Layer thickness for the PSS/PADMA combination, as a function of the number of deposition cycles, does not depend on whether the multilayer has been dried between layer pairs, as shown in Figure 1.[30] For a given number of layers the experimental variable with the greatest influence on the amount deposited is the salt concentration. In Figure 2 the thickness (which is assumed to be proportional to the amount deposited) of a 10-layer pair film shows an almost linear dependence on salt concentration between 10^{-2} and 2 M. This is in contrast to the early findings of Lvov and Decher,[3] who reported that the thickness of a layer pair of PSS/poly(allylamine hydrochloride), PAH, was proportional to the ionic strength squared. Recent work by Lösche et al.[31] on the same system has established a linear relationship of layer pair thickness with salt concentration. Significantly, the steady-state increment per layer pair for PSS/PDADMA (e.g., 270 Å/layer pair in 1 M NaCl, from Figure 1) is 7 times higher than the increment for PSS/PAH[31] under the same conditions. This demonstrates the importance of polyelectrolyte type in determining ultimate film thickness.

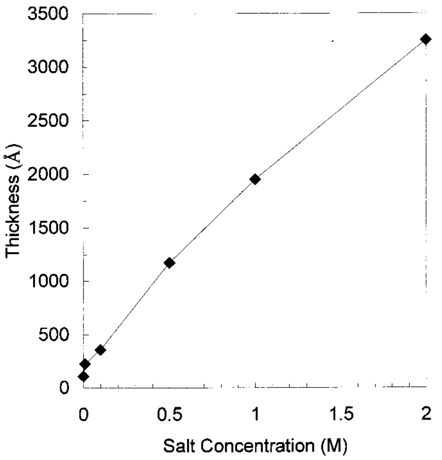


Figure 2. Film thickness vs salt concentration (NaCl in the polymer solution) for multilayers with 10 layer pairs each. Other conditions as in Figure 1.

The adsorption of polyelectrolytes onto an oppositely charged surface is an ion exchange phenomenon,[32] where charged segments replace small ("salt") ions compensating the surface charge, as in eq 1. Pol^- and Pol^+ are charged polymer segments, Pol^-Pol^+ is an ion pair, and M^+, A^- are salt counterions. The subscript "m" refers to the multilayer surface or, more precisely, a region close to the surface. If the salt ions are radiolabeled, it is possible to observe, in situ, the displacement of these ions by polyelectrolytes.[33] We have found, for example, that

$$\mathrm{Pol^-M^+}_{(m)} + \mathrm{Pol^+A^-}_{(aq)} \rightleftharpoons \mathrm{Pol^-Pol^+}_{(m)} + \mathrm{M^+}_{(aq)} + \mathrm{A^-}_{(aq)} \quad (1)$$

at low salt concentration polyelectrolyte segments are very efficient at seeking out surface charge.[34] From a first-order analysis, it appears that an appropriate model would be the adsorption of a charged polymer on an oppositely charged planar substrate, which has been treated theoretically and experimentally in some detail.[35] Charged polymer segments compete with added salt ions for charged surface sites. For adsorption via a purely electrostatic mechanism, at some point the concentration of salt ions, c_{sc}, is sufficient to displace all the polymer from the surface. This desorption transition has been examined theoretically by Wiegel,[36] by Muthukumar,[37] and by van de Steeg et al.,[38] who predict c_{sc} to scale as $(\alpha\sigma_0)^{0.9}$ where α is the average charge per repeat unit and σ_0 is the surface charge density. The dependence on molecular weight, M, is rather weak ($c_{sc} \sim M^{-1/5}$). For a fully charged polyelectrolyte ($\alpha = 1$) on a surface of high charge (e.g., $\sigma_0 = 0.2$ C m^{-2}) c_{sc} would be a physically unreachable several hundred M.[39] For weak polyelectrolytes, however, desorption might occur much earlier.

