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Stability of Self-Assembled Polymer Films Investigated by Optical Laser Reflectometry

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We studied the influence of post-treatment rinsing after the formation of self-assembled polyelectrolyte films made with the weak base poly(allylamine hydrochloride) (PAH) and the strong acid poly(styrene sulfonate) (PSS). The stability of the film was studied using optical fixed-angle laser reflectometry to measure the release of polymeric material and AFM experiments to reveal the change of morphology and thickness. We found that the polymer films were stable upon rinsing when the pH was the same in the solution as that used in the buildup (pH 9). The films released most of the polymeric material when rinsed at higher pH values, but a layer remained that corresponded to a PAH monolayer directly bound with the silica surface. Films containing at least four bilayers were stable upon rinsing at lower pH values, but the stability of thinner films depended on the type of the last polymer deposited. They were stable in the case of PSS as an outermost deposit, but they released a large part of their material in the case of PAH. The stability results were determined using a simple model of the step-by-step assembly of the polymer film described formerly.

Introduction

Self-assembled polymer films (also called multilayer films) have received much attention since first described by Decher et al. in the early 1990s.¹ They are easily obtained by the successive and alternate adsorption of two polyelectrolytes of opposite charges. In some cases, they are constructed with polymers bound via hydrogen bonds or a combination of electrostatic and hydrogen bonds.^{2,3} The plethora of recent papers and reviews addressing the buildup and the properties of these films has contributed much to our knowledge of the field.⁴ Given the broad range of materials and applications potentially available, there is every reason to pursue the study of macromolecular polymer assembly.^{5–7} Moreover, the layer-by-layer assembly process facilitates the elaboration of mixed or complex nanostructured materials containing small molecules, ions, proteins, DNA, or other particles.^{8–10} One of the most encouraging perspectives of polymer self-assembly is the design of membranes for the controlled release of medicinal or other active molecules by

tuning the permeation properties through the appropriate choice of the polymers and (or) the buildup procedure.^{11–15}

Although much has been learned and debated regarding the main factors affecting the construction of polymer films using the layer-by-layer process, less attention has been given to their stability. It is, however, of crucial importance to address this aspect of the elaborated materials in view of their use and the development of new applications. Several studies have shown that polyelectrolyte films are sensitive to the modification of the environmental conditions, with respect to the conditions of the buildup of the film. This is the case with a change in pH when one polymer is a weak base or a weak acid,¹⁶ a change in salt content,¹³ or a change in temperature.¹⁷ Since the layer-by-layer process relies mostly on electrostatic binding between two oppositely charged macromolecules, one would expect the physicochemical parameters affecting electrostatic interaction forces to alter both the binding of the film to the surface and the cohesion of the film. However, the study of film stability is complicated by the largely irreversible character of interactions involving macromolecules, particularly in the case of the adsorption and complexation of polyelectrolytes, which are the two principal reactions involved in the growth of self-assembled polymer films.

Several papers^{16,18–20} have investigated the role of pH in the buildup of weak polyelectrolyte films, but few have addressed

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the effects of a change in pH after film buildup. The pH-induced alterations of polymer films include a change in morphology,²¹ thickness,¹³ wettability;²² a release of part of the materials;²³ and sometimes a complete destruction.²⁴ Of course, the behavior depends on the polymers used but also on the construction process, film thickness, and sometimes the type of molecule last deposited²⁵ or the deposition of a preliminary layer of polymers.²⁶ The destruction of the multilayer films has been observed at low pH values for the polyelectrolyte pairs poly(methacrylic acid) (PMAA)-poly(4-vinyl pyridine) quaternized (QPVP)²⁷ and in acid and basic medium for PMAA/PVP²⁸ and PMAA/PAH (polyallylamine, HCl).^{21,24} However, an increase in the molecular weight of the polyelectrolytes has been shown to prevent the destruction of the film but not the swelling.²⁴

The stability of multilayers is of great interest in the study of encapsulated material release.^{29,30} Several studies have been devoted to this property by Sukhorukov et al.,^{31–33} who made capsules in which the porosity of the membrane depended on the pH of the rinsing solutions. Upon change in pH, the polyelectrolyte membrane switched back and forth between an open and a closed state for the release of Dextran molecules.

