Early steps of the film growth mechanism in self-assembled multilayers of PAH and PSS on silica

Polymer uptake, charge balance and AFM analysis

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Abstract

This study investigates the growth of self-assembled polyelectrolyte films with strong polyacid (poly(styrene sulfonate), PSS and a weak polybase (poly(allylamine hydrochloride), PAH at pH 9. Addressing the deposit of the first 3 bilayers, we focus on the successive adsorption isotherms, the effect of maintaining a constant pH, the charge balance and the counterions co-adsorption in the successive steps. We also present stepwise AFM images of the film grown on a silica wafer, showing a very heterogeneous morphology with bumps and valleys, totally unlike the expected regular superposition of bi-dimensional polymer layers. Finally, a sketch of the growth mechanism is proposed, featuring most of the experimental observations in the study.

Keywords: Self-assembled polyelectrolyte multilayers; PSS; PAH; Counter ion co-adsorption

1. Introduction

Encapsulation for the controlled release and targeting of active materials has been extensively studied in recent decades [1]. With this aim, a number of procedures, such as interfacial polymerization, co-acervation and liposomes were developed to produce solid shells on solid and liquid cores [2]. In the early nineties there appeared a new method that has since drawn great interest from the scientific community. It consists in alternately depositing oppositely charged polymers onto a substrate (the core) up to the desired thickness or shell permeability [3–5]. In addition to controlled release self-assembled polyelectrolyte multilayers have other potential applications in electronics [6] optical devices [7], membranes [8], electrocatalysis [9] and many other areas [10]. This method is advantageous

in that the process is very easy to apply to a variety of substrates including solid particles [11,12] and emulsions [13]. Procedures were found to synthesize hollow capsules suitable for further filling with active ingredients [14,15]. Controlled release was performed with an appropriate choice for the thickness and porosity of the shell, the polyelectrolytes properties (hydrophobic, hydrophilic) and the incorporation of counterions [16–19]. Remote release can be triggered by using thermosensitive [20] or pH charge dependant polymers [21]. Despite the fact that much work has been carried out with a number of polymer pairs, self-assembled polyelectrolyte shells have not found yet a true industrial outlet. This is certainly due to a lack of technical know-how. Moreover, recent reviews on the subject show that many theoretical and practical aspects of the interaction parameters during the growth of the polymer films remain ambiguous and actively debated [22,23]. In order to progress in the control of the assembly of macromolecules it is necessary to gain more and better knowledge on the dependence of film construction on the main experimental

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factors: polymer charge densities, pH, ionic strength and type of electrolytes. In a previous study, we addressed the influence of pH and salt concentration on the progressive weight uptake of alternating layers of a strong cationic polyelectrolyte, poly(dimethylaminoethyl methacrylate chloride), MADQUAT, and a weak polyacid, poly(acrylic acid), PAA [24]. It was seen that much information could be drawn from a simple charge balance, reflecting the contribution of electrolyte (counter) ions in the neutralization of the layer. Our aim in the present work was two-fold: to continue the investigation in the reverse case of the strong anionic polymer poly(styrene sulfonate) (PSS) and a weak polybase, poly(allyl amine, HCl) (PAH) and to examine the pH drift when mixing the polymers, since a change in pH may induce an alteration in the polymer assembly.

Investigations into the growth of PSS-PAH layers has already been reported in the literature, with contradictory results advocating either linear growth (constant weight deposit at increasing step number) [25,26] or exponential growth (the weight uptake of one polymer increases constantly in successive steps) [27,28]. The layer by layer growth of the film is related to the charge densities and the charge-charge stoichiometry in neighboring polycation and polyanion layers. In general, it is thought that high ionization of polyions results in a lower growth rate and lower ionization gives thicker layers. Therefore, for weak polyelectrolytes (as PAH in this investigation) the pH is a determining parameter of the growth. The other important factor in the neutralization stoichiometry is the incorporation of small electrolyte ions in the film, since they may neutralize part of the polymer charge densities. Moreover, we have formerly reported that the strong binding of small ions with one polyelectrolyte (at higher ionic strength) may hamper the binding of the other polymer [29]. In the present study, we investigated the layer by layer growth and the charge balance in the earlier steps of the film construction. We aimed to establish precisely the charge ratio and the contribution of the small ions in the polycation-polyanion binding, and the possible relation with the successive polymer uptake.