In order for polyelectrolyte to *accumulate* at the surface with added salt, an additional "chemical" interaction, X_s, of polymer with surface must be invoked:[38] essentially, there are additional contributions (e.g., hydrophobicity, dipolar interactions) to a net negative free energy term. In ion exchange terminology, this would correspond to a preference of polymer segment (over counterion) for surface signaled by a selectivity coefficient of >1.[40]

Hydrophobicity and Solvent Quality. The mechanism of interaction is charge compensation (the term is used here instead of "electrostatic"),[41] and the driving force is the multiplicity of segment−segment contacts acting cooperatively. In a crude approach, the binding free energy scales as the number of charges on the polymer, and the entropic release of small counterions accounts for strong binding.[32] A specific affinity of one polymer segment for another (polymer for surface) is characterized by X_s.[32] Recognizing the hydrophobic nature of the polymer/polymer contact, this affinity has been termed ion pairing.[27,32]

We can estimate the magnitude of X_s from the ion exchange literature. For example, the equilibrium constant for ion uptake relative to lithium for a sulfonate site in a slightly cross-linked polystyrene gel ranges from 1 to 7 for small ions.[40] This preference of one ion over another is not strong and represents 0−5 kJ mol^{-1} (0−2 kT). This result is similar in magnitude to oppositely charged polyion segment−segment free energies estimated previously.[27,42,43] Since we are considering adsorption in terms of ion exchange, we expect that different ions with differing affinity should modulate the adsorbed amount. In ion exchange, as a rule, the ion that swells the exchanger the least binds more strongly.[40] In other words, the least hydrated ion pair should be the most stable. For example, in the alkali metal series $\mathrm{Li}^+ \rightarrow \mathrm{Cs}^+$, the least solvated ion (Cs^+) binds the strongest to sulfonate exchanger. Multivalent species are much stronger binders than univalent ones.

The effect of salt type on polymer adsorption can be viewed from two complementary perspectives. First, a stronger binding salt ion would be functionally equivalent to adding more salt. Second, a less solvated, stronger binding ion would decrease the solvation energy of solution polymer (depicted with a condensed counterion[44] in eq 1), which would drive the polymer to the interface.

In Table 1 are summarized the thicknesses of multilayers with 10 layer pairs prepared from solutions containing different salt ions. Results for an anion series, using sodium as cation, and a cation series, holding the anion constant (chloride), are tabulated. The activity, rather than the concentration, was fixed at 0.33 for the sake of thermodynamic rigor. The trend reveals that the least hydrated ions[45] yield thicker films. Although the concentration is also increasing slightly due to decreasing activity coefficients, this change is not sufficient to account for the large increases in film thickness. The results for the proton appear (not surprisingly) anomalous given the hydration number, but in ion exchange the proton and lithium ion behave similarly.[40]

Table 1. Multilayer Deposition of 10 Layer Pairs of PDADMAC and PSS, 1 mM Each, on Si Disk at 600 rpm; Deposition Time, 5 min; 3 × 1 min Rinses in Fresh Water between Each Layer

salt	$a/\lambda/M$[a]	n_{cation}[b]	n_{anion}[c]	multilayer thickness,[d] Å
NaF	0.33/0.632/0.52	3.5	2.7	430
NaCl	0.33/0.681/0.48	3.5	2.0	903
NaBr	0.33/0.697/0.46	3.5	1.9	900
NaI	0.33/0.723/0.45	3.5	1.6	n/a[e]
HCl	0.33/0.757/0.43	2.7[f]	2.0	705
LiCl	0.33/0.739/0.44	5.2	2.0	820
NaCl	0.33/0.681/0.48	3.5	2.0	903
KCl	0.33/0.649/0.50	2.6	2.0	1200
RbCl	0.33/0.634/0.52	2.4	2.0	1466
CsCl	0.33/0.606/0.54	2.1	2.0	1420

[a] $a/\lambda/M$ = activity/activity coefficient/concentration. [b] Hydration number of cation in aqueous solution. [c] Hydration number of anion in aqueous solution. [d] Ellipsometric thickness, ±3%. [e] PDADMAC solution precipitates in NaI. [f] Hydration number for $\mathrm{H_3O^+}$ ion.