In the simple adsorption of a polymer layer, it has been shown that the amount adsorbed is not the same at a given pH whether the adsorption was made directly at that pH or via the release of an excess of polymer adsorbed at another pH where the molecules were weakly charged.³⁴ The literature contains a large number of examples showing that polymer adsorption is either not or only partially reversible upon dilution of the bulk solution, change of salt content, change of pH, etc.^{23,35,36} The stability of single polymer layers remains unclear; that of multistep deposited films is even more ambiguous.

The present paper addresses the stability of self-assembled polymer films formed with the weak base poly(allylamine hydrochloride) (PAH) and the strong acid poly(styrene sulfonate) (PSS) on silica. After construction at pH 9 in 10^{-2} M NaCl solutions, the films containing a variable number of polymer layers were immersed in polymer-free solutions at different pH values. Alteration or destruction of the films was monitored using the evolution of a laser reflectometric signal in time. In addition, some samples were examined with AFM to determine the morphological changes.

Materials and Methods

Substrates. Oxidized silicon wafers with silicon oxide layers at different thicknesses (113 and 300 nm, measured by ellipsometry, UVISEL Jobin Yvon) were purchased from ACM. The wafers were cleaned in piranha solution (1:3 v/v H_2O_2 and H_2SO_4 mixture) for 25 min, then extensively rinsed with and stored in ultrapure water (Milli Q-Plus system, Millipore) until use.

Polyelectrolyte Solution. The polyelectrolytes used to build the polymer films were a weak base, poly(allylamine hydrochloride) (PAH, MW = ~ 70 kDa), and a strong acid, poly(styrene sulfonate) (PSS, MW = ~ 70 kDa), obtained from Sigma-Aldrich and Alfa Aesar, respectively. The refractive index increment of the PAH solutions was $dn/dc = 0.2255 \text{ cm}^3/\text{g}$. The ionization ratio was about 0.4 at pH 9,³⁷ which is the pH for film construction. The refractive index increment of the PSS solution was $dn/dc = 0.1707 \text{ cm}^3/\text{g}$. Refractive indices were determined with a Mettler Toledo refractometer RE50. The polyelectrolyte solution concentration was 0.01 g/L. A constant ionic strength (10^{-2} M) was maintained by the addition of an appropriate amount of NaCl in all experiments. The pH was adjusted with the NaOH and HCl solutions.

Optical Fixed-Angle Reflectometry. The reflectometer constructed in our laboratory was similar to that of Dijt et al.,³⁸ and the apparatus was described in a former report.³⁹ Briefly, the reflectometer was equipped with an impinging jet cell into which the solution was injected through a cylindrical channel drilled into the prism. This geometry led to the formation of a stagnation point in the center of the cell to which the molecules are transported by convective diffusion. The polarized laser beam (He–Ne, 632.8 nm) reflected by the adsorbing substrate in the cell was decomposed by a beamsplitter in the parallel (p) and perpendicular (s) components with respect to the plane of incidence. The respective intensities (I_p and I_s) were measured with photodiodes, and the reflectometric signal S was calculated from

$$S = \frac{I_p}{I_s} \quad (1)$$

Practically, the output was expressed as the ratio of $(S - S_0)/S_0$, which is usually related to the surface excess as follows:⁴⁰

$$\frac{S - S_0}{S_0} = \frac{\Delta S}{S_0} = \frac{(R_p/R_s) - (R_p/R_s)_0}{(R_p/R_s)_0} = A_s \Gamma \quad (2)$$

where S_0 and S are the values of the signal defined in eq 1 when the polymer-free solutions are injected and in the course of the adsorption experiment, respectively. Eq 2 infers that $\Delta S/S_0$ is proportional to the surface excess Γ (mg m^{-2}), as Γ is a sensitivity coefficient that depends on several experimental parameters:⁴⁰ the thickness and refractive index of the substrate, the refractive index increment of the polymer solution (dn/dc), and the refractive index of the adsorbed layer (n_{ads}).

