Macromolecules 2001, 34, 3736−3740

Polyelectrolyte Multilayers Containing a Weak Polyacid: Construction and Deconstruction

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Received October 3, 2000; Revised Manuscript Received February 7, 2001

ABSTRACT: The growth of multilayers made from a combination of a weak polyacid and a strongly dissociated polycation is studied as a function of salt concentration and molecular weight. Film thickness reaches a maximum at around 0.3 M salt and then decreases quickly. Preformed multilayers are shown to decompose rapidly and, for high molecular weights, completely when exposed to aqueous solutions of NaCl of concentration >0.6 M. The apparent dissociation of multilayer polyelectrolyte complexes is due to competition for polymer/polymer ion pairs by external salt ions. Similar experiments aimed at decomposing multilayers by protonating the weak acid, thus decreasing polymer/polymer interactions, lead to incomplete loss of polymer, probably due to additional hydrogen bonding from the protonated weak acid. A model based on ion exchange/swelling of multilayers is used to explain their stability and permeability as well as the dependence of film thickness on salt concentration and type.

Introduction

Ultrathin polymer films may be deposited on a substrate by exposing it, in an alternating fashion, to solutions of oppositely charged polyelectrolyte.[1−4] Each immersion cycle contributes a reproducible and, eventually, constant increment to the film thickness. Several key experimental variables control the buildup of multilayered films in these systems.[3,5] For a given pair of strongly dissociated polycations and polyanions, the concentration of salt in the deposition solution appears to exert the strongest influence on the thickness of each polymer layer, which is approximately proportional to salt concentration.[5,6] Variables of lesser impact include salt composition, molecular weight, polymer concentration, and deposition time.[5]

Many of the polyelectrolytes employed for multilayers are either weak acids or their salts (such as carboxylates)[7−9] or protonated forms of weak bases (for example, poly(allylamine), poly(ethylene imine), and other polyamines).[1−4] The use of one or more polymers bearing weak acid/base functionality affords the possibility of controlling the average charge per repeat unit and thus the extent of interaction between charged polymers. Most of the initial work, and a substantial number of continuing studies, are performed under pH conditions which ensure that the polyelectrolyte remains in its most highly charged form (for example, protonated poly(allylamine), PAH). A number of recent studies, notably those of Rubner et al.,[7−9] have probed the complex behaviors for weak polyacid/polybase pairs that occur over a wide range of “pH space”. Depending on the pH, both polyanion and polycation can be weakly or strongly charged, leading to fine control over the thickness of each deposited polymer layer.[8,10] Under certain deposition conditions, phase separation of multilayer components yields unusual microporous ultrathin films.[9]

Less attention has been paid to the influence of salt concentration (ionic strength) on the buildup of weak polyacid/base-containing multilayers. In a study employing poly(allylamine) and poly(styrenesulfonate), PSS, Clark et al.[11] showed that the adsorption of polymers on carboxylate and oligo(ethylene glycol) functionalized monolayers was strongly dependent on the ionic strength of the deposition solution. Selective deposition of polyelectrolytes on substrates offers the possibility of pattern formation and processing using multilayers.[4,11−13] In certain applications, selective (or nonselective) deposition would ideally be followed by quantitative removal of the thin film, preferably in ambient under mild conditions. An additional benefit would be realized if processing were to be based solely on aqueous solutions.

Focusing here on a multilayer system in which one of the polyelectrolytes is poly(acrylic acid), a weak acid, and the polycation is strongly dissociated under all conditions, we investigate the interplay between pH and salt concentration. Our most significant finding is full multilayer deconstruction and desorption over a relatively narrow range of salt concentration.

