Polyelectrolyte Multilayers of Weak Polyacid and Cationic Copolymer: Competition of Hydrogen-Bonding and Electrostatic Interactions

Eugenia Kharlampieva and Svetlana A. Sukhishvili*

Department of Chemistry and Chemical Biology, Stevens Institute of Technology, Hoboken, New Jersey 07030

Received July 25, 2003; Revised Manuscript Received October 22, 2003

ABSTRACT: We report on the competitive role of hydrogen bonding and electrostatic interactions in growth and stability of polyelectrolyte multilayers (PEMs) in a wide range of pH. The system was a cationic copolymer of acrylamide and dimethyldiallylammonium chloride (PAAm-DMDAAC) containing 50% cationic units and poly(methacrylic acid) (PMAA) as a polyacid. The amounts of polymers adsorbed and ionization of carboxylic groups within a film were quantified using in situ FTIR-ATR (Fourier transform infrared spectroscopy in attenuated total reflection). The results were contrasted with the stability of films formed from polyacrylamide (PAAm) and PMAA. In the PAAm/PMAA system, interlayer adhesion occurred through hydrogen-bonding interactions, and the multilayer decomposed at $\mathrm{pH} > 5.5$. However, the PAAm-DMDAAC/PMAA multilayers produced at low pH could be stabilized at a pH as high as 8 with transition to electrostatic interactions. With films deposited at $\mathrm{pH} = 2$ from low ionic strength solutions, asymmetric release of PMAA was observed with no mass loss for the polycation in the range of pH 2−7. With thicker PAAm-DMDAAC/PMAA films, deposited at $\mathrm{pH} = 2$ in the presence of 0.15 M NaCl, multilayers showed significant mass loss at $\mathrm{pH} > 5.5$. However, stable polymer multilayers could be produced in this pH range by growing PAAm-DMDAAC/PMAA multilayers at $\mathrm{pH} = 2$ and exposing them to higher pH values in the presence of 0.4 mg/mL PAAm-DMDAAC solutions.

Introduction

Layer-by-layer sequential adsorption of polymers on solid substrates is a promising technique for creating nanoscopic structures in self-assembled materials.[1−6] The technique produces polyelectrolyte multilayers (PEMs). Much progress has been made in recent years to understand the mechanisms of film growth, charge balance, and location of counterions.[1−8] Although in the majority of cases layered polymer films are formed by electrostatic interactions, the multilayer growth based on hydrogen-bonding interactions is also possible.[9−11] Recently, one of us demonstrated that multilayers can be produced from water-soluble uncharged molecules, such as polycarboxylic acids at low pH values and poly(ethylene oxide) or poly(vinylpyrrolidone).[11,12] The self-assembly was guided by intermolecular hydrogen-bonding interactions. The films could be controllably erased at a higher pH value, when ionization of a polyacid increased.[11,12] More recently, Rubner et al. developed thermal and photochemical techniques for stabilizing hydrogen-bonded multilayers and used this approach to produce micropatterned thin films.[13]

An alternative way to stabilize films at neutral pH values is the use of copolymers that combine centers for electrostatic and hydrogen bonding in one molecule. These systems provide an interesting switching between ionic interactions at high pH to hydrogen interactions at low pH in one polymer chain. In addition to fundamental interest, the properties of the produced films might be useful for various applications. For example, gradual rather than sharp pH response of films is sometimes desirable, since this allows better adjustment of the rate of drug release. Another example is the use of the transition between hydrogen and electrostatic interactions for controlled release of self-assembled molecules into the environment.

In the present work, we investigate self-assembly of a cationic copolymer that contains acrylamide units, with a weak polyacid. Using FTIR-ATR, we study in situ growth of multilayers at a wide pH range as well as the stability of multilayers at neutral and basic pH conditions. The work builds upon earlier studies of multilayers produced with weak polyelectrolytes[14] and polymer multilayers stabilized by hydrogen bonding[9−13] that involve homopolymers. In contrast to these previous studies, we study a collective effect of electrostatic and hydrogen bonding on film integrity. We find that, in the pH range from 5 to 7, self-assembly switches from a regime in which intermolecular adhesion is predominantly driven by hydrogen bonding to a regime where electrostatic interactions are dominant. We also report that in certain conditions hydrogen-bonding interactions can outweigh electrostatic repulsions, and a cationic copolymer can be self-assembled with a polyacid in conditions when a polyacid carries no charges. Since this work was completed, Schoeler et al. reported on the self-assembly of a weak polyacid and a hydrogen-bonded polycation of low charge density and found the multilayers were not stable at neutral and basic pH values.[18] In this study, we work with polycations of larger charge density and find ways to prevent mass loss from the films when multilayers are transferred from the regime with hydrogen bonding to the regime with electrostatic stabilization. The approach refers exclusively to systems with electrostatic interactions and fails for multilayers with purely hydrogen-bonding interactions.

Experimental Section

Materials. A cationic copolymer of acrylamide and dimethyldiallylammonium chloride (PAAm-DMDAAC) with M_w 5 000 000 was obtained from Nalco Chemical Corp. According

---

* To whom correspondence should be addressed.