2. Experimental procedures

2.1. Materials and chemicals

The sodium salt of poly(4-styrenesulfonate) (PSS) with an average molecular weight 70 kDa was purchased from Alfa Aesar. PSS is a strong polyacid that is totally ionized in the whole range of pH used in this study [30]. The poly(allylamine hydrochloride) (PAH) from Sigma-Aldrich had a similar average molecular weight. The titration curves of Petrov et al. [31] showed that PAH behaves as a weak polyacid with a median ionization constant $pK = 8.5$. The silica powder (Aerosil 200) from Degussa contained spherical particles with a median diameter of 12 nm. Aerosil 200 is a hydrophilic compound with a BET surface area $200 \pm 25 \text{ m}^2/\text{g}$. The particles form aggregates in water but polymer uptake density was calculated from the BET surface area. The surface charge density of silica, measured previously using acid-base titration [32], had an isoelectric point close to pH 3. The silica wafers substrates (orientation 100) for the prepa-

ration of films used in the AFM analysis were purchased from ACM (Villiers St Frederic 78640, France). They were 150 mm in diameter, with a silicon thickness $625 \pm 15 \text{ }\mu\text{m}$ and an outer silica layer of approximately 100 nm (ellipsometry).

2.2. Adsorption measurement

Adsorption experiments were performed by mixing 100 g of a silica dispersion (weight fraction of silica 5%) with 10 g of polymer solution at the same pH (pH 5 or 9) and different concentrations. The mixture was stirred for at least 1 h before analysis. The pH usually changed after mixing the polymer solution and the silica dispersion. Unless stated otherwise, the pH was restored to the initial value using 1 M NaOH or HCl aliquots. Uptakes of polymer were calculated from the amount remaining in the solution after centrifuging the particles (Sigma 1–15 K, 15 mn, 14 000 rpm). The polymer concentration was determined using total carbon titration for PSS and PAH (Shimadzu, TOC 5050) and UV spectroscopy (255 nm, Beckman DU 520) for PSS.

2.3. Layer by layer deposit on silica particles

The layer by layer (LbL) deposit of the two polymers was performed at pH 9 on the silica particles starting with PAH and further alternating solutions of PSS, PAH, etc. Up to 6 layers (3 bilayers) were deposited. No water washing was done between steps. In order to avoid the separation of the particles by filtration or centrifugation between successive steps to eliminate the residual polymer in the solution, we limited the addition of polymer so that little or excess remained in the solution. An indication for the choice of the appropriate amount of polymer was obtained from preliminary adsorption isotherms, as will be shown in the next section. Preliminary experiments certified that the small excess actually present (less than 10 ppm) did not alter the next polyelectrolyte deposit.

2.4. Layer by layer deposit on the silica wafer

The silica wafers were cleaned by immersion in a Piranha solution (3 parts of sulphuric acid 98% to 1 part of hydrogen peroxide 33%), rinsed and finally stored in Milli Q water. The deposit on the silica wafers was done by circulating the solutions (100 mg/L, pH 9) in an impinging jet cell similar to that used for reflectometric measurements [33]. No water washing was performed between the deposit steps. The deposit time, 5 min for each layer, was sufficient to obtain the plateau of adsorption (no variation in the reflectometric signal after 2 min). In this cell, the flow was perpendicular to the silica wafer. The AFM analyses were done at the stagnation point at which molecules were transported onto the surface by diffusion only.

2.5. Characterization of polymer films

2.5.1. Atomic force microscopy (AFM)

The AFM measurements were done in the air at room temperature (20–25 °C) using the SMENA atomic force microscope (NT-MDT, Moscow, Russia) and the tapping mode. An ultra-

sharp silicon tip cantilever was used (NanoAndMore GmbH, Wetzlar, Germany). The resonance frequency was ~ 250 kHz, the spring constant ~ 42 N/m and the scan rate 1 Hz. The instrument was calibrated with a silicon grid (Silicon-MDT).

2.5.2. Zeta potential

The electrophoretic mobility of the particles was measured using dynamic light scattering (Zetasizer Nano ZS, Malvern Instrument, England) on particles redispersed in air-equilibrated NaCl 10^{-3} M solution at pH 9. The scattering angle was 17° and the temperature 25°C . The zeta potential was calculated from the mobility using the Smoluchowski relationship [34].