In the cases of polyelectrolyte monolayer adsorption and after rinsing a self-assembled film at pH 12, the reflectometric output could be converted into the deposited weight using the relation⁴¹

$$\Gamma = \frac{1}{2a} \left(-b + \sqrt{b^2 + 4a \left(\frac{\Delta S}{S_0} - c \right)} \right) \quad (3)$$

where a , b , and c were determined for each pH after modeling of the interface.

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Table 1. Adsorption of PAH on Silica Wafer at Different pH Values (NaCl 10^{-2} M): Reflectometric Measurements

pH	4	5	9	10	11	12
Γ (mg m $^{-2}$)	0.10	0.13	0.47	0.51	0.58	0.11

AFM. AFM experiments were performed in a stand-alone SMENA scanning probe microscope (NT—MDT, SPM Accessories). AFM images were recorded for polymer films built at the stagnation point in constant force mode. During the scan, the deflection of the cantilever was maintained to a preset value by the feedback loop, and the topographic map of the surface was obtained by the vertical displacement of the scanner. Conical silicon tips were used on the AFM cantilevers. The force constant varied between 0.1 and 0.3 N/m to probe the samples.

Experimental Procedures. Reflectometric measurements started with the injection of a pH 9 polyelectrolyte-free solution containing NaCl 10^{-2} M for 5 min to record S_0 . The polyelectrolyte solutions were then injected alternately for 10 min to buildup the PAH/PSS films. No rinsing was done between adsorption steps. Since silicon oxide is charged negatively,⁴² the PAH solution was injected first.

At the end of the buildup, polymer-free solutions were circulated at different pH values but with the same salt concentration (NaCl 10^{-2} M). The rinsing steps lasted the time needed to reach a stationary value of the output.

Results

Elaboration of Polymer Films. Single Layer Adsorption of PAH on Silica. The adsorption of a single layer of PAH on silica was measured in the reflectometric cell at different pH values from a polymer solution at a concentration of 10 mg L $^{-1}$ and NaCl 10^{-2} M. The film was further rinsed with a PAH-free solution at the same pH and ionic strength, which did not induce any change in the output. The variation of the adsorption with pH reported in Table 1 revealed a maximum at pH 11, which is to be expected since the driving force for adsorption is mostly electrostatic. At low pH values (pH 4), the surface charge density of silica is very low and that of PAH is high; therefore, the adsorption is significantly lower than at pH 10 where reverse conditions apply. The lower adsorption of PAH at pH 11 and 12 can be explained by its lower charge density and lower screening capacity when compared to the small counterions Na $^{+}$, which adsorb preferentially. The same adsorption trend was found for the weak polybase poly(vinyl imidazole) (PVI) on silica, with maximum adsorption at about pH 8.⁴³ Note that it is difficult to compute the charge balance between adsorbate and substrate after completion of adsorption with precision since the known charge density of each isolated compound (PAH and SiO $_2$) increases significantly upon interaction.¹⁰

Five Bilayer Polymer Films. Films containing five bilayers were deposited on silica at different pH values in the reflectometric cell by the successive and alternate adsorption of PAH and PSS from solutions of each polymer containing also NaCl at a concentration of 10^{-2} mol L $^{-1}$. These films were further rinsed by circulating a polymer-free solution at the same pH and salt concentration as the buildup system. All experiments were repeated 3 times and yielded similar results within a range of 5%. Figure 1 presents the stepwise output of the reflectometer after each addition of a polymer solution. Since silica is negatively charged, the first polymer added was PAH. Considering that the step height is approximately proportional to the deposited amount,⁴⁰ we can note that the deposited weight of the polymer

Figure 1. Variation of the reflectometric signal for the buildup of self-assembled films at different pH values. After construction, the films were rinsed at the same pH as the buildup.

varied considerably with the pH, exhibiting a maximum at about pH 10. Again, this result is explained by the dependence on pH of the charge densities of PAH and silica. PSS is a strong acid that is fully ionized at all pH values explored in this investigation. In addition, PSS only binds with the positive PAH molecules; it does not adsorb directly on silica. Therefore, since the adsorption of PSS is limited to approximately the level of charge neutralization of the preceding deposited film, it is actually determined by the adsorption of PAH, which means that the dependence of the film growth on pH follows from the dependence of the adsorption of PAH on silica in the first step.

