Mechanism of Polyelectrolyte Multilayer Growth: Charge Overcompensation and Distribution

Joseph B. Schlenoff* and Stephan T. Dubas

Chemistry Department and Center for Materials Research and Technology (MARTECH), The Florida State University, Tallahassee, Florida 32306-4390

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ABSTRACT: A mechanism for distributing excess polymer surface charge is used to model the growth of multilayers of strongly charged polyelectrolytes. Two parameters are required for the semiempirical analysis: the surface, or unrestricted, charge overcompensation level, ϕ, which is assumed to decrease exponentially from the film surface to bulk, and the characteristic length for this decay, l_{cp}, which is termed the charge penetration length. Modeling of the data reveals that only modest levels of polymer charge overcompensation are required to account for large increments in polymer thickness, realized at high salt concentration, since the excess charge is distributed over several "layers". Experimentally, ϕ appears to be roughly independent of salt concentration. The thickness increment is primarily controlled by l_{cp}, which is about 2.5 nominal layers for the system studied. Whereas the growth conditions and polyelectrolyte type lead to the formation of intrinsically compensated multilayers in this work, conditions for obtaining extrinsic compensation are also discussed. Kinetic vs thermodynamic limitations for polymer addition during a deposition cycle are contrasted.

Introduction

A uniform multilayer of polyelectrolytes may be deposited on a hydrophilic substrate by exposing it to solutions of polyanions and polycations in an alternating fashion.[1−5] Polyelectrolyte multilayers represent a subset of layered multicomposites by sequential adsorption (LAMSA). The LAMSA strategy encompasses a host of particle−particle,[6] molecule−particle,[7−11] and molecule−molecule systems,[5] including the strongly dissociated polyelectrolyte pair discussed herein. Much of the current intense interest in LAMSAs is motivated by the undemanding experimental requirements for their synthesis.[5,12]

Several generalizations may be made regarding the formation of LAMSAs from polyelectrolytes only, at least for strongly charged polymers of high molecular weight. First, the polyelectrolyte adsorption process is irreversible on the time scale of multilayer assembly: a property that is required for stable multilayer growth.[13] Irreversibility includes the lack of spontaneous desorption, desorption resulting from competition with small (salt) ions, and stripping of surface polymer by its oppositely charged solution counterpart.[14] Second, the most important variable for determining multilayer thickness (besides the number of layers) is the salt concentration of the solution used for deposition.[1−5] An approximately linear dependence of layer thickness on salt concentration has been noted.[15,16] Third, polymers in two-component multilayers are not stratified into well-defined layers but are dispersed and interpenetrating.[5,15,17] (In this respect, the localized microscopic disposition of polymer molecules resembles solution-precipitated polyelectrolyte complexes.[18−21]) If an additional labeled polymer is included in the layering, composition modulation in the substrate-normal direction may be observed over length scales longer than the thickness of a layer.[5,17,22] Additional variables are ranked in rough order, from significant to subtle, as follows: dielectric constant of the deposition solvent, identity of the salt, deposition time, polymer concentration, polymer molecular weight.[16] For weak polyelectrolytes, the degree of ionization becomes an important consideration.[23]

Mechanistically, the importance of surface charge overcompensation and reversal in polyelectrolyte multilayers, PEMs, has been emphasized, since each exposure deposits a reproducible quantity of material and reverses the charge on the surface, leaving it primed for the next layer of polymer.[1−5,14] Theoretical treatments of molecule−molecule and molecule−surface charge overcompensation have predicted modest overcompensation.[24−29] Recent experiments on strongly dissociated polyelectrolyte pairs, such as poly(diallyldimethylammonium), PDADMA, and poly(styrenesulfonate), PSS, have shown that, in the presence of salt, several equivalent monolayers of polyelectrolyte accumulate on the growing multilayer with a single exposure.[14,16] Extension of classical theory for the adsorption of polymers at impermeable surfaces would not predict a thick layer of polymer.[25] To account for this, we depicted excess polymer surface charge distributed over several interpenetrating layers of polycation and polyanion.[14,16]

In this paper we provide a coordinated theoretical and experimental analysis of the PSS/PDADMA system. We combine our results with earlier findings,[14] concerning the mechanism of charge balance in the surface and bulk of growing multilayers, to provide a semiempirical picture of the mechanism for buildup of multilayers.

Experimental Section

Polymers were deposited on silicon wafers (Si⟨100⟩, 0.5 mm thick, 1 in. diameter, undoped, polished on one side, Topsil Inc.) according to published procedures.[16] Wafers were cleaned in 70% H_2SO_4(conc)/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, 1:1:5 v/v, rinsed in water, and blown dry with a stream of N_2. Polystyrenesulfonate, (sodium salt, molecular weight, MW, 5 × 10^5, Scientific Polymer Products) and poly(diallyldimethylam-

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* Corresponding author.