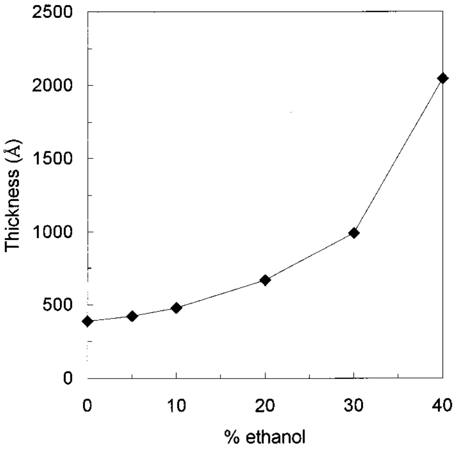


Figure 3. Thickness vs wt % ethanol for a 10-layer-pair multilayer of PSS/PDADMA from water/ethanol mixtures with 0.1 M NaCl. Other conditions as in Figure 1.

An extreme case is given by the results for iodide ion, which forms such a hydrophobic complex with $\mathrm{PDADMA_{(aq)}}$ that it precipitates. Lesser solvation of solution polymer segments would decrease intrapolymer segment repulsion, allowing more to accumulate at the surface. Arguments invoking neutralization of charge and lowering of electrostatic repulsion would point in the same direction.

An alternative to adding different counterions to make the solvent "poorer" (higher X, polymer−solvent interaction parameter) would be to vary the solvent itself, decreasing the dielectric constant so that the solvation energy for the charged, hydrophilic polyelectrolyte becomes less favorable. This should also drive the polymer to the interface. Such an experiment is summarized in Figure 3, which shows the effect on multilayer thickness of increasing the organic fraction in a water/ethanol solvent. At ethanol concentrations past 40% the polymers start to precipitate, suggesting the Θ condition is to be found near this point. It is clear that solvent composition offers another degree of control in multilayer formation.

Surface hydrophobicity can be controlled by selection of surface counterion. For example, a 10-layer-pair PSS/

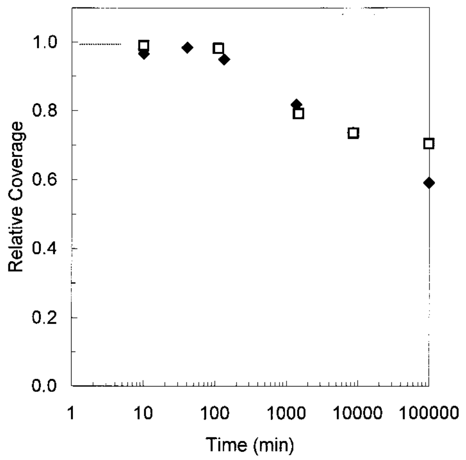


Figure 4. Kinetics of exchange of ^{14}C-labeled PM2VP as the last (terminating) layer on a 10.5-layer-pair multilayer of PSS/PDADMA. Multilayers were made with 0.1 M NaCl and exposed to 10 mM PDADMAC in 0.1 M NaCl (squares) or with 1.0 M NaCl and exposed to 10 mM PDADMAC in 1.0 M NaCl (diamonds). Coverage relative to the initial count rate is plotted as a function of immersion time in the exchanger solution.

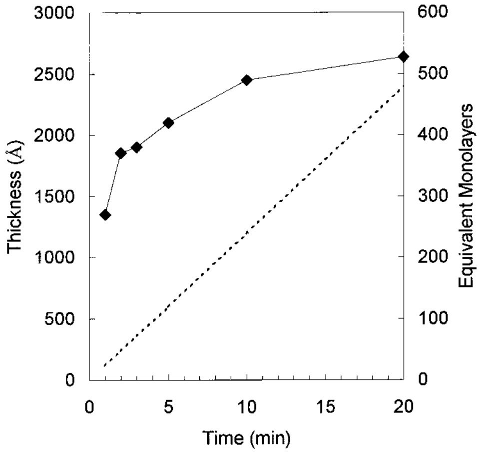


Figure 5. Thickness vs deposition time for *each* layer for 10 layer pairs of PSS/PDADMA deposited from 1.0 M NaCl. Polyelectrolyte concentration 1 mM; 300 rpm rotation rate. Also plotted is an estimate of the number of equivalent monolayers (φ) of polymer arriving at the surface as a function of time. If 20φ is required for each layer, short-time coverage is flux limited, but at longer times (>2 min) it is not.