10.1021/ma0350821 CCC: $25.00

Table 1. Calibration Constant Used To Calculate the Amount of Different Polymers Deposited within Multilayers

absorbance band, cm^{-1}	band assignment	polymer	calibration constant, abs units m^2 mg^{-1}
sum of 1701, 1670, and 1552 cm^{-1} bands	COOH and COO^-	PMAA	0.175
sum of 1640 and 1625 cm^{-1} bands	amide I region	PAAm	0.15
sum of 1640 and 1625 cm^{-1} bands	amide I region	PAAm-DMDAAC	0.05

to the manufacturer, the polymer contained 50% cationic units. Polyacrylamide (PAAm) with M_w 1 300 000 was purchased from Aldrich. Poly(methacrylic acid) (PMAA) with M_w 150 000 was purchased from Scientific Polymer Products, Inc. To eliminate possible traces of residual monomer, the samples were dialyzed against deionized water using tubing with a molar mass cutoff of 3000 Da. The dialysis was continued for 3 days (with the water bath frequently changed to purified water during that time), after that all samples were freeze-dried.

Poly(4-vinylpyridine) (PVP) with M_w 200 000 was purchased from Scientific Polymer Products, Inc. This sample was quaternized with ethyl bromide in ethanol solution using well-established methods[19,20] to obtain a polymer with 90% of pyridinium units (Q90) as determined by infrared spectroscopy.

In these experiments, the solvent was D_2O rather than water. This eliminated overlap of the IR spectra of polymers in the 1700−1500 cm^{-1} region with the strong water band. D_2O with 99.9% isotope content was purchased from Cambridge Isotope Laboratories and was used as received. Though the acidity was therefore determined by deuterium rather than hydrogen ions, we nonetheless refer to it as pH rather than pD. One should note, however, that hydrogen-to-deuterium exchange has an effect on the dissociation constants of acid groups, usually resulting in a relatively small (0.2−0.6) increase of pK_as of acidic groups in deuterium oxide as compared to their dissociation in water.[21]

To control pH and ionic strength, concentrated HCl and the inorganic salts $Na_2B_4O_7 \cdot 10H_2O$, Na_2HPO_4, and NaH_2PO_4 (General Storage, pure grade) were used as received.

The H_2O used for glassware cleaning was deionized and further purified by passage through a Milli-Q System (Millipore).

Pretreatment of the ATR Crystal. Multilayer films were deposited on a hydrophilic Si crystal which was oxidized using the procedure described elsewhere.[22] To enhance the adhesion of polymers to the substrate, the surface was first modified by a precursor layer. For this, Q90 was allowed to adsorb from a 0.1 mg/mL solution at pH = 9.2. Adsorption occurred, probably due to electrostatic attraction at this high pH. After waiting 20 min, the amount adsorbed reached a saturated value of ~1.5 mg m^{-2}, and the polymer solution was replaced by a pure buffer (0.01 M borate buffer at pH = 9.2). Then the liquid cell was filled with 0.1 mg/mL solution of PMAA at pH = 9.2 and after waiting 20 min was replaced by a buffer solution at the same pH. After that buffer solution at pH = 9.2 was replaced with a 10^{-2} M phosphate buffer solution at a lower pH. Substrate with its precursor film was used for multilayer deposition at a constant pH from 2 to 8.

Deposition of the Multilayers. Multilayers were deposited using a layer-by-layer technique. The protocol for in-situ multilayer deposition within the flow-through ATR−FTIR liquid cell was slightly different from the technique of alternate dipping that is commonly used for multilayer deposition and can be found in an earlier publication.[12] Briefly, 0.1 mg/mL solution of PAAm-DMDAAC or PAAm was allowed to adsorb onto the surface of the modified Si crystal for 20 min, and after that the polymer solution was replaced by buffer without polymer. PMAA was then deposited in a similar way, and the deposition cycle was repeated. Except for the two pretreatment polymer layers, all deposition solutions were kept at a constant pH during multilayer growth cycles.

FTIR-ATR Measurements. The amounts of polymers adsorbed and the degree of ionization of the carboxylic groups were quantified by in-situ FTIR-ATR from calibrated intensities of the vibration bands of $-COO^-$, $-COOH$, and the amide I bands. The layer-by-layer adsorption was monitored by infrared spectroscopy using attenuated total reflection. Infrared spectra were collected using a Bruker Equinox-55 Fourier transform infrared (FTIR) spectrometer equipped with a narrow-band mercury cadmium telluride detector. The attenuated total reflection (ATR) optics and the thermostated custom-built adsorption cell (Harrick Sci.) were placed in a dry air-purged compartment within the internal compartment of FTIR spectrometer.

The ATR surface was a rectangular Si crystal of dimension 50 mm × 20 mm × 2 mm (Harrick Scientific) whose beam entrance and exit surfaces were cut at 45°. The methods to oxidize the crystal surface in a controlled way and to clean the cell elements were described elsewhere.[22]

Interferograms were collected at 4 cm^{-1} resolution, and the number of averaged scans was 120. To obtain the absorbance spectra analyzed below, each interferogram was divided by the corresponding background, measured for the same ATR cell with the same D_2O buffer solution. Background spectra were obtained with the ATR crystal covered with the precursor film (one-layer Q90).