Another feature in Figure 1 is the progressive increase of the deposited weight in the successive adsorption steps. This is clearly seen in higher steps for PSS at pH 9, 10, and 11 and it is illustrated and discussed in a previous work at pH 9.⁴⁴ This phenomenon has been reported in several papers where distinction was drawn between a linear and an exponential growth of the film with the step number.^{45–47} In the first case, each polymer adsorbed the same amount in successive steps; in the second case, at least one of the two polymers progressively adsorbed an increasing amount. These different growth rates have been explained differently.⁴ Several investigations support that the progressive increase in adsorption of one polymer is caused by the diffusion of this polymer throughout the deposited film,⁴⁸ rather than a straight deposition on the existing film, which would produce a constant deposited weight. In many cases, the stepwise growth of the film changes from exponential to linear.⁴⁹ Our former investigation addressing the charge balance of PAH/PSS films on colloidal silica showed that PSS macromolecules bind with amine groups far inside the formerly deposited PAH layers, thus demonstrating the penetration of the last deposited PSS in the film.⁴⁴ The same phenomenon did not appear to take place with PAH.

In the case of PAH at pH 11, the reflectometric output sometimes presented a peculiar shape with a sharp increase and a slow decrease that lasted for most of the recording, about 10

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Figure 2. Reflectometric signal induced by rinsing with solutions at different pH values of a single PAH layer adsorbed at pH 9 (NaCl 10^{-2} M in all measurements). The different traces correspond to the repetition of the experiments.

mn (Figure 1). These overshoots have been described in the literature, mentioning two principal causes: either a fast adsorption process followed by the dissolution of a polyelectrolyte complex⁵⁰ or a slow rearrangement of the macromolecules in the film consecutive to the initial adsorption step.⁵¹ Both explanations make sense; however, parallel measurements using reflectometry and a quartz microbalance did not show any decrease in film weight during the overshoots.^{51,52} Moreover, recent calculations have revealed that the drift of the reflectometric output may result from an optical artifact related to the change of the refractive index and/or the thickness of the polymer film.^{53,54} In our opinion, no desorption took place during the overshoot.

Stability of Polymer Films. Polymer Layers Rinsed at the Same pH and Ionic Strength as the Buildup. When rinsed with polymer-free solutions, at the same pH and salt concentration as the buildup, no alteration in reflectometric output was detected. All films were stable, which is reminiscent of the known irreversibility of the adsorption of single polymer layers.⁵⁵ Similar observations have been reported in other investigations, which also showed that although the output signal was not affected by rinsing, it did induce a much higher adsorption in the subsequent steps, and the overshoots vanished.²³

Polymer Layers Rinsed at Different pH Values as the Buildup pH. A single layer of PAH was adsorbed on silica at pH 9, and then a polymer-free solution at different pH values was circulated in the cell. Figure 2 shows that the polymer layer was stable upon rinsing with a solution at pH 9 (the buildup pH) or above. Conversely, the polymer desorbed partially in more acidic solutions: the lower the pH, the more it desorbed (Table 2). As stated previously, unless there is a significant contribution of specific interactions (i.e., nonelectrostatic binding forces), polyelectrolytes adsorb up to slightly above the neutralization of the surface charge. Thus, in these experiments, we found that

Table 2. Remaining Amount of Polymer after Rinsing a Single PAH Layer Formed in NaCl 10^{-2} M Solution at pH 9

rinsing pH	3	4	5	9	12
remaining film wt (mg m ⁻²)	0	0.1	0.35	0.53	0.53

the desorption of PAH did indeed follow from the decrease in the silica charge density. Table 2 gives the remaining amount of polymer after rinsing: the polymer weight was calculated using the relation (pH 5) and the appropriate values of the parameters $a-c$.⁴¹

The stability of the film when rinsing with solutions at higher pH values behaves similarly to PVI on silica.³⁶ Since the adsorbed amount is generally limited kinetically by an electrostatic barrier and not thermodynamically, it is process dependent. In many cases, as here, adsorption at a given pH is higher when it is obtained by the release of polymer adsorbed at a more favorable pH value than when it is adsorbed directly from the solution at that pH. This phenomenon will be discussed further in the last section.