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monium chloride), PDADMAC (MW 300−400 000, Aldrich), were dialyzed extensively against distilled water using 3500 molecular-weight-cutoff dialysis tubing. All polymer solution concentrations are quoted with respect to the monomer repeat unit.

Sequential adsorption of polyelectrolytes was performed by hand dipping or with the aid of a robot. In the latter case, deposition was done on spinning wafers affixed to a stainless steel shaft rotating at 600 rpm. Between alternate exposure to two polymer solutions, there were three rinses of fresh water. Rinse and polymer solution volumes were approximately 50 mL each. The deposition time for each layer was 5 min. Polymer concentrations were 1 mM with a rotating substrate or 10 mM with a static substrate. The concentration of salt (NaCl) was varied from 0 to 1.0 M.

Thicknesses were determined using a Gaertner Scientific L116B Autogain ellipsometer with 632.8 nm radiation at 70° incident angle. The refractive index for multilayers was 1.54. Wafer surfaces included approximately 8−10 Å of native silicon oxide. Counting of radioisotope (^{35}S, β, $E_{\max} = 0.167$ MeV, $t_{1/2} = 87$ days) was performed with a piece of plastic scintillator ($3 \times 20 \times 30$ mm, SCSN81) positioned on the end of a RCA 8850 photomultiplier tube biased to 2200 V with a Bertan 313B power supply. A Philips PM6654C frequency meter interfaced to a PC collected the counts.[30,31] Background with this setup was ca. 1 cps, and the signals from the experiments below were in the range 3−1000 cps.

The radiochemical study employed multilayers with 14 (i.e., terminated with PSS) or 15 (terminated with PDADMA) layers. $H_2{}^{35}SO_4$, provided HCl free (ICN Radiopharmaceuticals, 1490 Ci mol^{-1}), was used as a stock. Of this, 25 μCi was added to 50 mL of 10^{-4} M Na_2SO_4 to yield a specific activity of 5 Ci mol^{-1} $^{35}SO_4{}^{2-}$. Wafers constructed with polymer solutions of different salt concentrations were exposed to labeled sulfate for 15 min under stirred conditions and were then blown dry with a jet of nitrogen prior to counting. As a standard, a few microliters of labeled sulfate was allowed to dry on the surface of the scintillator.

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

Film thicknesses for PDADMA/PSS multilayers are plotted, in Figures 1−3, as a function of layer number[32] for deposition solutions containing 0, 0.5, and 1.0 M salt. The increment per deposition cycle is less toward the beginning of multilayer buildup, imparting an upward curvature to the data. This familiar PEM feature is more noticeable for concentrated salt solutions. Eventually, the thickness adopts a linear, or steady-state, dependence on layer number. The sensitivity of PDADMA/PSS multilayer assembly to variables such as salt and polymer concentration, salt type, solvent quality, and deposition time was evaluated recently.[16] All these variables impact film formation to some extent, but the major factor is the salt concentration. The commercial (Aldrich) PDADMA is branched, as is usually obtained for high conversions of the monomer.[20] Unbranched PDADMA (molecular weight 300 000, generously provided to us by R. Klitzing) yielded multilayers of equivalent thickness (±5%) as the Aldrich material, which is an indication that the level of branching in the commercial polymer does not influence the buildup of multilayers.

The role of surface charge in determining and limiting the increment of polymer added per deposition cycle was probed in a recent study using radiolabeled counterions.[14] With the strongly dissociated polyelectrolytes PSS and PDADMA a constant surface charge develops during multilayer buildup. The surface charge, propagated and inverted by sequential adsorption steps, is overneutralized (overcompensated) on each step. A steady-state thickness increment vs layer number appears when the level of overcompensation is constant. In this mechanism, the salt concentration determines adsorbed amount (layer thickness) by controlling surface charge. Here, we measure the surface charge directly using radiolabeled sulfate as counterion. The method of removing excess label from the surface of the multilayer (by a jet of gas) was somewhat less precise than the in-situ self-exchange method used previously,[14,31] but we verified, using blanks, that less than 5% of the counts came from residual electrolyte wetting the wafers.