In most experiments the penetration depth of the evanescent wave was large relative to the thickness of the multilayers. (For example, the penetration depth of the evanescent wave was 0.47 μm at 1643 cm^{-1} for the Si crystal that we used.) Consequently, it was not necessary to correct data for the decay of electric field with the distance from the surface of the crystal. Simple calculation showed that this assumption held up to a film thickness of about 500 Å. For a dried film, this corresponds to the adsorbed amount of about 50 mg m^{-2}. (In this estimate, a density of 1 g cm^{-3} was assumed.) For films thicker than 500 Å, the measured intensity was corrected for decreasing intensity of the evanescent wave. The correction was small; for example, it was 5% for the films with 60 mg m^{-2} total mass deposited.

If measurements were performed in the presence of polymer solutions, the signal included contributions from the polymer solution in addition to those from the adsorbed polymer layers. Their respective contributions were easily separated when the polymer solution was replaced by pure buffer after each adsorption cycle. The contribution of the solution value was about 1% of the total signal for a solution concentration of 0.1 mg/mL.

The adsorbed amount of polymers and the degree of ionization of PMAA molecules within the multilayer were calculated from calibration constants which were independently determined by measuring the infrared absorbance of polymer solutions of known concentrations as they are brought into contact with a nonadsorbing surface. The detailed procedures include integration of intensity of the absorbing species in the evanescent wave as a function of distance from the crystal surface and have been described previously.[23−25] Calibration of the amount adsorbed was also described in detail earlier for both QPVP[26] and PMAA.[12] The calibration constants for Q90 and PMAA were taken from our earlier study. The ratio of extinction coefficients for the charged and uncharged groups in PMAA were reported earlier. In particular, equal values were found for the extinction coefficients of the 1701 and 1552 cm^{-1} PMAA absorption bands.[12] The calibration constants for PAAm and PAAm-DMDAAC were determined in this study using integral intensities of the 1600−1680 cm^{-1} amide I band. The calibration constants for all polymers used in this work are given in Table 1.

Figure 1 shows a representative infrared spectrum of a PAAm-DMDAAC/PMAA film deposited on the Q90/PMAA-pretreated Si surface at pH = 6. The spectrum shows three major peaks: an absorption band at 1701 and 1671 cm^{-1} associated with stretch vibrations of uncharged carboxylic groups (ν, C═O), a broad band at 1640 and 1625 cm^{-1}

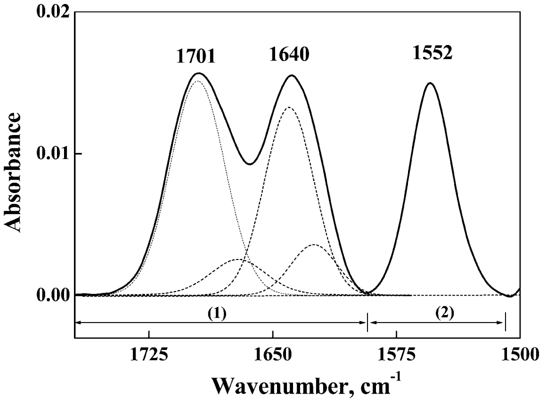

Figure 1. Representative FTIR-ATR spectrum of the nine-layer PAAm-DMDAAC/PMAA film with PMAA included into the top layer. Absorbance is plotted against wavenumber. The measurement was obtained in D_2O solution using 0.01 M phosphate buffer at pH = 6. Multilayers were deposited at pH = 6. The spectrum was obtained by dividing the spectrum of the adsorbed multilayers by that of a Si crystal with precursor layer in a pure buffer solution. The spectrum integration and curve-fitting intervals 1760−1590 and 1590−1505 cm^{-1} are shown by arrows.

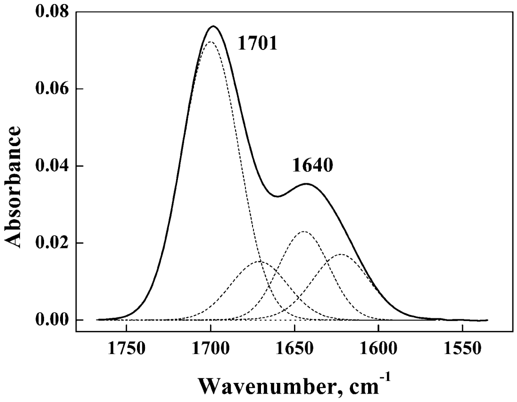

Figure 2. Spectral decomposition of a FTIR-ATR spectrum of the nine-layer PAAm-DMDAAC/PMAA film in the 1760−1570 cm^{-1} region. PMAA is included as the top layer. Absorbance is plotted against wavenumber. Conditions are the same as in Figure 1, except that multilayer deposition and measurements were done at pH = 2.