Experimental Section

Poly(diallyldimethylammonium chloride), PDADMA (molecular weight, MW, (3−4) × 10^5), and inorganic salts were used as received from Aldrich. Poly(acrylic acid), PAA, was obtained from Polymer Sources Inc. (Quebec). Two PAA samples, representing “high” and “low” MW, had $M_w = 84\ 500$, $M_w/M_n = 1.07$ and $M_w = 5200$, $M_w/M_n = 1.09$, respectively. Polymer solutions were 1 mM (based on the repeat unit) in various concentrations of $NaCl_{(aq)}$. All deposition and rinse solutions were stabilized to the pH of the PAA deposition solution with the addition of acid, base, or buffer. Multilayers were deposited robotically[5] on spinning (300 rpm), 1 in. diameter, 0.5 mm thick, polished Si (100) wafers (Topsil Inc.) which had been cleaned with “piranha” (70% H_2SO_4(conc)/30% $H_2O_{2(aq)}$: *caution*: piranha is a strong oxidizer and should not be stored in closed containers) and rinsed in water. Deposition time was 5 min per layer with 3 × 30 s rinses in water between layers. Multilayers were dried with a stream of nitrogen prior to thickness measurement. Thicknesses were determined using a Gaertner Scientific L116B Autogain ellipsometer with 632.8 nm radiation at 70° incident angle. A refractive index of 1.54 was employed for the multilayer.

Multilayers were exposed to NaCl solutions of increasing concentration up to 1.0 M. For the variable pH study, multi-

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10.1021/ma001720t CCC: $20.00

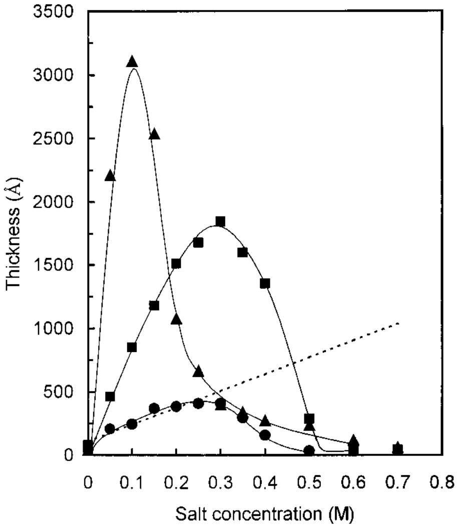


Figure 1. Thickness of a 20-layer PAA/PDADMA multilayer on silicon wafer deposited from 1 mM polymer solution containing various concentrations of NaCl. Squares: PAA molecular weight 84 500, pH 11 deposition solution. Circles: PAA (MW = 5200), pH 11. Triangles: PAA (MW = 5200) from pH = 5 solution. Solid lines are a guide to the eye. The dotted line is from a previously reported PSS/PDADMA multilayer system.[5]

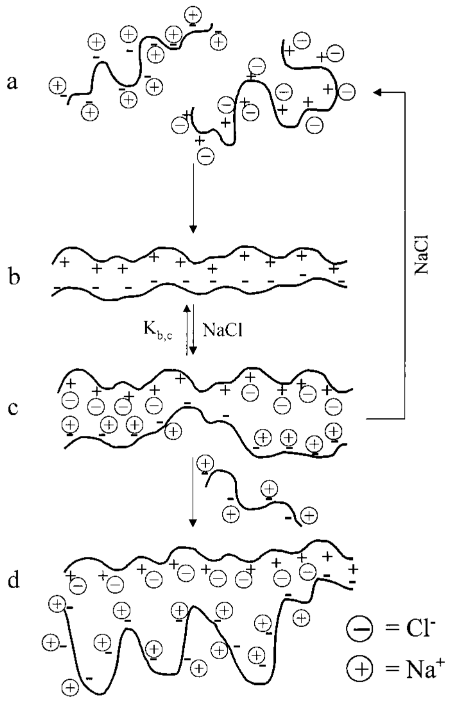
layers were exposed to increasingly acidic baths adjusted to a total ionic strength of 0.1 M using NaCl. Baths for controlling pH used HCl (pH 1−4), NaOH (12−10), and the following buffer/pH combinations: TRIS/8.4, phosphate/6.5−7.0, acetate/4.6−5.5, biphthalate/4.0.