PDADMA multilayer (terminated with PDADMA) was deposited on an APT-treated substrate. The multilayer was exposed to 2×10^{-5} M $NaCl_{(aq)}$, to ensure the surface charge was compensated by chloride ions, and blown dry. The contact angle of a 10 μL droplet was 41 ± 7°. The wafer was then immersed in a solution of 10^{-5} M perfluorooctanesulfonic acid, to exchange with Cl^-, and dried. The contact angle was 107 ± 4°. This contact angle remained unchanged after the sample was rinsed in pure water, immersed in 1.0 M NaCl for 10 min, and then rinsed in water again. The low-energy surface appears to be quite stable, perhaps due to aggregation of the perfluoroalkane chains on the surface.

Kinetics and Irreversibility. One might argue that the irreversible nature of the adsorption process is immediately apparent from consideration of Figure 2 and eq 1. Since a deposition cycle terminates with a rinse in water, an increase in film thickness with additional salt is not expected if the polymer were adsorbed in the thermodynamically reversible limit: the polymer would desorb in pure water. This, by itself, is not sufficient evidence for irreversibility in high-affinity polymer adsorption. As pointed out by Fleer et al.,[46] a pseudo-constant surface excess of polymer exists at all experimentally attainable polymer concentrations. Two additional experiments were designed to probe the extent of irreversibility. In the first, a radiolabeled positive layer (^{14}C-labeled PM2VP) was adsorbed on top of a 10-layer-pair PSS/PDADMA multilayer that had been deposited from either 1.0 or 0.1 M NaCl. After rinsing, the modified multilayers were immersed in 10 mM PDADMAC in 0.1 or 1.0 M salt to allow for exchange of labeled for unlabeled positive polyelectrolyte. As with our previous studies on similar exchange experiments on adsorbed polymers,[33] no evidence for desorption was found on the time scale of hours (Figure 4). After a few days a small fraction of polymer exchanged, and even after several weeks (note the logarithmic time axis of Figure 4) only 30–40% had exchanged. The desorption/exchange results were similar for both salt concentrations.

In the second experiment, separate wafers were coated with polymers deposited according to *one* of the following sequences:

1 M salt + 1 mM PDADMAC →
0.1 M salt + 1 mM PDADMAC → rinse → rinse →
1 M salt + 1 mM PSS → 0.1 M salt + 1 mM PSS →
rinse → rinse → repeat

or

0.1 M salt + 1 mM PDADMAC →
1 M salt + 1 mM PDADMAC → rinse → rinse →
0.1 M salt + 1 mM PSS → 1 M salt + 1 mM PSS →
rinse → rinse → repeat

Other experimental conditions were the same (600 rpm, 20 layers total, 5 min deposition time for each layer). The multilayers had the same thickness (1950 Å). We conclude that the amount of polymer deposited is controlled by the *highest (rather than the last) salt concentration polymer-containing solution to which the surface has been exposed* during a cycle. A thin layer, having been deposited from low salt concentration, is able to reconform to accommodate more polymer, but once adsorbed, polymer does not desorb.

If irreversible, one might expect the kinetics to be diffusion-controlled over much of the range of experimental coverage (“hit-and-stick”). If this were the case, plots of film thickness vs deposition time, or polymer concentration, as in Figures 5 and 6, respectively, should attain plateau values early on (“high-affinity” behavior in the latter case). Also provided in Figure 5 is an estimate of the number of equivalent monolayers of polymer arriving at the interface.[47] Apart from the first few minutes, there is plenty of flux to the surface. Both Figures 5 and 6 approach the expected form, but there is significant material adding to the multilayer throughout. There are two possible explanations for this. It has been suggested that a like-charged electrostatic barrier prevents the approach of additional polymer.[27] This argument has been used for single-layer adsorption of polyelectrolytes.[32] A gradually increasing amount with time is certainly consistent with such a barrier. How-