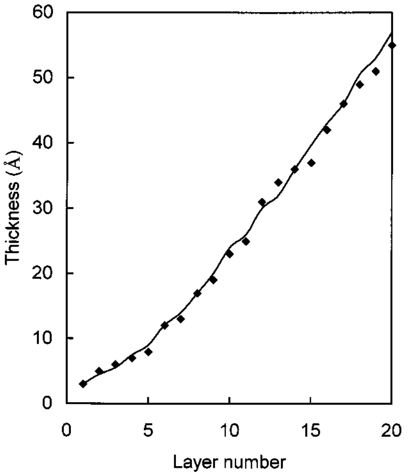


Figure 1. Thickness as a function of the number of layers for a PSS/PDADMA multilayer deposited on silicon wafer from polymer solutions containing no salt. Odd layers are from PDADMA; even from PSS. Polymer concentration 10 mM; 5 min deposition time with three water rinses between layers. Solid line is a fit to eqs 9 and 10 with $\phi = 1.72$ and $l_{cp} = 7.5$ Å. The thickness of the first layer, t_1, was measured to be 3 Å.

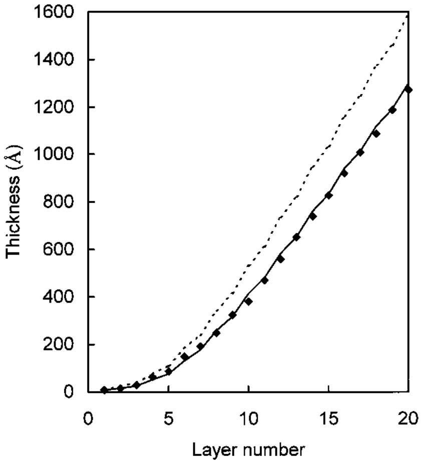


Figure 2. Thickness vs layer number for PSS/PDADMA deposited from 0.5 M NaCl. Other conditions as in Figure 1. Here, t_1 was found to be 8 Å, and fit parameters were $\phi = 1.95$ and $l_{cp} = 185$ Å. The dotted line corresponds to the same ϕ, with $l_{cp} = 225$ Å.

In Figure 4 the areal surface charge density is plotted as a function of salt concentration for PDADMA/PSS multilayers consisting of 14 (PSS-terminated) and 15 (PDAMA-terminated) layers (by this thickness, the multilayer has developed its steady-state behavior). For the 15-layer films, the pseudolinear dependence of the

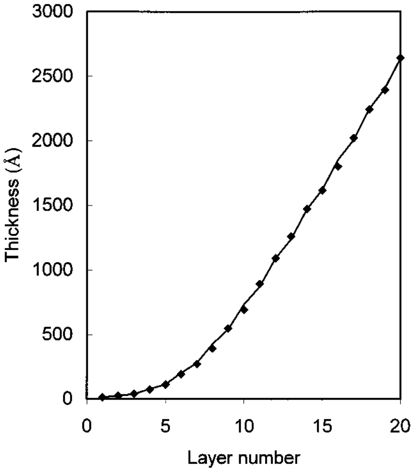


Figure 3. Thickness vs layer number for PSS/PDADMA deposited from 1.0 M NaCl. Other conditions as in Figure 1; $t_1 = 12$ Å, $\phi = 1.86$, and $l_{cp} = 425$ Å.

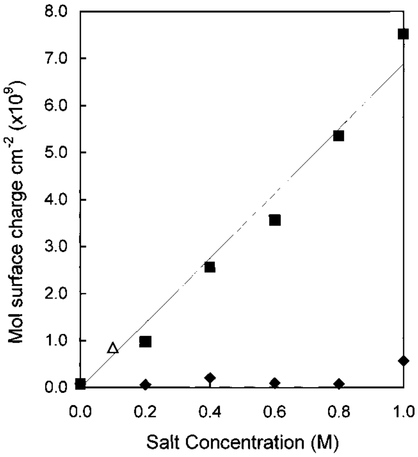


Figure 4. Positive surface areal charge density for 15-layer PSS/PDADMA multilayers (PDADMA-capped, squares), and 14-layer multilayers (PSS-capped, diamonds) made from solutions containing 1 mM polymer and different NaCl concentrations. Multilayers were robotically deposited on silicon wafers spinning at 600 rpm. The probe for surface charge was ^{35}S-labeled sulfate ion. No surface or bulk positive polymer excess charge is observed for the PSS-capped multilayer (i.e., the multilayer contains no negative salt ions). The solid line is a guide to the eye. The open triangle is from a similar strongly dissociated polyelectrolyte system.[14]

surface positive charge tracks that of the thickness.[16] When the surface bears a negative charge (14 layers), no sulfate ion is adsorbed, indicating the presence of only one salt ion within the multilayer. This implies the polymer that is not in excess is completely ion-paired with its oppositely charged partner throughout the multilayer, in disagreement with atomic force measurements on multilayers.[33,34] These latter studies, suggesting the coexistence of unpaired positive and negative polymer segments, were performed on different polymers, including a weakly dissociating cation.