Results and Discussion

To provide pH dependence for one species only, the polycation in all cases was high MW PDADMA. PAA is a weak polyacid which exhibits gradual dissociation over a range of solution pH values (unlike a typical monomeric carboxylic acid) and is about 50% protonated at pH 5 and completely ionized above pH 9.[14] Deposition of PAA/PDADMA on spinning silicon wafers yielded uniform, reproducible multilayers. The thickness of a 20-layer multilayer for narrow MWD PAA samples of MW 84 500 and 5400 was measured as a function of deposition solution salt concentration (Figure 1). There are several marked differences in behavior of this system compared to a previously studied strong polyelectrolyte system (PSS/PDADMA),[5] also summarized in Figure 1. Although an initial increase in film thickness is observed with PAA, the films become thinner for salt concentrations above 0.5 M. Eventually, no multilayer formation can be detected. Films made from the higher molecular weight PAA are also significantly thicker, in contrast to the trends generally observed for other multilayer systems, for which no MW dependence is reported.[2,3]

The low molecular weight PAA could be induced to form thicker films by lowering the pH. The average increment per PAA/PDADMA layer pair goes from a maximum of about 40 Å to about 310 Å on decreasing the pH from 11 to 5. Stable, reproducible thicknesses could not be obtained for the high MW PAA at pH 5, perhaps due to the instability of a loose, highly hydrated thick film under the conditions of shear employed here. The enhancement in thickness at low pH can be compared to the results of Shiratori and Rubner,[8] who, using the PAA/PAH pair, found a large increase in thickness at pH 5. These authors explained the enhanced adsorption in terms of an increased concentration of polymer loops for the partially charged polyelectrolytes.

Scheme 1. Various Stages during the Formation, Swelling, and Decomposition of a Polyelectrolyte Multilayer[a]



[a] In (a) the solution-phase polymers are compensated by counterions. When the polymers associate during multilayer formation, (b), and after the final rinse step, polymer charges are compensated by other polymer charges (polymer/polymer ion pairs, intrinsic compensation). Salt added to the external bathing solution forces some swelling (extrinsic compensation) (c). If the swelling is sufficient, the multilayer decomposes (shown by the arrow) back into individual, or perhaps loosely associated, solution-phase polymer strands. In the presence of additional polyelectrolyte of one type (here negative), overcompensation occurs near the surface (d), giving the excess surface charge reversal required for adsorption of the next polyelectrolyte. During the adsorption of a polyelectrolyte layer in multilayer buildup, steps b → c → d occur simultaneously.

The unusual maximum in film thickness as a function of salt concentration seen in Figure 1 may be explained by an ion exchange model for polyelectrolyte adsorption.[5,15−19] The interaction of polyelectrolyte charges is represented in Scheme 1. As we have discussed,[20] complexes formed by polyion interactions are similar whether they are in multilayers or whether they remain as solution-dispersed, quasi-soluble “symplexes” (also known as “polyelectrolyte complexes”).[21] Thus, many of the arguments concerning overcompensation and ion exchange in multilayers may be transposed to symplex formation. For the purposes of the present discussion, however, we assume that the polymer strands depicted in Scheme 1a are incorporated into a multilayer on complexation (1a → 1b).

Ion exchange phenomena in multilayers come into play from two perspectives. The first involves the displacement, by charged polymer segments, of small salt (counter)ions compensating any excess surface charge. During multilayer formation, the polymer charges pair and salt is displaced. The displacement of surface counterions has been observed directly using radiolabeled salt ions.[16,18,22] The polyelectrolyte complex in

1b, representing the material within a multilayer, is entirely salt-free following the final rinse step: polymer charges within the bulk of the multilayer balance with a 1:1 stoichiometry—termed "intrinsic" charge compensation.[22]

In the presence of salt ions within the bathing solution a second ion exchange process is possible (1b → 1c) where polymer/polymer ion pairs are forced apart, yielding some extrinsic compensation, due to the chemical potential of solution salt. At some point, depending on the strength of the polymer/polymer ion pair (i.e., the equilibrium constant for 1b → 1c), the polymer chains are sufficiently extrinsically compensated that their interaction is inadequate to form polyelectrolyte complexes and multilayers cannot be built. (Salt-induced polyelectrolyte dissociation is also depicted in Scheme 1.) Thus, a maximum is observed in the ionic strength vs thickness relationship. The appropriate energy balance at this point is probably between a highly hydrated, salt ion compensated polyelectrolyte and the few remaining polymer/polymer ion pairs that are barely sufficient to hold the polyelectrolyte complex together. The degree of extrinsic compensation required for this transition would be of great interest. The apparent dissociation of polyelectrolyte complexes at high ionic strength is discussed by Dautzenberg et al.[21]