associated with amide I vibrations, and a band at 1552 cm^{-1} from asymmetric stretching vibrations of carboxylate groups (ν_a, COO$^-$). The intensities of the peaks shown in Figure 1 were then integrated by curve-fitting using Galactic Grams/32 software. In each series of experiments, the same curve-fitting file with fixed band centers and widths was applied to all spectra for consistency. Integration was performed in two spectral regions: 1760−1590 cm^{-1} (region 1) and 1590−1505 cm^{-1} (region 2). Peak integration in region 1 was performed with peak centers fixed at 1701, 1671, 1640, and 1625 cm^{-1} and the peak widths of 39, 40, 35, and 33 cm^{-1}, respectively. A peak centered at 1671 cm^{-1} was introduced in curve-fitting to account for the asymmetric shape of the 1701 cm^{-1} peak, as was discussed earlier.[12] An example of the curve-fitting procedure in region 1 is shown in Figure 2. The sum of intensities of the 1640 and 1625 cm^{-1} peaks has been used to determine the calibration constants for PAAm-DMDAAC and PAAm. For integration in the spectral region 2, the width of the 1552 cm^{-1} peak was fixed at 32 cm^{-1}.

Results and Discussion

Self-Assembly of PAAm/PMAA and PAAm-DMDAAC/PMAA Multilayers. The layer-by-layer deposition of PAAm/PMAA and PAAm-DMDAAC/PMAA was monitored by in-situ FTIR−ATR experiments. Prior to deposition of multilayers, precursor layer was first deposited on the substrate to create a large density of functional groups. The deposition procedures are described in the Experimental Section. In both systems, at a concentration of 0.1 mg/mL, typically 90% of polymer was deposited during the first 15 min. At longer time, adsorption would continue to grow with almost linear increments of about ∼5% of mass increase per hour for at least another 2 h. This slower kinetics is also observed in the deposition of hydrogen-bonding polymers[12] as well as polyelectrolytes[26] and probably reflects slow conformational rearrangements of adsorbed polymer chains. The adsorption was usually interrupted within 20 min, when polymer solutions were exchanged for a buffer solution.

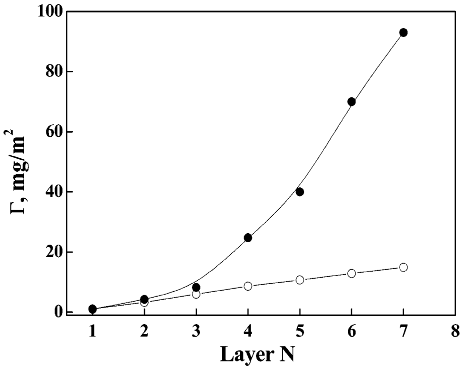

Figure 3. Layer-by-layer deposition of PAAm-DMDAAC/PMAA film at low ionic strength conditions (open circles) and at high ionic strength conditions (filled circles). The experiments were done at pH = 2 using D_2O solutions of phosphate buffer adjusted with hydrochloric acid. High ionic strength solution contained 0.15 M NaCl at pH = 2.

Figure 3 shows the growth of the PAAm-DMDAAC/PMAA multilayer at pH = 2. As seen in Figure 2, the FTIR-ATR spectrum of the multilayer does not contain the 1552 cm^{-1} −COO$^-$ vibrational band, suggesting that PMAA is completely un-ionized at these conditions. Although the PAAm-DMDAAC copolymer contains density of positive charges (an estimated intercharge distance is ∼0.7 nm), stable PAAm-DMDAAC/PMAA multilayers are produced at low ionic strength conditions, with relatively small amounts of polymers deposited at each step (1 mg m^{-2} of PMAA and 1.5 mg m^{-2} of PAAm-DMDAAC per layer). The mechanism of such self-assembly is drastically different from a more common charge-compensation mechanism of multilayer growth. In the produced multilayers, hydrogen bonding provides interlayer adhesion while unfavorable electrostatic repulsions between the PAAm-DMDAAC cationic units destabilize the film. The fact that a cationic polymer can be self-assembled on a surface with a neutral polymer by means of hydrogen bonding is unusual and suggests that the degree of counterion binding in the film is probably high. We were not able, however, to determine this value in our experiment. Also seen in Figure 3, when the self-assembly is performed in 0.15 M NaCl solution, unfavorable electrostatic repulsions between the cationic units of PAAm-DMDAAC are screened, yielding larger amounts of polymer deposited per layer. In this screened regime of deposition, incremental layer thickness is comparable with that obtained in purely hydrogen-bonded PAAm/PMAA systems. Note that in a control experiment we showed that ionic strength has no effect on the self-

Table 2. Growth of Seven-layer PAAm-DMDAAC/PMAA and PAAm/PMAA Films at Various Deposition Conditions As Determined by in Situ FTIR-ATR

polymer system	growth conditions[a]	amount deposited, mg/m^2	regime of growth
PAAm/PMAA	pH 2	64	I (stable)
PAAm/PMAA	pH 6	0	IV (inhibited)
PAAm-DMDAAC/PMAA	pH 2	17	I (stable)
PAAm-DMDAAC/PMAA	pH 6	50	II (stable)
PAAm-DMDAAC/PMAA	pH 7		III (unstable)
PAAm-DMDAAC/PMAA	pH 8		III (unstable)

[a] All polymers were deposited from 0.1 mg/mL D_2O solutions containing 0.01 M phosphate buffer. To obtain solution at pH = 2, hydrochloric acid was added to the buffer. The substrate was an ATR silicon crystal covered with a pretreatment polymer layer (see Experimental Section).