A final component within the multilayers is water, some weakly and some strongly bound.[15,21] The water content, which depends on the relative humidity, was approximately 15 wt % under our ambient conditions.[21] We do not include water in our simulations (i.e., the thickness measurements are assumed to be made under dry conditions).

Internal Layering: Implications of Intrinsic Compensation. The results from the preceding section reinforce those from a prior study, in which we found, using radiolabeled salt ions, that small ions do not participate in charge balance within as-made PSS/PDADMA multilayers, a feature which we termed "intrinsic" compensation.[14] Intrinsic compensation in thick PEMs requires interpenetration of polymers: a significant constraint. For example, it is not possible to have density fluctuations (distinct stratification, composition oscillations[35]) for two components that are intrinsically compensated. For three components, wherein one is labeled, density fluctuations are possible and have been observed (i.e., Bragg reflections are seen), but the material in any nominal layer is actually interdiffused over several layers.[5,17,22] Well-defined layering would be important for certain applications requiring anisotropic properties, such as conductivity in two dimensions. The question is, are there materials and experimental conditions that would yield sharp rather than such "fuzzy" layering? The following categories of materials/approaches may lead to distinct layering:

(i) Forced Intrinsic Compensation. Post-buildup processing steps can induce excess polymer charge of one type within the multilayer. Such steps include thermolytic or photolytic elimination of charged groups (as we have shown previously),[14] electrochemical injection of charge into the multilayer (also demonstrated),[36,37] or the introduction of charge via pH changes when the multilayer includes weakly acidic polyelectrolytes.[23] Layering observed in poly(phenylenevinylene)-containing PEMs[38] may fall in this category, with a contribution from (iii) below.

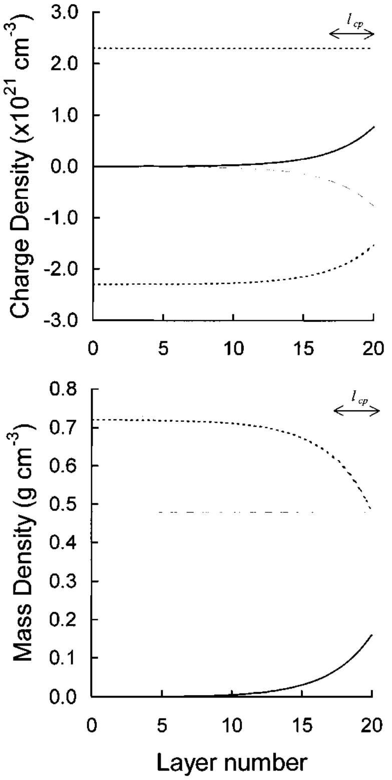
(ii) Particle/Polymer Systems. A mixture of organic polyelectrolyte and inorganic or organic particles would be conducive to stratification due to the rigid, impenetrable nature of the particle. Multilayers incorporating platelike clay minerals can show Bragg diffraction,[7,39] although the minerals may not be localized in one continuous plane.

(iii) High Ratio Neutral/Charged Systems. As the material balance within a multilayer tends toward a larger fraction of uncharged hydrocarbon (for example, from hydrophobic side chains or sparsely charged repeat units), phase separation is possible. Examples of systems with high neutral/charge ratio forming layers have been observed.[3,40] Intrinsic compensation is a balance between entropy loss imposed by localizing segments and free energy gains from ion pair formation. One might expect an intrinsic → extrinsic phase transition as more polymer is held together by fewer ion pairs.

(iv) Minimal Thickness Layering. If the layer thickness is approximately the dimension of a monomer repeat unit or less, ion pairs and hydrophobic parts can exist within different strata. This mechanism of layering is likely only with rigid polymers.

Stratification is not a requirement for good bulk orientation within multilayers. For example, an optically active PEM[41-43] may have chromophores aligned well along a particular axis, with poor structural correlation in the plane of the substrate, akin to the nematic phase in liquid crystals. A corollary is that high-quality orientation, leading to stable second-order nonlinear optical activity, observed within certain thin films,[42,43] does not directly imply good stratification. A gradient in hydrophobicity that probably accompanies the gradient in counterion concentration may be critical in achieving orientation within multilayers.