3. Results

3.1. Successive and alternate adsorption isotherms

Fig. 1 compares the adsorption of PAH on silica between pH 5 and pH 9 as a function of the equilibrium concentration (unadsorbed) in the solution. These two pH were chosen in order to screen the deposit properties at different ionization ratios of PAH at pH 5 when the charge ratio (percentage of protonated groups) is close to 1 and pH 9 when it is close to 0.4. the pH in these experiments was not adjusted after mixing the silica and the polymer. The increase in adsorption with pH shown in Fig. 1 was to be expected for two reasons. First, the surface charge density of silica increases with pH and that of PAH decreases. Based on the charge compensation principle, which should roughly apply here, more polymer is required to neutralize the surface of silica at pH 9 than at pH 5. Second, it has been well demonstrated that polyelectrolyte adsorption is determined kinetically by an electrostatic barrier between formerly deposited and incoming macromolecules [35]. In the present case, adsorption at pH 9 is less prone to induce an electrostatic barrier since PAH is only slightly charged. The charge balance will be examined more thoroughly in the last section. Quantitatively the adsorption of PAH on silica resembles that of the weakly basic poly(vinyl imidazole), which showed a maximum about pH 8 [36].

Fig. 2 shows the successive adsorption isotherms of PAH and PSS on silica at pH 9. In this case the pH was corrected after mixing the silica and the polymer solutions. Considering the adsorption of PAH on SiO_2 , we see that PAH adsorbs more on SiO_2 when the pH is corrected after mixing (0.75 mg m^{-2}

Fig. 1. Adsorption isotherms for PAH at pH 5 (■) and 9 (◆) (pH not adjusted).

Fig. 2. Adsorption isotherms for PSS (◆) and PAH (■) at pH 9 (adjusted pH).

in Fig. 2) than when it is not (0.60 mg m^{-2} in Fig. 1). This is understandable since the pH after mixing was 7.4, i.e. the surface charge of silica was lower and that of PAH was higher than when the pH was restored at pH 9. Data for the adsorption of PSS were obtained by using a PAH pre-covered silica substrate. The PAH pre-coverage was 0.7 mg m^{-2} , which is somewhat below the saturation of the silica surface, in order to minimize the amount of unadsorbed polymer in the solution. In a separate experiment, the supernatant of the PAH pre-covered silica dispersion was analyzed and showed that the amount of dissolved PAH was below 10 mg/L and that no precipitation was seen after addition of the PSS solution. Addition of PSS (preset at pH 9) in the dispersion of precovered silica (preset at pH 9) caused an increase in pH that was corrected before the adsorption measurements. This will be explained further on.

Similarly to the above example, further successive adsorptions of PAH and PSS were performed at controlled pH 9. Fig. 3 summarizes the final data from the 1st (PAH) to the 6th (PSS) polymer adsorption. It is important to note (remember?) that each isotherm in Fig. 3, save the “first” one for PAH on silica, was measured on a former layer of the polymer with an opposite charge at a coverage corresponding to the top of the steep rise for that polymer. The successive polymer coverages prior to each isotherm in Fig. 3 are reported in Table 1. For instance, the isotherm for layer 6 in Fig. 3a (3rd PSS layer, 3 mg m^{-2} at the plateau) was obtained on a film made with the successive deposits of PAH (0.7 mg m^{-2}), PSS (1.15 mg m^{-2}), PAH (0.8 mg m^{-2}), PSS (1.24 mg m^{-2}) and PAH (0.88 mg m^{-2}).

Table 1 also indicates the plateau values for each adsorption isotherm (Γ_p). We see a larger difference for PSS than for PAH between the top of the steep rise and the saturation plateau. This difference increased with the step number, which will be attributed later to a significant rearrangement of the polymer film upon adsorption of PSS. In addition, plateau values revealed a progressive increase in adsorption for each polymer, but clearly a larger increase for PSS than for PAH. In the former case the adsorption doubled between the 1st and the 3rd PSS layer, whereas the increase was only 25% for PAH. Similar figures were obtained with other polymer pairs, but with no evidence that the cationic or the anionic polymer growth was systematically higher. In the case of PSS-PAH, the former generally adsorbs more than it did here, but this may also depend on the pH

Table 1
Summary of adsorption data for the 3 first PAH-PSS bilayers

	Layer 1	Layer 2	Layer 3	Layer 4	Layer 5	Layer 6
Polymer added	PAH	PSS	PAH	PSS	PAH	PSS
Γ (mg m ⁻²)	0.7	1.15	0.8	1.24	0.88	1.89
Γ (monomère/nm ²)	4.5	3.4	5.2	3.6	5.7	5.4
Γ_p (mg m ⁻²)	0.75	1.45	0.85	1.85	0.95	3
V_{NaOH} 1 M (mL)	2.05 ± 0.16		1.20 ± 0.16		1.00 ± 0.16	
V_{HCl} 1 M (mL)		1.70 ± 0.16		1.60 ± 0.16		2.60 ± 0.16