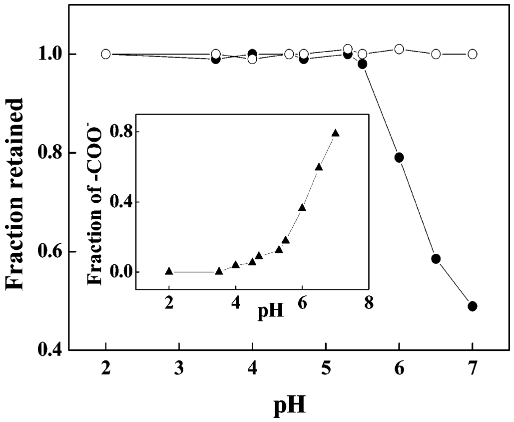

Figure 4. pH-triggered response of eight-layer PAAm-DMDAAC/PMAA film. The relative mass loss of PAAm-DMDAAC (open circles) and PMAA (filled circles) is plotted as a function of pH. The multilayer was deposited at pH = 2 in 0.01 M buffer. The total amount adsorbed was 20 mg m^{-2}. The experiments were done in D_2O, which contained 0.01 M phosphate buffer adjusted with hydrochloric acid for lower pHs. The inset shows the average ionization of PMAA within the multilayer film.

assembly of PAAm with PMAA at pH = 2 where both polymers are uncharged.

The unique aspect of the PAAm-DMDAAC/PMAA system is the switching between hydrogen-bonding and electrostatic interactions that can be achieved by changing the environmental pH. The pH dependence of the self-assembly was studied in experiments of two types. In experiments of the first type, multilayers have been deposited at a specific pH value; these results are shown in Table 2. In experiments of second type, multilayers were deposited at pH = 2 and then exposed to buffer solutions with increasing pH values; these results are illustrated in Figure 4 and discussed later in the paper.

Table 2 summarizes the results of PAAm-DMDAAC/PMAA and PAAm/PMAA multilayer growth in a wide range of pH. There are striking differences in the film growth of these two systems. With the purely hydrogen-bonded PAAm/PMAA system, large amounts of polymers (64 mg m^{-2} per 7 layers) are deposited at pH = 2, but there is no film growth at pH = 6 where a significant fraction of carboxylic groups of PMAA become ionized (pK_a of PMAA is about 6−7). Since the association between PAAm and PMAA chains is primarily driven by hydrogen-bonding interactions, the decrease in the density of the hydrogen-bonding groups below a critical value results in dissociation of PAAm and PMAA chains. This is similar to the concept of critical minimum charge density developed for electrostatically stabilized multilayers.[27,28] In contrast to the PAAm/PMAA system, stable PAAm-DMDAAC/PMAA multilayers can be deposited at pH = 6. The incremental amount of PAAm-DMDAAC and PMAA deposited at this pH were larger than those obtained at acidic pH values (see Table 2). This is probably related to stronger intermolecular interactions between the polycation and the polyacid chains at pH = 6. At this pH, about half of the carboxylic groups of PMAA were ionized, and both hydrogen-bonding and electrostatic interactions contributed to intermolecular adhesion. At even higher pH values (pH ≥ 7), the growth of PAAm-DMDAAC/PMAA multilayers was not stable. In this regime, during deposition of the polycation, about 10 mg m^{-2} of PAAm-DMDAAC was deposited to the surface, but this amount was then removed from the surface during PMAA deposition. A similar regime of unstable growth, also called the "adsorption−desorption" regime, was reported earlier by other groups for different pairs of polyelectrolytes.[18,27−29] In a series of control experiments using turbidity measurements of polyelectrolyte solutions, we have demonstrated that there is intermolecular adhesion between PAAm-DMDAAC and PMAA chains at pH ≥ 7. In control experiments with PAAm-DMDAAC and PMAA solutions, we confirmed that while an insoluble PAAm-DMDAAC/PMAA complex is formed at a ratio of charged units close to unity, the polyelectrolyte complex is solubilized in an excess of PMAA charged units. The latter models the situation with multilayer growth at high pH values when the substrate is exposed to large concentrations of PMAA. It also shows direct correlation between the formation of water-soluble polyelectrolyte complexes in solution and the "adsorption−desorption" regime of multilayer deposition, in good agreement with the recent work by Kovačevič et al.[30]

Although PAAm-DMDAAC/PMAA multilayers cannot be prepared at pH ≥ 7, stable multilayers can be produced by using lower pH for multilayer deposition with subsequent exposure of films to buffer solutions at high pH. Figure 4 shows the evolution of mass adsorbed when a PAAm-DMDAAC/PMAA multilayer was prepared at pH = 2, with no additional salt added, and then sequentially exposed to a buffer solution with an increasingly high pH. One sees that when pH increases, the multilayer selectively releases PMAA to the solution. The inset in Figure 4 shows changes in ionization of the self-assembled polyacid during pH increase. Note that the PMAA ionization increased in the pH range from 5 to 7, in good agreement with the reported pK_a of 6 for PMAA.[12] For multilayers formed primarily by electrostatic interactions, one would expect that a weak polyacid is more ionized compared to free polyacid in solution.[14,18,31] However, this effect was not observed in the case PAAm-DMDAAC/PMAA multilayers. The reason is probably that the effect of DMDAAC units to increase the fraction ionization of PMAA is compensated by the effect of AAm units that tend to decrease PMAA ionization because of the hydrogen bonding between AAm and −COOH groups. An important point in Figure 4 is that release of PMAA correlated with changes in PMAA ionization. The release kinetics was relatively fast. For example, a steady state was reached after about 15 min at pH 6. Figure 5 shows the evolution of charge balance within the multilayer with the pH of the external solution. It is interesting that