Scheme 1. Sketch of Charge Density vs Distance (Upper Panel) from the Substrate (in Terms of Nominal Layer Number), and Mass Density vs Distance (Lower Panel) for an As-Made 20-Layer Pair PSS/PDADMA Multilayer Measured under Dry Conditions[a]



[a] The curves were modeled according to eq 4 with $l_{cp} = 200$ Å and $\phi = 1.5$. The system assumes intrinsic compensation within the bulk of the multilayer (layers 0–10),[14] that is, 1:1 polymer charge stoichiometry and no salt ions. The final deposition is from PDADMAC. In the upper panel, contributions from positive and negative polymers 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}. In the lower panel, the PDADMA is shown as the dashed line and the PSS as the dotted line. The solid line is the excess, chloride-compensated PDADMA.

If deposition is performed from concentrated salt solutions, several equivalent monolayers of polymer accrue on a single deposition.[16] We have suggested that this large polymer excess charge is actually accommodated in the substrate-perpendicular direction over a length scale equal to several “layer thicknesses”.[14,16] Such a spreading of excess polymer charge is depicted in Scheme 1, which offers perspectives based on charge conservation or mass balance. The former shows how charge is balanced by polymer segments or salt ions, and the latter is useful for determining thickness increments (see Figures 1–3).

Scheme 1 incorporates several elements that have been established experimentally for these strongly dissociated polyelectrolytes. First, the bulk of the PEM is intrinsically compensated, in contrast to the region near the surface, where small counterions balance excess polymer charge.[14] Second, both polymers are present at all points, since they are interpenetrating.[5] This coexistence extends to the surface, allowing excess polymer to be distributed smoothly into the multilayer, rather than existing as a thick layer of loops and tails at the surface.

It is important, in this discussion, to differentiate between *polymer* interpenetration and *charge* penetration length (l_{cp}). Although strong mixing is consistent with the experimentally established interpenetration of polymers,[5,15,17] the length of penetration of excess charge is not necessarily the same as the range of physical penetration or diffusion of a polymer as it adds to the multilayer. The operational definition of the “degree of interpenetration” depends on the method used to measure this overlap. For the same system, an estimate of the spatial distribution of one “layer” of polymer obtained from neutron or X-ray structural studies[5,15,17,38] would differ from methods based on charge[37,44,45] or energy[46–48] transfer depending on the range of the interaction.

Linear Regime (Steady-State Growth). The key to multilayer propagation is charge overcompensation. At the multilayer/solution interface, the charge of the last-added polymer compensates the previous one by a factor ϕ. If $\phi = 1$, the opposite polymer charges are in exact stoichiometic ratio. $\phi - 1$ is the overcompensation factor (for example, if $\phi = 1.5$, the charge is overcompensated by 50%). In the model below we assume that ϕ is the same for the positive and negative polymers, which has been shown for PSS/PDADMA pair.[55] The charge increment per deposition cycle may then be converted to mass and thickness increment.

The adsorption of the first layer of polyelectrolyte, the subject of extensive theoretical and experimental attention,[24] seems to be somewhat anomalous. The charge from the first (PDADMA) layer far exceeds the nominal surface charge of bare native silica surface at “ambient” pH values of ca. 5. Previous studies have shown the surface excess of polymer to be a weak function of polymer or salt concentration.[24,49] Other interactions, including hydrogen bonding, dipolar, or hydrophobic forces, may be responsible for controlling the thickness of this initial layer.

Within the bulk or interior of a thicker multilayer, a charge balance condition is imposed by intrinsic compensation (i.e., the bulk *charge* densities of PSS and PDADMA are equal). c_{bulk}^{+} (c_{bulk}^{-}) are the bulk *mass* densities (g cm^{-3}) of positive (negative) polymer

$$c_{\text{bulk}}^{+} = f^{+}\rho \tag{1a}$$

$$c_{\text{bulk}}^{-} = f^{-}\rho \tag{1b}$$

f^{+} (f^{-}), the bulk volume fraction of positive (negative) polymer, is defined by

$$f^{+} = \frac{M^{+}\alpha^{-}}{M^{+}\alpha^{-} + M^{-}\alpha^{+}} \tag{2a}$$

$$f^{-} = \frac{M^{-}\alpha^{+}}{M^{+}\alpha^{-} + M^{-}\alpha^{+}} \tag{2b}$$

M^{-} and M^{+} are the molar mass of the respective negative or positive repeat unit, and α is the degree of dissociation per repeat unit; $\alpha < 1$ accounts for the possibility that the polymer might be a partially dissociated weak polyelectrolyte, or each repeat unit might not be fully charged. It takes *more* polymer to neutralize charge if $\alpha < 1$. In the present work, both polyelectrolytes are strongly dissociated ($\alpha = 1$).The density, ρ, of pure polymer or multilayer is assumed to be the same (here 1.2 g cm^{-3}).