Incorporated amount in the construction of the film (Γ), plateau values from Fig. 3 (Γ_p), volume of base or acid 1 M to maintain pH 9.

in the experiment. In fact, PSS was found to adsorb less than PAH at pH 5.5 and pH 7, which might be linked to the higher charge density of PAH at lower pH [37]. In a recent study involving the polymer pair MADQUAT (strong cationic polymer)-PAA (weak anionic polymer), growth was much higher for the fully charged polycation than for the weak polyacid PAA [24].

3.2. Variation of pH upon polymer mixing

The change in pH upon adsorption of a polymer is an interesting phenomenon that has generally been ignored in former studies. The direction of the pH drift provides information concerning the adsorption mechanism. Fig. 4 summarizes the variation of pH upon the successive additions of each polymer. One set of data relates to the uncontrolled procedure and the other

to the case in which the mixture was returned to pH 9 after the addition of each polymer. Starting at pH 9, the addition of PAH caused a decrease to pH 7.2. In the case where no adjustment was made, the next addition of PSS increased the pH to about 8.3. With further additions of PAH, PSS and PAH, respectively, the pH decreased to about 8.1, increased to 10 and eventually decreased to 8.9. When the mixture was returned to pH 9 after each addition of polyelectrolyte (i.e. back to the horizontal line in Fig. 4), the drift induced by the next addition varied more symmetrically with respect to pH 9. We see also that the drift diminished progressively, more so after the addition of PAH than of PSS. The amount of base or acid required to restore pH 9 is reported in Table 1.

The change in pH reveals the occurrence of several reactions in the adsorption process:

- The first addition of PAH in the silica dispersion caused a decrease in pH (pH 9 to pH 7.2) due to the release of protons from the silanol groups. The reason was that the polycation neutralized the surface charge of silica, which induced increased ionization in the silanol groups. The phenomenon is described below by two binding equilibria for PAH:

SiOH and SiO⁻ are the silanol group and its ionized form, respectively. NH₃⁺_{PAH} is a protonated aminogroups on PAH. Although unprotonated NH₂ groups forming Hydrogen bond with SiOH groups are not to be excluded, they are not necessary for the purpose of this study.

Fig. 3. Adsorption isotherms for PAH (a) and PSS (b). Odd and even numbers refer to PAH and PSS respectively. In 3a, layer 1 of PAH was deposited on silica (◆), layer 3 was the 2nd layer of PAH deposited on SiO₂/PAH/PSS (■), layer 5 was the 3rd layer of PAH deposited on SiO₂/PAH/PSS/PAH/PSS (▲). In 3b, Layer 2 was the 1st layer of PSS deposited on SiO₂/PAH (◆), layer 4 was the 2nd layer of PSS deposited on SiO₂/PAH/PSS/PAH and layer 6 was the 3rd layer of PSS deposited on SiO₂/PAH/PSS/PAH/PSS/PAH (▲). Intermediate adsorbed polymer densities are given in Table 1.

Fig. 4. pH variation versus time and addition step number, pH 9 with adjustment after mixing (▲) and without adjustment (■).

Fig. 5. Zeta Potential of PAH/PSS covered silica particles in NaCl 10^{-3} M pH 9. PAH outer layer (1, 3, 5) PSS outer layer (2, 4, 6).

- Adsorption of PSS on PAH-covered silica caused an increase in pH (pH 9 to pH 10.4), which is attributed to an increase in the protonation of PAH:

Adsorption of PAH on the formerly deposited PSS layer induced a decrease in pH, revealing an additional interaction of PAH with uncovered parts of silica. In this case as well, additional protonation of the amino groups may take place as above, but the dominant effect was that from the silica surface:

These equations demonstrate that the pH drift – its magnitude and its direction – is an indication of the polyelectrolyte binding mechanism. For example, the data in Fig. 4 reveal that PAH still reached the silica surface at the 5th deposit. This will be discussed further on, in the last section.

3.3. Zeta potential

Electrophoretic mobility was measured after each deposit step. Zeta potential values reported in Fig. 5 show the usual alternation between positive and negative charge excess [24]. Values about ± 40 mV are known to correspond to surface saturation for polyelectrolyte adsorption [38].