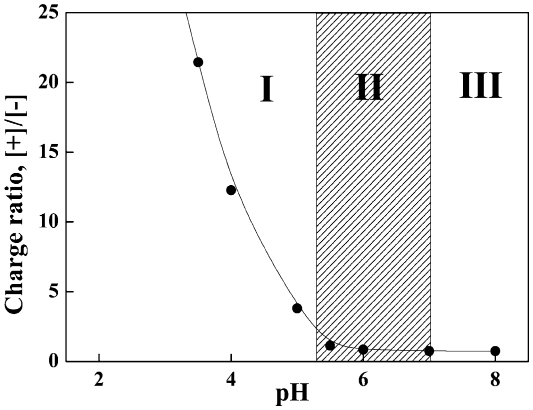

Figure 5. Ratio of positive to negative charges within eight-layer PAAm-DMDAAC/PMAA films as a function of pH. Conditions are the same as in Figure 4. Different regimes of multilayer stability are shown as regions I, II, and III.

the charge balance within the PAAm-DMDAAC/PMAA film changed from a large excess of positive charges at low pH toward unity at neutral pH values. We suggest that three regimes for the multilayer charge balance and stability can be discerned. At pH < 5.5 (regime I), self-assembly is primarily driven by hydrogen-bonding interactions between amide groups of PAAm-DMDAAC and carboxylic groups of PMAA. We have recently also suggested that an important contribution to multilayer stability at low pH values comes from carboxylic acid cyclic dimers and oligomeric associated structures.[32] In this region, multilayers are stable despite of unfavorable repulsions of positive charges in the polycation, and PMAA is not released into solution. At 5.5 < pH < 7 (regime II) the fraction of ionized carboxylic acid groups rapidly increases. While negative charges accumulate within the film, PMAA chains are released to solution to bring the charge balance of the film back to unity. Finally, at pH > 7 (regime III) where PMAA is highly ionized, hydrogen bonds are not formed and interlayer adhesion occurs exclusively through electrostatic interactions. In this regime, the multilayer growth was unstable and deposition proceeded through a sequence of adsorption–desorption events.

It was meaningful to make comparison with multilayers deposited exclusively due to hydrogen-bonding interactions. We found that the charge evolution and pH regimes for multilayer stability in a PAAm/PMAA system were strikingly different from those found for PAAm-DMDAAC/PMAA films. Figure 6 shows that PAAm/PMAA multilayers disintegrate at a narrow pH range from 5.5 to 6, after a critical charge density is reached (~8%). These regimes are shown in Figure 7. In regime I, hydrogen bonding largely contributes to the interlayer adhesion. The PAAm/PMAA film is uncharged at pH = 2, and an excess of negative charge is accumulated within the film when the pH is increased. In contrast to the PAAm-DMDAAC/PMAA system, the multilayers contain an excess of negative charge that grows with pH and finally results in multilayer disintegration at pH > 5.5. The characteristic feature of regime IV shown in Figure 6 is the lack of intermolecular adhesion between PAAm and PMAA chains. The observation of complete film destruction at high pH values is consistent with other studies on hydrogen-bonded multilayers.[11−13]

Thicker PAAm-DMDAAC/PMAA multilayers prepared at pH = 2 in the presence of 0.15 M NaCl showed a different pH response. When these multilayers were exposed to buffer solutions with increasingly high pH, a large mass loss was observed over a pH range from 5 to 7. This is illustrated in Figure 8. The inset in Figure 8 shows that the mass loss correlated with the ionization changes of PMAA. Note that the amount of polymer remaining adsorbed at pH = 6 was the same as the amount deposited in an independent experiment with deposition done directly at pH = 6 (see Table 2). At pH ≥ 7, however, the multilayer was almost completely destroyed. The observed mass loss is probably associated with the formation of water-soluble complexes in solution. Using turbidity measurements, we have confirmed the association of PAAm-DMDAAC/PMAA chains at pH > 7. The difference in the pH response of thick and thin films is partially due to the stabilizing effect of the substrate on thin films. In addition, with thick polymer layers, switching from hydrogen-bonding to electrostatic interactions and resulting chain rearrangements might cause easier layer fouling.