Overcompensation leads to excess charge density from the last-added polyelectrolyte, but only at the surface is ϕ "unrestricted" by bulk effects. At increasing length, l, from the interface into the multilayer, the level of overcompensation decreases in an exponential fashion.[50] The characteristic length of this decay is $l_{\mathrm{cp.}}$ The overcompensation gradient is "visualized" by the salt counterion profile, which is the mirror image of the excess polymer charge profile. l_{cp} does not necessarily represent the characteristic length scale over which the adsorbing polymer interpenetrates into the multilayer surface.[51] It is a range of charge overcompensation.

The excess polymer charge is balanced by small (salt) ions (Na$^+$ or Cl$^-$). The gradient in chemical potential of ions within the surface of the multilayer has been directly observed by Kiltzing and Möhwald[52] using pH-sensitive dye-labeled polyelectrolytes. For simplicity, we assume that the volume of the salt ion plus extra hydration is equal to the volume of the polymer segment of same charge (see Scheme 1).

We express the surface excess polymer concentration, $c^+_{\mathrm{ex},0}$ or $c^-_{\mathrm{ex},0}$ as

$$c^+_{\mathrm{ex},0} = \left(\frac{\phi - 1}{\phi}\right)c^+_{\mathrm{bulk}} \tag{3a}$$

$$c^-_{\mathrm{ex},0} = \left(\frac{\phi - 1}{\phi}\right)c^-_{\mathrm{bulk}} \tag{3b}$$

The excess charged polymer profile into the multilayer is assumed to follow an exponential decay[52]

$$c^+_{\mathrm{ex,l}} = c^+_{\mathrm{ex},0}\mathrm{e}^{-l/l_{\mathrm{cp}}} \tag{4a}$$

$$c^-_{\mathrm{ex,l}} = c^-_{\mathrm{ex},0}\mathrm{e}^{-l/l_{\mathrm{cp}}} \tag{4b}$$

The total areal excess polymer density, Γ (g cm^{-2}), the area under these profiles, is then

$$\Gamma^+ = c^+_{\mathrm{ex},0}l_{\mathrm{cp}} \tag{5a}$$

$$\Gamma^- = c^-_{\mathrm{ex},0}l_{\mathrm{cp}} \tag{5b}$$

Combining (1) and (3) with (5), and recognizing $t_n = \Gamma/\rho$, we obtain the thickness increment, t_n^+ (t_n^-) for one positive (negative) layer

$$t_n^+ = 2\left(\frac{\phi - 1}{\phi}\right)l_{\mathrm{cp}}f^+ \tag{6a}$$

$$t_n^- = 2\left(\frac{\phi - 1}{\phi}\right)l_{\mathrm{cp}}f^- \tag{6b}$$

The factor of 2 in eq 6 is included because the adding polymer neutralizes existing surface charge and then overcompensates by the same amount.

The total thickness, t, with contributions from positive and negative polymers, is

$$t = 2l_{\mathrm{cp}}\left(\frac{\phi - 1}{\phi}\right)(f^+n_{\mathrm{odd}} + f^-n_{\mathrm{even}}) \tag{7}$$

where n_{odd} and n_{even} are the number of PDADMA and PSS layers, respectively. Note that for strongly dissociated polymers ($\alpha^+ = 1$ and $\alpha^- = 1$, or $\alpha^+ = \alpha^-$), $n_{\mathrm{even}} = n_{\mathrm{odd}}$, and any combination of M^+ and M^-

$$t = n\left(\frac{\phi - 1}{\phi}\right)l_{\mathrm{cp}} \tag{8}$$

Initial Nonlinear Growth Regime: Overall Expression. For thin films, toward the beginning of multilayer buildup, the decaying excess charge profile is truncated by the impenetrable substrate/multilayer interface. The increment for the next adsorption step, eq 6, is effectively limited by a function of the form $1 - \mathrm{e}^{-t/l_{\mathrm{cp}}}$. As the film grows, the increment reaches the steady-state value, imparting an upward curvature to the thickness vs layer plots. This curvature will be more marked for higher salt concentrations (thicker layers).