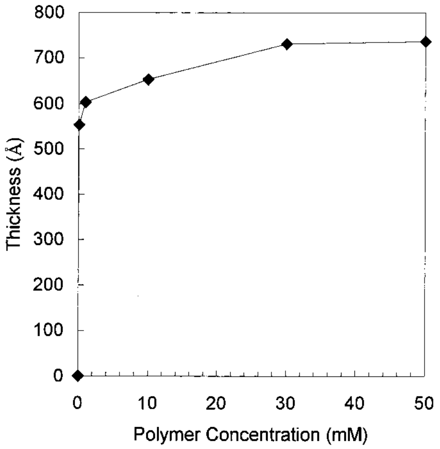


Figure 6. Thickness vs polymer concentration (for both polymers) for 5 layer pairs. Other conditions as in Figure 1.

ever, at these high salt concentrations the electrostatic interactions within the polyelectrolyte should be sufficiently screened for the polymer to behave as though it were neutral. In this regime it is more likely that steric interactions limit the addition of more polymer. This repulsion, an excluded-volume effect, would probably be coupled with slow conformational changes on the surface or within the top few layers. Such slow rearrangements are well-known in polyelectrolyte adsorption.[48,49] We have found complete self-exchange is possible for polyelectrolytes at the liquid/liquid and solid/liquid interface,[50] despite strongly adsorbing hydrophobic segments, which one would not expect if there were a repulsive electrostatic barrier in operation. In contrast, diblock (brush-forming) polyelectrolytes could not be exchanged,[34] probably due to steric (excluded volume) interactions.

The literature on polyelectrolyte multilayers contains a wide range of estimates (seconds to hours) of the "time required to form a layer." The formation of most of a layer is probably limited by mass transport of polymer to the surface. The remainder will be added under a slower regime of permeation though surface polymer and rearrangements. Solution mass transport is a function of the solution concentration and hydrodynamics, which should be specified in comparing layer formation times. For example, if solution transport were diffusion limited, it would take 1000 times longer to make a layer 10 times thicker from a solution that was 10 times more dilute. Convective diffusion, as employed here, would speed up deposition, compared to diffusion alone. Furthermore, since smaller molecules diffuse faster, and wide distribution molecular weight polyelectrolytes have been almost universally employed for PEMs, an irreversibly formed multilayer will incorporate a significantly lower molecular weight fraction of polyelectrolyte than the nominal M_n of the polymer sample.

Excess Charge. The key to polyelectrolyte multilayer propagation is surface charge reversal.[5] Each deposition step must leave the surface primed for the next immersion in oppositely charged polymer. This phenomenon is not intuitive: is has been generally assumed that polyelectrolyte associations have a 1:1 charge stoichiometry.[29] The addition of polymer is irreversible on the whole-molecule scale, as shown above, but mobility of short stretches of polymer (an adsorbed "correlation length") must occur in order to accommodate more polymer. Additional theoretical treatments of overcompensation (overcharging) are now emerging.[51−55]

According to the theory for single-layer polyelectrolyte adsorption, in the absence of added salt adsorbed layers should be thin and should overcompensate surface charge only slightly,[35,38] leading to minimal polymer buildup when the process is reiterated. This trend is observed here: with no salt added (the only source of ions is from the polymer itself, 10^{-3} M) the thickness of a 10-layer-pair film was about 60 Å. The estimated coverage (assuming a density of 1.2 g cm^{-3}) would be about 7×10^{-8} g cm^{-2} layer pair^{-1}. The coverage for a dense monolayer, φ, of PSS/PDADMA monomer pairs (molecular weight 310 g mol^{-1}) would be about 9×10^{-8} g cm^{-2}. Thus, the increment is slightly less than 1 monolayer (1φ) per cycle. For a similar system, radioisotopically labeled PSS and poly(*N*-methyl-2-vinylpyridinium), using no salt and 10^{-4} M polymer, a coverage of 3×10^{-8} g cm^{-2} per layer pair (0.3φ) was obtained.[26]

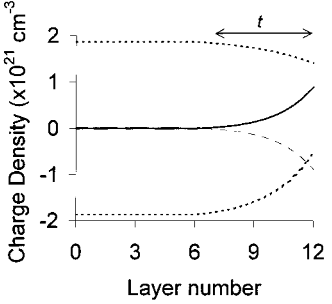
Significantly higher coverages are obtained when salt is added (see Figure 2). For example, 320 Å per layer pair (obtained with 2 M salt) corresponds to 3.8×10^{-6} g cm^{-2} or about 40φ! The single-layer adsorption theory, while a good starting point for discussion, does not predict such high amounts.