When the solution contains an excess of one of the polyelectrolytes, additional polymer adds to the surface of the multilayer, whereupon the surface charge is neutralized, or compensated, then overcompensated (Scheme 1d), reversing the sign of the surface charge and inverting the population of surface counterions from cations to anions (or vice versa).[22] This surface charge reversal is a critical, nonintuitive step that permits repeated, steady-state increments of oppositely charged polymer to add.[1−4] In the presence of sufficient salt, a substantial amount of polymer can add to the surface (much more than an equivalent monolayer of polymer repeat units), and a model has been developed to account for the spreading of this polymer excess charge through several layers.[22,23] In this model, overcompensation at the surface, caused by enhanced degrees of freedom ("loops," an entropy argument), is inhibited within the bulk of the multilayer because of steric repulsive interactions between polymer segments (excluded volume). Salt, and the swelling it causes, relieves some of these repulsions, permitting a longer range for the distribution of excess charge and a greater thickness increment per "layer".[23]

During the buildup of a polyelectrolyte multilayer, swelling and overcompensation steps depicted in Scheme 1 are, in reality, occurring simultaneously, as is the deconstruction at high salt concentration. Scheme 1 provides a complete framework for understanding the interplay between salt effects and multilayer stability, thickness, swellability, and permeability as follows:

Thickness Dependence on Salt Concentration. As more salt is added, swelling the multilayer, excess charge can be spread more efficiently into the multilayer surface, as discussed above.

Polymer Type. The influence of polyelectrolyte types on multilayer buildup depends on the relative strength of the polymer/polymer ion pair, i.e., the 1b → 1c equilibrium constant, $K_{b,c}$ (Scheme 1). Strongly interacting segments (low $K_{b,c}$) cannot be easily swollen, so the thickness increment will be lower.

Stability. This also depends on $K_{b,c}$. Stronger ion pairing will yield more salt-resistant multilayers.

Permeability. The permeability of multilayers to small ions[24−26] depends on the membrane concentration of these ions, which will be greater if $K_{b,c}$ is larger.

Salt Type. Hydrophobic salt ions, more effective at displacing polymer/polymer ion pairs ($K_{b,c}$ larger), will give thicker films but will cause the dissociation of polymers sooner. The former effect has been observed experimentally.[5]

The current example, PAA/PDADMA, in comparison to PSS/PDADMA may be used to illustrate these relationships (Figure 1). Specifically, PAA/PDADMA multilayers are more easily swollen by salt and thus give thicker, but less stable, films than PSS/PDADMA. If the polymer/polymer interactions are decreased further by neutralizing some of the PAA charges (lower pH), the layers are even thicker, but the polymer complexes begin to dissociate at lower salt concentration.

Molecular weight is not specifically considered in the reasoning above. The contrasting behaviors of low and high MW PAA at pH 11 (where the PAA is fully ionized) are explained by fewer contact points per molecule for the former due to the lower molecular weight. Whether the surface coverage can be rationalized by equilibrium or kinetic effects is more subtle. An equilibrium argument might consider the total number of cooperatively acting interactions per molecule and would conclude greater adsorption by larger molecules. However, the ratio of extrinsic to intrinsically compensated polymer segments (free, in a "loop":bound, in a "train") may well be independent of molecular weight. Furthermore, the maximum in layer thickness occurs at about the same salt concentration (Figure 1) for both molecular weights, as does the decomposition of multilayers (vida infra), suggesting the affinity of PAA for PDADMA is unaffected by molecular weight. We believe that the differences in coverage are due to the relative speed with which the PAA on the surface can be stripped off the surface by solution PDADMA. From a strictly thermodynamic perspective, polyelectrolyte complexes, if soluble, should be more stable in solution than they are on a surface, since additional degrees of freedom are afforded in the former. Soluble polyelectrolyte complexes can be formed if one polymer is in great excess or if the polymers have very different chain lengths.[21] In the present case, both conditions hold when the multilayer capped with low MW PAA is immersed in PDADMA. Thus, there is a greater loss of PAA to the solution.