Stability of SiO₂(PAH/PSS)_x Layers. PSS terminating films with different numbers of bilayers, SiO₂(PAH/PSS)_x, with x varying between 1 and 5, were produced at pH 9 and subsequently washed with polymer-free solutions at different pH values between 4 and 12. The washing solutions contained the same concentration of NaCl (10^{-2} M) as the buildup solution. To facilitate comparison, the outputs for a given value x were set graphically at the same level at the end of the buildup (i.e., before beginning the rinsing experiments). In fact, the buildup experiments were highly reproducible: differences between the output in the last adsorption step did not exceed 5% for any film sequence.

The results in Figure 3 may be summarized as follows. Films were not stable when the pH of the rinsing solution was more basic than the buildup pH; they released most of the macromolecules. On the contrary, no alteration in the films was detected upon rinsing with a solution that was more acidic than the buildup pH. Assuming that the remaining polymer film was a single layer, after rinsing at pH 12, the remaining polymer density was calculated from the final output and eq 3. Values collected in Table 3 show a progressive increase with the number of bilayers in the film (0.69, 0.97, 1.24, and 1.72).

AFM pictures were consistent with the reflectometric observations. Figure 4 shows the typical morphology of a polymer film containing five bilayers deposited from polymer solutions at pH 9 and NaCl 10^{-2} M. Films were characterized by a continuous polymer background with a mean thickness of about 13 ± 3 nm and small thicker islands.⁴⁴ In a former study, we showed that the islands contained aggregates of PAH/PSS complexes.⁴⁴ The origin of the particular features of the film will be discussed in the last section. After rinsing at pH 4, the picture showed no significant difference, as was to be expected from the stable reflectometric measurements, whereas rinsing at pH 12 caused a considerable alteration in which most of the islands disappeared.

Stability of SiO₂(PAH/PSS)_x PAH Layers. Similar experiments were performed with films ending with PAH instead of PSS; they can be written as SiO₂(PAH/PSS)_x PAH, with x varying between 1 and 4. These films were also unstable (Figure 5 and Table 3) upon rinsing at a pH above the buildup pH (pH 10–12) and stable upon rinsing at a lower pH, except in the case of films with three layers: SiO₂(PAH/PSS)₃ PAH (12% weight loss) and less so with five layers: SiO₂(PAH/PSS)₅ PAH (2% weight loss). The remaining amount of polymer after rinsing at pH 12 showed no significant trend with the film thickness (0.93, 0.52, 0.92, and 1.43).

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Figure 3. Reflectometric signals upon rinsing with solutions at different pH values of films containing: (a) one bilayer, (b) two bilayers, (c) three bilayers, and (d) five bilayers. All experiments in solutions of NaCl 10^{-2} M. The different traces correspond to the repetition of the experiments.

Table 3. Polymer Release (wt %) and Remaining Weight (mg m^{-2}) after Rinsing at Different pH Values of Films Built at pH 9^a

no. of layers	pH				
	4 (%)	5 (%)	9 (%)	11 (%)	12 (%)
1	100	34	0	0	0 (0.53)
2	0	0	0	29	45 (0.69)
3	12	2	0	18	44 (0.93)
4	0	0	0	26	63 (0.97)
5	2	0	0		87 (0.52)
6	0	0	0	25	71 (1.24)
7	0	0	0		77 (0.92)
8	0	0	0	27	75 (1.72)
9	0	0	0		86 (1.43)
10	0	0	0	33	90 (1.24)

^a All experiments in NaCl 10^{-2} M solution.

Reconstruction of Films after Rinsing at pH 12. Films with the composition $\text{SiO}_2(\text{PAH/PSS})_x$ PAH and $\text{SiO}_2(\text{PAH/PSS})_{x+1}$ were prepared and then rinsed successively with a solution NaCl 10^{-2} M at pH 12 and 9. After stabilization of the output, a new solution of polyelectrolyte at pH 9, either PAH or PSS, was introduced in the cell to attempt the reconstruction of the film broken at pH 12. Figure 6a–d shows the successive steps of the experiment for different film compositions ($x = 2$ or 3), the film construction, rinsing at pH 12, rinsing at pH 9, and the introduction of PAH or PSS. In the case of the film construction, the two stepwise curves corresponded to the repetition of the experiment, which aimed to test each of the polymer solutions. From Figure 6, we see that only PSS could adsorb on the film that remained after the successive rinsing at pH 12 and 9, which clearly means that this film was positively charged (i.e., contained an excess of PAH). In a more quantitative way, we see also that the output

after PSS adsorption reached a roughly similar value in all experiments ($\Delta S/S_0 = 0.10$, be aware of the different scales): approximately 3 mg/m^2 .