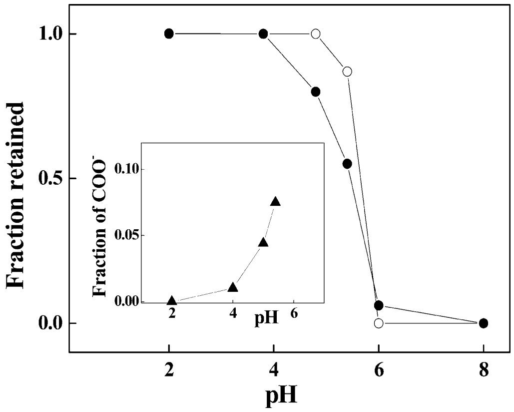

Figure 6. pH-triggered multilayer disintegration of eight-layer PAAm/PMAA film. The relative mass loss of PAAm (open circles) and PMAA (filled circles) is plotted as a function of the pH. The multilayer was deposited at pH = 2 in 0.01 M buffer. The total amount adsorbed was 70 mg m^{-2}. The experiments were done in D_2O, which contained 0.01 M phosphate buffer adjusted with hydrochloric acid for lower pHs. The inset shows the average ionization of PMAA within the multilayer film.

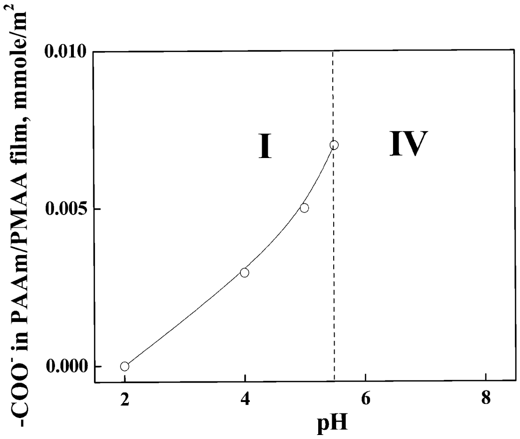

Figure 7. Amount of negative charges accumulated within eight-layer PAAm/PMAA film with an increase in pH. Conditions are the same as in Figure 4. Region IV corresponds to the decomposition of the film at pH > 5.5.

The fact that PAAm-DMDAAC and PMAA chains adhere to one another at high pH values was used to stabilize the multilayers whose pH response is shown in Figure 8. In these experiments, multilayers were

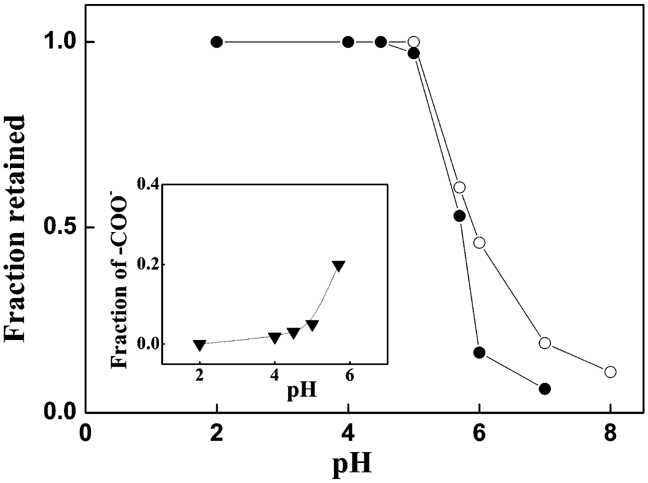

Figure 8. pH-triggered disintegration of seven-layer PAAm-DMDAAC/PMAA film. The mass loss of PAAm (open circles) and PMAA (filled circles) is plotted as a function of the pH. The multilayers were deposited at pH = 2 in the presence of 0.15 M NaCl. The total amount adsorbed was 95 mg/m^2. The experiments were done in D_2O, which contained 0.01 M phosphate buffer adjusted with hydrochloric acid for lower pHs. The inset shows the average ionization of PMAA within the multilayer films.

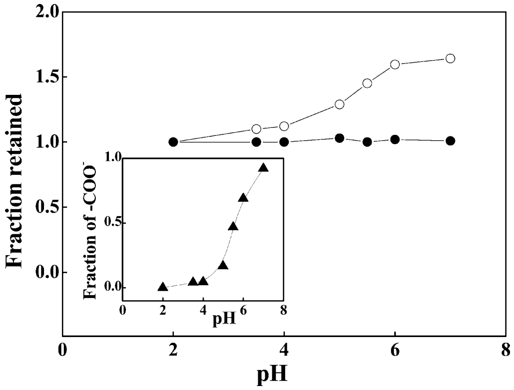

Figure 9. Stabilization of seven-layer PAAm-DMDAAC/PMAA film in PAAm-DMDAAC solutions. The mass evolution of PAAm-DMDAAC (open circles) and PMAA (filled circles) are shown as a function of pH. Conditions are the same as in Figure 8, except that experiments were done in the presence of 0.4 mg/mL PAAm-DMDAAC solution. The inset shows the average ionization of PMAA within the multilayer films.