To further probe the stability of PAA/PDADMA multilayers, as-made films were subjected to increasing salt concentration and the thickness monitored (Figure 2). For both MW PAAs, multilayers were stable in salt concentrations up to ca. 0.4 M and then started to dissociate, with the "desorption" transition complete by 0.6 M. Loss of an intact multilayer on immersion in 1 M salt (pH 11) was more rapid than could be measured (ca. 3 s). As discussed above, since the transitions for the low MW and high MW PAA occur over the same range, the interaction energy between PAA and PDADMA does not appear to be a strong function of molecular weight. The dissociation of PAA from PDADMA is caused by salt ions successfully challenging polymer/polymer segment ion pairs. The degree of extrinsic compensation required for the polymer/polymer interaction to be weakened to the point that the multilayer

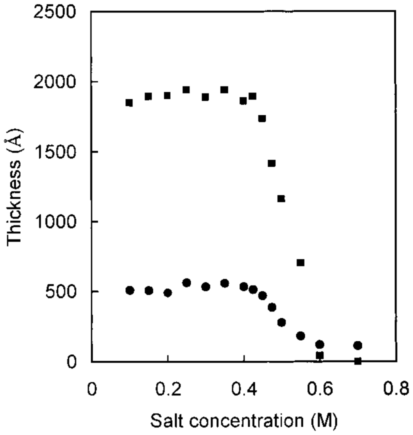


Figure 2. Thickness of 20-layer PAA/PDADMA, prepared with 84 500 MW (squares), and 5200 MW (circles) PAA, as a function of salt concentration. The deposition, soaking, and rinsing solutions were maintained at pH 11.

decomposes (Scheme 1) is similar in concept to the minimum charge density on a polyelectrolyte for multilayer formation, addressed by Laschewsky et al.,[4,27] although extrinsic compensation brings with it added hydration (salt-compensated polymer segments are more hydrophilic than polymer/polymer ion pairs), which enhances the repulsion between polymers more than would a hydrated neutral segment.[28]

Additional effects should be considered when comparing the nature of the polyelectrolyte complexes as they exist within the multilayer[20] (Scheme 1b–d) compared to solution complexes.[21] The deconstruction of the multilayer may actually yield very loosely associated complexes, i.e., not true solutions of individual polyelectrolyte molecules. These complexes have insufficient structural integrity to maintain a layer but do not fully dissociate. Classical polymer adsorption theory[29] details a small loss of conformational entropy (of order $0.2kT$ per segment) when a polymer adsorbs at a surface. Associated strands of polyelectrolyte in solution will have slightly greater configurational entropy. Thus, a complex in solution might be a little more stable than a complex within a multilayer.

We estimate the critical fraction of extrinsic compensation for dissociation, y_{crit}, using the data of Hoogeveen et al.,[30] who found that stable multilayers between PAA and quaternized poly(vinylimidazole) would exist for a degree of quaternization of 0.18 and above. This would suggest a value for y_{crit} of ca. 82%. This figure is probably an upper limit for the PAA/PDADMA salt-induced decomposition, due to the additional hydration effect of the charged segments. It is worth noting that a y_{crit} of 80% still leaves an average of about 15 polymer/polymer ion pairs on a PAA chain of molecular weight 5400.

With the low MW PAA, a small thickness remained at high salt concentrations (Figure 2). According to the manufacturer, the PAA polymers are prepared by anionic polymerization of *tert*-butyl acrylate, followed by hydrolysis to prepare the acid. The initiator is *sec*-butyllithium with about 3 units of α-methylstyrene. The PAA chains thus have a short, hydrophobic end, which is believed to be responsible for the small residual amount of PAA observed for the low MW material.