Discussion of Stability Experiments. The results of the stability experiments described previously are easily understandable given our current knowledge of the buildup of self-assembled polymer films. In a former study, we showed that there were two stages in the initial steps of film growth: the earlier one, during which the surface is active via the adsorption of PAH, and the later one, during which growth relied solely on interactions between the two polymers. These two stages of the buildup are shown schematically in Figure 7 and will be outlined briefly next.

In the first stage, the adsorption of PAH is limited electrostatically, slightly above the neutralization of the surface charge of silica.^{10,55} At this point, the effective surface potential (streaming or zeta potential) is about 40 mV.¹⁰ An important feature at this stage is that a significant part of the surface remains polymer-free (Figure 7). In the second stage, PSS adsorbs only on the formerly deposited PAH macromolecules. It is also limited electrostatically, up to a surface potential near -40 mV . Detailed investigations have shown PSS to bind with the free protonated groups of PAH after displacement of the Cl^- counterions. It also binds with a large amount of newly ionized amine groups thanks to the additional protonation due to the electrostatic screening of PSS. At pH 9, we found that the binding with PSS increases the ionization of PAH to about 30%.¹⁰ Finally, as suggested by Hoogeveen et al.,²³ we presume that many of the bonds formed between PAH and silica surface in the first step break upon adsorption of PSS and free silanol groups to make new bonds in ensuing steps. Once bound, the two macromolecules form hydrophobic entities, much like they do in solution through a coacervation process.⁴ A few bonds between PAH and silica keep the complexes attached to the substrate.

Figure 4. AFM contact mode topographic images of SiO_2 (PAH/PSS)₅ films. Effect of rinsing with NaCl 10^{-2} M solution at different pH values and the corresponding z-profiles along an arbitrary horizontal line. (a and b) Film after buildup at pH 9; (c and d) film rinsed at pH 4; and (e and f) film rinsed at pH 12.

Figure 5. Reflectometric follow up of the buildup of films at pH 9 and consecutive injection of the solutions at different pH values (NaCl 10^{-2} M): (a) films containing three layers and (b) films containing nine layers. The different traces correspond to the repetition of the experiments.

In the third adsorption step, PAH binds both with unbound silanol groups and with sulfate groups pointing out of the macromolecular complexes. In the fourth step, again PSS may only bind with PAH, enlarging existing PAH-covered aggregates and forming new aggregates with the isolated PAH molecules deposited in the third step. The process continues until the entire

silica surface is covered with macromolecular aggregates (step 6 in Figure 7). In subsequent stages, which constitute the second growth regime, the two polymers adsorb only via polymer–polymer interactions (i.e., the surface no longer contributes to the adsorption process). The transition step between the two growth stages depends on the many parameters influencing the

Figure 6. Reflectometric followup of the buildup of films at pH 9,¹ consecutive rinsing at pH 12² and pH 9,³ and injection of PAH and PSS solutions at pH 9.⁴ All experiments in NaCl 10⁻² M solutions. (a) SiO₂(PAH/PSS)₂PAH, (b) SiO₂(PAH/PSS)₃, (c) SiO₂(PAH/PSS)₃PAH, and (d) SiO₂(PAH/PSS)₄. The different traces correspond to the repetition of the experiments.