3.4. AFM characterization of the PE film

AFM pictures of the first bilayers formed on the silica wafer are presented in Fig. 6. They show a strongly inhomogeneous film with bumps about 200 nm wide and large valleys). Bumps were about 60 nm high, with a maximum height of 90 nm. On average, the height of bumps varied little with the number of bilayers, but their density did. The number of bumps above

60 nm, for example, increased from 4 to 35 between 1 and 3 bilayers. When experimenting a scratching technique described formerly [39], we found that a thin polymer layer a few nm thick was deposited between the bumps. The evolution of this layer with the film growth is under study. Several AFM images taken in a liquid cell, which required no intermediate drying, showed the same features. This indicates that the film morphology was not significantly modified by the sample drying. A question may be raised about the possible difference between polymer deposits carried out on the silica wafer (as shown in AFM pictures) and those carried out on the silica particles (adsorption isotherms and charge balance data). Earlier studies strongly suggest that the polymers adsorb similarly in both cases. In the case of MADQUAT/PAA, the difference for the first 5 bilayers was less than 20% between the uptakes on the silica wafer (measurements using reflectometry and a quartz microbalance) and on the particles (using carbon analysis) [24,29].

4. General discussion and charge balance

4.1. Polyelectrolyte adsorption is ruled kinetically

Polyelectrolyte adsorption on a charged substrate reaches more or less charge compensation, i.e. the charge density (C m^{-2}) of the adsorbed polymer equals that of the surface. However, in the case of monolayer adsorption, it is generally found that the electrokinetic potential after adsorption has the same sign as the adsorbed polyelectrolyte, which means that there is an excess of polymer charge density in comparison with the structural surface charge. Using the Gouy-Chapman relationship for diffuse layer charge density [40] one may calculate that the charge excess corresponding to a potential about 50 mV is very small in comparison with that of the polymer (less than $1 \mu\text{C cm}^{-2}$). Theoretical studies carried out by Cohen-Stuart et al. [35] and experimental illustrations [41] have shown that once the surface potential reaches a given value, an electrostatic repulsion is created in the interface that prevents additional molecules from reaching the substrate. In other words, polyelectrolyte adsorption is kinetically limited, with a threshold for surface saturation when the zeta potential reaches about ± 40 mV [24]. This all applies well to the present measurements.

4.2. Shape of adsorption isotherms

Adsorption isotherms presented in Figs. 1 and 2 have the usual profile with a steep rise and a saturation plateau. The steep rise is explained by the strong electrostatic attraction between the polymer and the substrate with an opposite charge. The plateau is determined by the kinetic barrier, as explained above. In the case of monolayer adsorption, the intermediate section is attributed to the selectivity of adsorption with respect to the molecular size in polydispersed samples [42,43]. In the case of PSS, the gradual broadening with the adsorption step number suggests a more complicated phenomenon that we attribute to an adsorption induced rearrangement of the molecules in the film. We note that PAH isotherms did not produce the same figure, but

Fig. 6. AFM images ($10\ \mu\text{m} \times 10\ \mu\text{m}$, z scale is between 0 and 100 nm) of the PAH/PSS for 1 bilayer (A), 2 bilayers (B), 3 bilayers (C), three-dimensional image for the 3 bilayers film (D), enlarged part of C ($3\ \mu\text{m} \times 3\ \mu\text{m}$) (E), z profile along the white line in E (F).

kept a rectangular profile. Again, the two polymers did not react similarly with respect to adsorption.

4.3. pH drift and pH adjustment

As stated above, the pH drifts in Fig. 4 revealed part of the binding mechanism for the polyelectrolytes, but more quantitatively, the amount of acid or base required to return to pH 9 measured the change of ionization of the polyelectrolyte and (or) the substrate upon adsorption at constant pH. Note that when the pH decreased between 9 and 7.23 upon adsorption of the first PAH layer, the net uptake of protons was $(9.9 \times 10^{-6} \text{ (H}^+ \text{ mol L}^{-1}) / 5.02 \times 10^{-2} \text{ } \Gamma \text{ (mol L}^{-1}) = 2 \times 10^{-4} \text{ mole per mole of PAH unit}$, which is negligible. However, when returning to pH 9 the increase in adsorption was $(0.7 - 0.53) = 0.17 \text{ mg m}^{-2}$ and the concomitant addition of hydroxyl ions was $2.05 \times 10^{-3} \text{ mol}$. Since the silica surface area was 1000 m^2 and the molar weight