exposed to higher pH values not in pure buffer solution, but in a solution containing one of the macromolecular constituents of the film. In particular, PAAm-DMDAAC/PMAA multilayers were deposited at pH = 2, with PMAA as the top layer. The films were then transferred to a higher pH buffer containing 0.4 mg/mL PAAm-DMDAAC. As seen in Figure 9, PAAm-DMDAAC adsorbed onto the film at all pH values. The amount adsorbed was small at pH < 5 where ionization of a polyacid was small. A significant increase of the mass adsorbed occurred at pH > 5, where ionization of the polyacid significantly increased (see inset in Figure 9). The increase in the PAAm-DMDAAC adsorption correlates with the onset of a charge-compensation mechanism of polycation adsorption at neutral and basic pH. The cationic copolymer adsorbed to the multilayer to compensate for the excessive negative charge within the film produced by an increase in the pH. It is important that with 0.4 mg/mL PAAm-DMDAAC solutions the polycation completely prevented the release of PMAA from the PAAm-DMDAAC/PMAA films. With lower concentrations of PAAm-DMDAAC (e.g., 0.2 mg/mL), PMAA was partially released from the multilayer when the pH was increased. This points to the importance of the kinetic factor in multilayer stabilization. The requirement for this stabilization seems to be that the polycation adsorption kinetics should be faster than the release rate of PMAA from the film. The above mechanism of film stabilization fails to work in systems with no intermolecular adhesion at high pH values. A control experiment in the PAAm/PMAA system showed that the presence of PAAm in solution had no effect on multilayer stability.

In summary, we find different regimes of multilayer stability corresponding to variations of external pH. In a regime with hydrogen-bonding interactions, charge imbalance may occur in the system due to stabilization of the film with hydrogen bonds. After a transition regime, an electrostatic mechanism sets in and the film sustains the balance of charges. In this regime, the charge balance requirement determines the multilayer response to increasing pH. The system may respond to increased ionization of the polyacid by releasing the excessive amounts of the polyacid. In a different scenario, emerging negative charges in the film are compensated through the adsorption of additional amounts of cationic polymer from solution, with no release of macromolecular components from the multilayer.

Acknowledgment. We thank Tom Cattabiani (Stevens Institute of Technology) for many discussions. This work was supported by the National Science Foundation under Award DMR-0209439.

References and Notes

(1) Decher, G.; Hong, J.-D. *Makromol. Chem., Macromol. Symp.* **1991**, *46*, 321.
(2) Decher, G. *Science* **1997**, *277*, 1232.
(3) Lvov, Yu.; Haas, H.; Decher, G.; Möhwald, H.; Mikhailov, A.; Mtchedlishvily, B.; Morgunova, E.; Vainshtein, B. *Langmuir* **1994**, *10*, 4232.
(4) Cheung, J. H.; Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2712.
(5) Schlenoff, J. B.; Ly, H.; Li, M. *J. Am. Chem. Soc.* **1998**, *120*, 7626.
(6) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
(7) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592.
(8) Graul, W. G.; Li, M.; Schlenoff, J. B. *J. Phys. Chem. B* **1999**, *103*, 2718.
(9) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717.
(10) Wang, L. Y.; Fu, Y.; Wang, Z. Q.; Fan, Y.; Zhang, X. *Langmuir* **1999**, *15*, 1360.
(11) Sukhishvili, S. A.; Granick, S. *J. Am. Chem. Soc.* **2000**, *122*, 9550.
(12) Sukhishvili, S. A.; Granick, S. *Macromolecules* **2002**, *35*, 301.
(13) Yang, S. Y.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 2100.
(14) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.
(15) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.
(16) Chen, K. M.; Jiang, X. P.; Kimerling, L. C.; Hammond, P. T. *Langmuir* **2000**, *16*, 7825.
(17) Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2001**, *123*, 5368.
(18) Schoeler, B.; Poptoshev, E.; Caruso, F. *Macromolecules* **2003**, *36*, 5258.
(19) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 246.
(20) Margolin, A. L.; Izumrudov, V. A.; Švedas, V. K.; Zezin, A. B.; Kabanov, V. A.; Berezin, I. V. *Biochim. Biophys. Acta* **1981**, *660*, 359.
(21) Salomaa, P.; Schaleger, L. L.; Long, F. A. *J. Am. Chem. Soc.* **1964**, *86*, 1.
(22) Frantz, P.; Granick, S. *Macromolecules* **1995**, *28*, 6915.
(23) Sperline, R. R.; Maralidharan, S.; Feiser, H. *Langmuir* **1987**, *3*, 198.

(24) Harrick, N. J. *J. Opt. Soc. Am.* **1965**, *55*, 851.
(25) Frantz, P.; Granick, S. *Langmuir* **1992**, *8*, 1176.
(26) Sukhishvili, S. A.; Granick, S. *J. Chem. Phys.* **1998**, *109*, 6861.
(27) Schoeler, B.; Kumaraswamy, G.; Caruso, F. *Macromolecules* **2002**, *35*, 889.
(28) Glinel, K.; Moussa, A.; Jonas, A. M.; Laschewsky, A. *Langmuir* **2002**, *18*, 1418.
(29) Sui, Z.; Salloum, D.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 2491.
(30) Kovačevič, D.; van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A. *Langmuir* **2002**, *18*, 5607.
(31) Mendelsohn, J. D.; Barrett, C. J.; Chan, V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017.
(32) Izumrudov, V.; Sukhishvili, S. *Langmuir* **2003**, *19*, 5188.

MA0350821