Figure 7. Sketch of the growth mechanism of the step-by-step self-assembly of two polyelectrolytes of opposite charge. Step 1: electrostatically limited adsorption of the positive polymer (PAH on silica). Step 2: formation of polymer complexes by adsorption of the negative polymer (PSS) on the first deposited PAH. Step 3: adsorption of the positive polymer on the polymer complexes PAH/PSS and on uncovered parts of silica. Step 4: adsorption of PSS on preformed PSS/PAH aggregates and formation of new pAH/PSS aggregates with isolated PAH molecules, etc. Step 6: the surface is completely covered with polymer aggregates, and further adsorption of the polyelectrolytes relies only on polycation–polyanion interactions.

polymer–surface and polymer–polymer interactions. In the case of PAH/PSS in 10⁻² M NaCl solutions, the transition took place around step number 5;⁵⁴ in the case of Madquat/PAA polymers, we reported a transition between steps 4 and 6, depending on the pH and ionic strength.⁵³ For the PSS-poly(methyl vinylpyridinium) (PVP⁺) pair, Hoogeveen et al.²³ found a transition beyond the third layer on TiO₂ and the sixth layer on SiO₂. AFM images (Figure 5) are consistent with the mechanism described previously: aggregates show up as small islands that vary in size and

number at each adsorption step.⁴⁴ The mechanism described previously was well-illustrated by Picart et al. in the buildup of films with poly(L-lysine) and hyaluronic acid on glass.⁵⁶

With this knowledge in mind, we now discuss the results obtained in the present investigation. Concerning the first PAH layer, as stated previously, the system behaved as expected from the principle that polyelectrolyte adsorption is limited for

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kinetic reasons at the level of surface charge neutralization.^{57,58} Since lowering the pH decreased the surface charge density, part of the PAH molecules desorbed, leaving nearly the required amount for charge neutralization. When rinsing at pH 3, all molecules deposited at pH 9 left the surface since it was uncharged at this pH value. At pH 4 and 5, the remaining amount of PAH was 0.1 and 0.35 mg m⁻², respectively (accuracy 5%). However, although the isolated PAH molecules were not charged, they remained adsorbed after rinsing at pH 12. There is an interesting point to mention here: in the case of direct adsorption of PAH at pH 12, the amount adsorbed was 0.11 mg m⁻² (Table 1), which is significantly lower than the amount remaining on the film made at pH 9 after rinsing at pH 12 (0.5 mg m⁻²). The same phenomenon has been described for the adsorption on silica of another weak polybase: PVI.³⁶ We found that PVI adsorbed about 40% less from a solution at pH 10 than via the release at pH 10 of the excess of polymer adsorbed at pH 8. This phenomenon was explained by a kinetic phenomenon associated with the time required to detach and rearrange the entangled chains of the polymer. There is much evidence from the literature that polyelectrolyte adsorption is controlled kinetically, via the formation of an electrostatic barrier between the deposited molecules and those coming from the solution.^{35,57} One consequence is the lack of reversibility and a large dependence of the polymer uptake on the experimental protocol, as we see here. Instead, when the pH was switched from the buildup at pH 9 to pH 4 and 3, the release of PAH was immediate because the charge density of the PAH molecules increased strongly, which created an expelling force by electrostatic repulsion.

Films of higher ranks (four adsorption steps and above) built at pH 9 were stable when the pH was lowered, but they released part of the macromolecules in more basic media, which was contrary to the behavior of the PAH monolayer. The stability in acidic media is explained by the cohesive strength of the macromolecular aggregates. When the pH was switched to lower values, the charge density of PAH increased and so, consequently, did the number of electrostatic bonds between PSS and PAH (for isolated macromolecules, the amine groups are totally protonated at about pH 7 and below). Although no bonds were expected between PAH and silica at pH 4 and below (shown previously by the total desorption of the single PAH layer), the hydrophobic PAH/PSS aggregates were not released from the interface due to the cohesive strength of the whole polymer film.

Conversely, the film broke at a pH higher than the buildup pH, due to the decrease in the charge density of PAH and the corresponding decrease in the bonds between PAH and PSS. In addition to the lower binding strength, the negative charge of PSS turned in large excess of the positive charge of PAH, which induced electrostatic repulsion between PSS molecules and with the negative silica surface. Therefore, one is inclined to think that the signal's decrease reveals the desorption of both kinds of molecules. The remaining amount of polymer showed no particular trend; it varied erratically between 0.5 and 1.4 mg m⁻², which was the same or significantly higher than the single layer of PAH adsorbed at pH 9 (0.53 mg m⁻²). We did show that the single layer of PAH formed at pH 9 was stable upon rinsing at pH 12, which we attribute to the electrostatic bonds remaining at this pH, owing to the charge induced on PAH by its interaction with silica and to the long time required to rearrange and release the excess of entangled macromolecules. In comparison, self-assembled polyelectrolyte films were not stable upon rinsing at