In a previous radiochemical study we accounted for the all charged species (polyions and salt ions) that could be employed in preserving net charge neutrality within a multilayer.[26] The steady-state increment of polymer per deposition cycle was rationalized in terms of a constant amount of surface charge overcompensation for both negative and positive layers. Upward curvature of thickness vs layer number plots, seen extensively at the initial stages of multilayer assembly, was explained as a transition of charge density from that at the surface of the substrate, σ_s, to the multilayer surface charge, σ_m. On substrates of higher charge, and with lower salt concentrations (e.g., 0.1 M, see ref 26), σ_m and σ_s are more closely matched, so curvature is minimized.

Since σ_m corresponds to several monolayers of polymer repeat unit, excess polymer charge must be spread out perpendicular to the substrate. Such a distribution of charge is consistent with the finding that material in a particular layer is interdiffused over several adjoining layers; i.e., significant interpenetration occurs.[5,22−24,31] Thus, a more refined picture of the multilayer surface would have excess polymer charge dispersed over several layers and not simply contained in a layer of loops and tails. Such a case is depicted in Scheme 1, which shows charge contributions from each polyelectrolyte and the resulting net polymer charge profile. Note that overall multilayer charge neutrality is maintained by salt ions. A minimum number of layers are required before the growth increment reaches its "true" steady-state value. At this point, the thickness of the layer of excess polymer charge corresponds to the "equilibrium" thickness, *t* (see Scheme 1).[56] The plot of thickness vs layer number (Figure 1) initially shows upward curvature before *t* is established. Charged species within the multilayer are depicted with exponential profiles. The theoretical background behind this scheme will be detailed in a forthcoming publication.

Experiments with the surface forces apparatus,[27] as well as the electrophoresis of multilayer coated particles,[57] have suggested that unpaired (uncomplexed) segments of the oppositely charged polymer coexist with the "surface majority" polymer. This is in contrast to

Scheme 1. Sketch of Charge Density vs Distance from the Substrate (in Terms of Nominal Layer Number) for an As-Made 6-Layer-Pair PSS/PDADMA Multilayer at 50% Relative Humidity[a]



[a] For deposition from 1.0 M NaCl, each layer would be ca. 100 Å thick. The final deposition is from PDADMAC. Contributions from positive and negative polymer are shown as dotted lines, and the net polymer charge density is shown as the solid line. The area under the latter curve would represent the polymer "surface" charge. Chloride counterions are represented by the dashed line. Charge density is estimated assuming a bulk density of 1.2 g cm^{-3} and a segment ion pair molecular weight of 310 g mol^{-1}. Several elements are incorporated into the sketch, including 1:1 stoichiometry within the bulk of the multilayer (layers 0 to 6),[26] intrinsic bulk compensation,[26] positive polymer excess charge distribution over 3 layer pairs[56] (thickness, *t*), decreasing positive and negative polymer density at the surface due to greater hydration, coexistence of polymers even at the multilayer surface,[27,67] and 20 vol % water in the bulk.[68]

our recent results where the surface charge was directly probed with small radiolabeled counterions.[26] In the latter case, polymers associate completely, and only one type of counterion was found at the surface. The disagreement may be explained partially by the fact that we employed very low salt concentration (10^{-4} M) to maintain high specific activity of the radiolabel, in which case there would be less competition by small ions for surface sites: our dilute conditions approach, in the limit, pure water. Additionally, the discrepancy could arise from the different polymers employed. The strong polyacid/weak polybase combination employed in the Lowack and Helm[27] study may form weaker ion pairs and therefore fewer polymer/polymer contacts. If this were the case, one would expect more effective competition by salt ions (eq 1), and complete desorption (at c_{sc}) might be achieved at lower salt concentrations. More weakly associated multilayers would also be more permeable to salt ions.[58]