The overall thickness of a film that includes a transition from nonlinear to linear growth is modeled as the sum of thickness increments, t_n,

$$t = \sum t_n = t_1 + \sum t_n^+ + \sum t_n^- \tag{9}$$

The anomalous first layer, thickness t_1, has been separated from the increments due to positive (odd) and negative (even) layers. The thickness increment from each layer ($n > 1$) is limited, at the beginning, by truncation of the excess charge profile by the substrate. Thus, for odd and even layers respectively

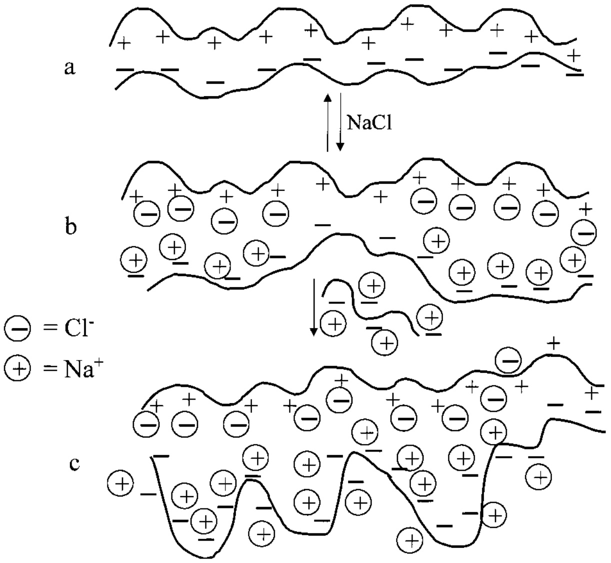
$$t_n^+ = 2l_{\mathrm{cp}}\left(\frac{\phi - 1}{\phi}\right)f^+(1 - \mathrm{e}^{-t/l_{\mathrm{cp}}}) \tag{10a}$$

$$t_n^- = 2l_{\mathrm{cp}}\left(\frac{\phi - 1}{\phi}\right)f^-(1 - \mathrm{e}^{-t/l_{\mathrm{cp}}}) \tag{10b}$$

Since the thickness, is not an explicit function of other variables, eqs 9 and 10 were evaluated using an iterative computer program. The program also minimized the deviations between experimental and calculated values for various pairs of surface overcompensation, ϕ, and charge penetration length, l_{cp}. The overall behavior of multilayer buildup is predicted well by eqs 9 and 10, as seen in Figures 1−3. The experimentally observed difference in increment between the PSS and the PDADMA layers, due the higher molar mass of the former, is reproduced in the fit, giving a stepped appearance. It is evident that, for the linear portion of the film growth, only the product ϕl_{cp} is unique, and many combinations of these two parameters would yield the correct slope. Clear separation between l_{cp} and ϕ can only be obtained if there is initial curvature to the data, since l_{cp} effectively delays the onset of steady-state growth. In the presence of such curvature, the model is reasonably sensitive to the choice of l_{cp}. For example, in Figure 2 the calculated behavior for a somewhat larger value of l_{cp} is presented. For data that do not exhibit curved and linear regimes, l_{cp} and ϕ would have to be measured independently by a surface-sensitive analytical technique, such as ESCA, or by obtaining the profile of deuterium-labeled polyelectrolyte by neutron reflectometry.[15,53]

Values for ϕ and l_{cp} for 1 M, 0.5 M, and salt-free solutions were 1.86, 425 Å; 1.95, 185 Å; and 1.72, 7.5 Å, respectively. There are several significant points that may be made concerning the proposed model. First, excess polymer charge is able to penetrate deeply into the multilayer. Second, because of this large l_{cp}, the level of overcompensation need not be high, even for very "thick" films.[54] In addition, ϕ appears to be a weak

Scheme 2. Interior of a Multilayer, Represented by Two Oppositely Charged Polymer Strands (a), Is Intrinsically Compensated As-Made; With the Addition of Salt, Extrinsic Compensation Occurs (b), as Ions Swell the Multilayer, Competing for Polymer Charge; in the Presence of Additional Polyelectrolyte, (c), Overcompensation from the Surface into the Film Is Seen



function of salt concentration, and the film growth is almost entirely controlled by excess charge penetration. For salt concentration M, the approximate relationship is $l_{cp} = 400M$. The independence of ϕ on salt concentration (thickness increment) is consistent with prior results from electroosmotic flow measurements of capillaries coated with multilayers,[55] where it was found that the apparent surface charge remained strictly constant as the thickness increment increased.

Clearly, several refinements of the model represented by Scheme 1 and eqs 9 and 10 are possible. For example, the volumes of hydrated salt ions are not the same as the polymer segments. Also, since the surface of the multilayer is probably more diffuse and hydrated, the profile of both polymers would likely decay toward the surface, with the last-added polymer decaying less.

Equilibrium vs Kinetic Limitations of Excess Surface Polymer. The concentration profiles depicted in Scheme 1 represent a mean-field model, that is, the composition and field experienced by adsorbing polymer are uniform in the plane of the multilayer. We can envisage two possible physical limitations for the field in the substrate-normal direction. The first argument has a thermodynamic basis. Overcompensation at the surface is a balance between the loss of polyelectrolyte degrees of freedom (an entropy argument) and the free energy gain from segment/segment hydrophobic ion pairing. Segment density increases from the multilayer/solution interface into the film, increasing the steric repulsion. Enhancing the configurational degrees of freedom by overcompensation is no longer energetically favorable within the multilayer because of this repulsion.