Figure 8. Turbidimetric followup of the influence of pH on the stability of PAH/PSS aggregates formed at pH 9 in solutions containing NaCl 10⁻² M. Change of pH with NaOH 1 M or HCl 1 M.

pH 12, but the remaining amount was at least that found for a single PAH layer. After destruction of the film at pH 12 and rinsing at pH 9, the attempts of adsorption, showing that PSS only can adsorb on the remaining film, show that this film was positively charged and very likely was a PAH layer directly bound with silica. We presume that the PAH/PSS aggregates forming the film (Figure 7) broke up when the electrostatic bonds became too low, due to the decrease in charge of PAH at higher pH values. As shown elsewhere,^{4,21,23,24,27,28} there is a critical polymer charge density below which polyelectrolyte films or aggregates do not form; therefore, in the case of weak polyelectrolytes, which are pH/charge dependent, there should be a critical pH for the stability domain. To illustrate more clearly the role of disaggregation in the film rupture, we prepared a mixture of the two polymers at pH 9 in the same conditions as the buildup in the reflectometric cell. As expected, the system was highly turbid, due to the formation of PAH/PSS aggregates. We did not characterize the precipitated units, we merely added a concentrated NaOH solution stepwise, under strong magnetic stirring, to raise the pH and measured the turbidity of the system continuously. Figure 8 shows that the suspension did indeed become perfectly clear at pH 12 (i.e., aggregates broke, and the two polymers dissolved completely).

An interesting feature was observed in the earlier steps of growth (see Table 2). Films ending with a PSS layer were completely stable in acidic media, whereas films ending with PAH released part of their content: 12 wt % after step 3 and 2 wt % after step 5. No release was detected upon acidification at step 7 and above. This is explained by the growth mechanism sketched in Figure 7. When PAH was the last layer deposited, a fraction of the molecules had adsorbed as discrete units on the silica surface, as illustrated by step 3 (or step 5, not shown) in Figure 7. Thus, when the solution became more acidic, a fraction of the isolated PAH desorbed upon electrostatic repulsion since the charge density of silica decreased and that of PAH increased. The same phenomenon took place in the desorption from a single layer of PAH in Table 2. In steps 2 and 4, there was no release of polymer from the film since all PAH molecules formed insoluble aggregates with PSS. As stated previously, polyelectrolyte aggregates are stable upon a decrease in pH since the binding strength of the polyelectrolyte complexes increases with the related increase of the charge density of PAH. Finally, we see that the stability of the PAH/PSS films is easily explained by the stepwise growth sketched in Figure 7, which is also

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consistent with AFM pictures in Figure 5 and other film characteristics described in former investigations.^{10,44} As expected, we also see that the stability of self-assembled polyelectrolyte films is intimately related to that of complexes formed in the solution (coacervates), as has been stated in the literature,⁴ but seems largely ignored in many investigations.

Conclusion

The stability of PAH/PSS films, and more generally the stability of polyelectrolyte films containing at least one weak polybase or polyacid, is strongly dependent on pH, due to the determining influence of electrostatic bonds between the two polymers. There is a critical pH, above or below which the film breaks, releasing a large part of the polymers. There are two reasons for the destruction of the film: (1) when one of the polymer charge densities becomes too low, the binding strength of the molecular aggregates, which act as the elementary bricks of the film, is no longer sufficient and the film breaks and (2) when the charge of one polymer in the film decreases, the uncompensated charge

of the other polymer creates a repulsive interaction between the molecules of that polymer, which induces a fast release of molecules. After the film broke, we found that the fraction remaining in the interface was the polymer bound electrostatically to the substrate and that the amount was close to, and just above, the monolayer formed by direct uptake from the solution. Our results show that the stability of self-assembled polymer films depends on two major factors: the strength of the binding between the surface and the polymer of opposite charges, which dominates at earlier steps of the buildup, and the strength of the binding between the two polymers in aggregates, which allows the cohesion of the film in later steps.

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