Since the degree of ionization of the PAA is pH-sensitive, it should, in principle, be possible to modulate the PAA–PDADMA ion pairing (or electrostatic) interactions by controlling the solution pH. At sufficiently low pH, the charges on the PAA would be too dilute to maintain cohesive forces throughout the multilayer and it should dissociate. Figure 3 summarizes the dependence of film thickness on pH for a PAA/PDADMA sample made at high pH and sequentially exposed to solutions of progressively lower pH but the same ionic strength (0.1 M). Although the thickness of the films made with high MW PAA does, indeed, decrease, suggesting desolvation and then loss of polymer, the change is more gradual than observed in Figure 2. Furthermore, total loss of polymer is not observed, and immersion in a bath of the original pH 11 solution results in a small increase in the residual film thickness. The results with low MW PAA show, again, some shrinkage but little loss.

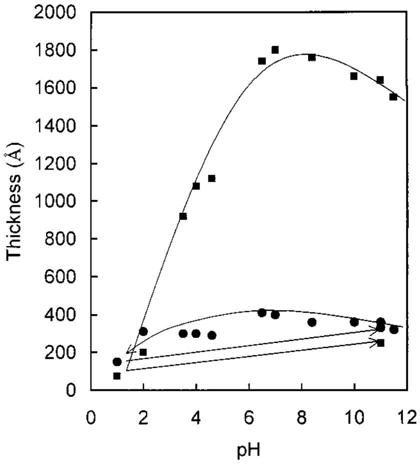


Figure 3. Twenty-layer PAA/PDADMA multilayers, prepared as in Figure 2, maintained at a constant ionic strength of 0.1 M and subjected to decreasing pH. Both the low- and high-MW samples were exposed again to pH 11 at the end of the run.

The observations in Figure 3 may be rationalized by the fact that PAA becomes more hydrophobic as it is deprotonated. Fully deprotonated PAA is also expected to show hydrogen-bonding interactions. Thus, at the same time that the electrostatic PAA–PDADMA interactions decrease, the PAA becomes less soluble and exhibits secondary attractive interactions. The convolution of these two opposing effects results in incomplete dissociation/solvation of the multilayer components.

Evidence of history-dependent behavior in attempting to use pH-induced dissociation was obtained by exposure of multilayers, built at high pH, to low pH with increasing salt concentration. Figure 4 shows such an experiment where samples were exposed to increasing salt concentration at pH 5 and then at pH 2. Instead of the full decomposition of the multilayer, which is expected under conditions where the both the pH and the salt concentration should be contributing cooperatively to multilayer dissociation, incomplete loss of thickness is seen. Again, the partial or full neutralization of the PAA does not permit full dissolution of multilayer components.

In summary, for the present system, modifying polycation–polyanion interactions via pH control is not equivalent to the use of salt concentration. All polymer components remain fully soluble at high pH and all salt concentrations employed, and a “clean” transition from coated to uncoated substrate is observed, with complete removal of polymer by a salt concentration of ca. 0.6 M

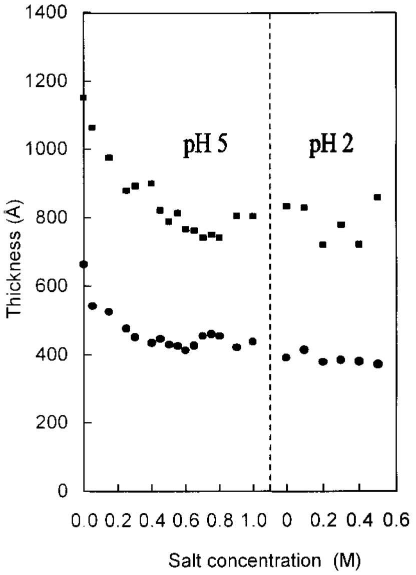


Figure 4. Twenty-layer PAA/PDADMA multilayers, prepared as in Figure 2, exposed to increasing salt solution at pH 5, followed by increasing salt solution at pH 2.

(the approximate ionic strength of seawater). The use of such mild conditions for removing a uniform polymer film may be a useful processing step in the application of polyelectrolyte multilayers.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation, Grant DMR 9727717, for support of this work.

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