How does additional salt permit overcompensation further into the multilayer (l_{cp} increases)? Scheme 2 is an aid to understanding our current hypothesis: in the presence of salt, compensation of polyelectrolyte charge within the as-made multilayer transforms from intrinsic to extrinsic. The polymer in Scheme 2b is actually highly swollen with salt ions and also contains more water, which is brought in with the salt. In the presence of one of the polyelectrolytes (the negative one in this example), more polymer can add, and the overcompensation extends further into the multilayer due to the effective decrease in segment−segment repulsion (the multilayer polymer is diluted by water and salt ions). Scheme 2 depicts the swelling and addition of polymer as two distinct steps, whereas they are, in reality, simultaneous. The swelling of multilayer by salt is shown as reversible, while the polyelectrolyte addition is irreversible, as demonstrated for the time scale of the multilayer construction experiment.[16]

An interesting transition is predicted by extrapolation of the salt concentration to the point where the remaining intrinsic compensation (polymer/polymer ion pairing) is no longer sufficient to keep the multilayer together, and it dissociates (i.e., additional salt no longer produces thicker films). This critical salt concentration is approximately 3.5 M for PSS/PDADMA. Given the importance of the intrinsic → extrinsic equilibria ("swellability") in the accommodation of excess charge and thus the film thickness, several projections may be made. First, multilayers with strongly associating polymer/polymer ion pairs will yield thinner films than those easily swollen by salt but will be more stable to higher salt concentrations. For example, the well-studied poly(allylamine)/PSS pair gives much thinner films than PSS/PDADMA but is stable to higher salt concentrations.[4] Second, the use of more hydrophobic salt ions in the multilayer solution will give thicker films (due to more effective competition with polyelectrolyte segments and thus greater swelling). This latter effect has been observed.[16] Finally, the ionic permeability of multilayers should be inversely related to the strength of their polymer/polymer ion pairing.

It is appropriate to view thermodynamic arguments with caution: although the adsorption/desorption of salt ions is fast and reversible, the adsorption of polymer is slow and irreversible. The net irreversibility of polyelectrolyte adsorption was demonstrated using radiolabeled polymer, which, when incorporated in a multilayer as the top layer, did not exchange with unlabeled material on the time scale of assembly.[13,14] Irreversibility is an essential (and fortuitous) property. If desorption were not kinetically limited, one might expect multilayer polymer to be stripped off the surface on exposure to a solution of its counterpart.

Small but measurable gradual changes in the adsorbed amount with time or polymer concentration[16,56] attest to nonequilibrium conditions. The critical question is, how far is the system from equilibrium? In the limit of extreme kinetic control, the field into the multilayer could be diffusion-controlled. In this mechanism, the diffusion of the polymer becomes restricted as the polymer penetrates the multilayer. Salt enhances diffusion of oppositely charged polymer into the surface[57] by freeing up individual segments via competitive ion exchange.[58] Polyelectrolyte conformational changes are known to be accelerated by the addition of salt.[59,60] In the fully interdiffusion-controlled (kinetic) limit, l_{cp} would also be the interpenetration length.

Our current thinking is that thermodynamics are mainly responsible for controlling the adsorbed amount, with a lesser, but significant, role played by kinetics (as seems to be common for polyelectrolytes). This conclusion is based on the well-known observation that multilayer thickness is essentially independent of molecular weight.[3,5] Specific to our polymers, multilayers made from the PDADMA used here were the same thickness for 5 × 10^4 and 8 × 10^5 narrow molecular weight distribution PSS at salt concentrations ≤ 1 M. If l_{cp} were kinetically limited, one would expect a strong dependence on molecular weight. Further, one does not see pockets of "marooned" extrinsic charge which one would expect if the system relied entirely on the diffusion of external polymer to compensate internal charge. Polymer excess charge (and the ions that balance it) can be transmitted instead by less demanding localized reconformations (like squeezing the walls of a toothpaste tube).

Conclusions

More work is needed to distinguish the mechanism limiting interpenetration. The question of the interdiffusion of a polymer layer and the dependence on molecular weight would be efficiently addressed using deuterium labeled layers and neutron reflectometry.[15] The two additional questions of prime importance that remain concern quantitative theoretical treatments for ϕ and l_{cp}. These can probably be predicted, with complete consideration of segment, solvent, and ion chemical potentials, by sophisticated self-consistent-field models, such as those developed by Scheutjens and Fleer and others.[24]

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