As-made PSS/PM2VP multilayers, where the final step is a rinse in pure water, contain no bulk salt ions. The charge compensation between positive and negative was thus termed "intrinsic": each positive polymer charge was balanced by a negative segment.[26] However, Sukhorukov et al.[59] have presented evidence to show that significant swelling of multilayers can take place in the presence of salt. This is quite reasonable, since salt would compete with polymer for internal charge (eqs 2 and 3). The multilayer may be

$$\mathrm{Pol^-Pol^+}_{(m)} + \mathrm{M^+}_{(aq)} + \mathrm{A^-}_{(aq)} = \mathrm{Pol^-M^+}_{(m)} + \mathrm{Pol^+A^-}_{(m)} \quad (2)$$

$$K_2 = \frac{[\mathrm{Pol^-M^+}_{(m)}][\mathrm{Pol^+A^-}_{(m)}]}{[\mathrm{Pol^-Pol^+}_{(m)}][\mathrm{M^+}_{(aq)}][\mathrm{A^-}_{(aq)}]} \quad (3)$$

highly loaded with salt ions when exposed to solutions of significant salt concentration. It is difficult experimentally, however, to distinguish between multilayer and solution ions under these conditions. When salt-loaded multilayers are immersed into water, the ions are expelled into solution as polymer segments now have no small ions with which to compete. All charged segments form ion pairs except for those at the surface belonging to the polymer that is in slight excess (overcompensation), which require salt ions for neutrality. This interesting "ion breathing"—uptake and release of salt as the sample alternates between salt and rinse solution—is presumably occurring throughout the history of multilayer assembly.

Under the constraints of intrinsic compensation, an increment per deposition corresponding to several equivalent monolayers requires significant interpenetration of multilayer components. Although it may be advantageous to accumulate polymer quickly for certain applications, interpenetration would not desirable for devices requiring defined stratification or orientation, such as noncentrosymmetric films for nonlinear optical (NLO) applications.[60,61] In a recently described PEM,[61] the intensity of second-order NLO response followed the expected quadratic dependence on film thickness, but each layer pair was only 1.2 nm thick.

Neglecting mean field approximations, a simple expression for desorption of the chain at high salt concentration can be obtained. For a stoichiometric polymer—polymer complex, if we define the fraction of polymer in the extrinsic form as *y*, the remainder, intrinsic, is $1 - y$, and desorption should occur at

$$n = \frac{y}{1 - y} \approx \frac{1}{1 - y}$$

where *n* is the degree of polymerization. Using eq 4

$$K_2 = \frac{y^2}{(1 - y){c_{sc}}^2} \approx \frac{1}{(1 - y){c_{sc}}^2}$$

and

$$c_{sc} = \sqrt{n{K_2}^{-1}}$$

This explains the preferential adsorption of high (relative to low) molecular weight polyelectrolyte at high salt concentrations.[62–64]

Conclusions

In conclusion, we have attempted to link the effects of experimental variables into a qualitatively consistent picture of the driving forces behind polyelectrolyte multilayer formation. Our findings emphasize the overall irreversibility, and hence stability, of film formation. In evaluating the mechanism controlling surface excess, extending the theory for flat, impenetrable monolayers to multilayers underestimates the adsorbed amount, since excess polymer charge can be dispersed in the *z*-direction. Factors that make the solvent "poorer, " such as hydrophobic counterions or modifers of low dielectric constant, tend to drive solution polyelectrolyte to the surface. Given the extensive interpenetration imposed by intrinsic compensation requirements, the direction of our analysis is very much toward viewing adsorption as polyelectrolyte complex (PEC) formation. In the classical model of Michaels,[29,65,66] oppositely charged polymers form structureless "scrambled egg", physically cross-linked precipitates, generally favoring a 1:1 stoichiometry. It is appropriate to compare PEMs and PECs because the former do not form truly 2-dimensional structures. One may expect the same profusion (confusion) of behavior modalities depending on experimental variables such as salt concentration and type and whether the polyelectrolytes are weakly or strongly dissociated (not investigated here). It is evident how molecular interpenetration in PEMs can occur, *during* the buildup, over several layers: opposite charges are available for polymer−polymer complexation through more than one layer.

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