of PAH was 93 g, it was easy to calculate a ratio of about 1.1 mol of hydroxyl ion per additional mole of adsorbed PAH unit when restoring pH 9. Part of these hydroxyl ions increased the surface charge of silica and the other part deprotonated the polymer. In other words, there was a considerable exchange of protons and probably a significant rearrangement of the polymer in the second step (return to pH 9) for the adsorption of the first PAH layer. This observation points to a possible cause of experimental uncertainties and discrepancies in the literature, since many investigations have not explicitly mentioned the pH control procedure and many have ignored the pH drift. As stated above, the shape of the intermediate part of the isotherms (between the steep rise and the plateau) may result from the rearrangement of the polymer film upon pH adjustment. This was more so for PSS than for PAH, as attested by the larger amount of acid (1.7, 1.6, 2.6 mL after PSS adsorption) than base (2, 1.2, 1 mL after PAH adsorption) required to correct the pH. In the case of PAH, the first

value (2 mL) was exceptionally high due to the large increase in the silica surface charge density. After adsorption of the first PSS layer, the pH was 10.4, the addition of acid (1.7×10^{-3} mol) to return to pH 9 increased the charge density of PAH and caused an additional uptake of PSS. The latter increase of adsorption was 0.16 mg m^{-2} (0.8×10^{-3} mol). Therefore, the increase of ionization of the amine groups (Eq. (2b) above) was about twice the additional negative charge of PSS ($1.7 \times 10^{-3}/0.8 \times 10^{-3}$). This is certainly due to the addition of acid, which caused a reorganization of the whole polymer layer. In the first step of adsorption (when the pH increased from 9 to 10.4), PSS formed macromolecular complexes with PAH and most of the sulfonate groups were neutralised with Na^+ counterions. When returning to pH 9, protons were available as needed to reach equilibrium at this pH. In the course of pH adjustment, Na^+ ions were released from PSS molecules and new bonds were formed between PSS (sulfonate groups) and PAH (protonated amine groups). Overall, the increase of the binding ratio between the two polymers was 30% (i.e. the increase in protonation of PAH/total adsorbed PSS units = $1.7 \times 10^{-3} \text{ mol} \times 100/5.8 \times 10^{-3} \text{ mol}$). Naturally, a concomitant change in the conformation of the macromolecules and in the film structure took place so as to adjust to the additional binding. This phenomenon was seen to amplify for the next PSS layers. In our opinion, this is one reason for the presence and the broadening of the intermediate part in the isotherm. The above interpretation corroborates other indications that successive polyelectrolyte layers interpenetrate [44], although there is no evidence here that true layers form.

4.4. Increase of adsorption with the step number

Fig. 3 and Table 1 show a stepwise increase of adsorption for both polymers, much more so for PSS than for PAH. A priori, the principal parameters that may influence the progression of the uptake are an increase in surface charge density, an increase in adsorption site density and a progressive change in the conformation of the adsorbing polymer. As seen above, a larger increase in PSS adsorption correlates with a larger uptake of protons by the underlying amine groups. Conversely, there is no opportunity for PAH to cause a symmetrical reaction since PSS is fully ionized. The different rate of growth for PSS and PAH presumably comes from the difference in their ionization ratio. A similar difference was observed in a previous study with MADQUAT-PAA, where the increase in adsorption was much higher for the fully charged cationic MADQUAT than for the weak polyacid PAA [24]. With regards to our results, we believe that the highly charged polymer determines film growth in the case of a strong-weak polyelectrolyte pair. However, as noted earlier, it is difficult to make any definitive statement from the reports in the literature since there is little information about pH control in deposit experiments.

4.5. Charge balance in the polymer film

The driving force for the successive adsorption of the polymer is essentially electrostatic. In order to distinguish more clearly

the different ionic contributions in early growth, we computed the charge balance in the deposited film stepwise.

For the first layer at pH 9, the values in Table 2 show charge compensation between the silica surface and the adsorbed polymer (PAH). The initial charge of silica was $-8.8 \pm 0.5 \mu\text{C}/\text{cm}^2$ [32], the charge density of the adsorbed polymer was $29 \pm 1.5 \mu\text{C}/\text{cm}^2$, the increase in silica charge density (calculated from the known addition of NaOH) was $-20 \pm 1.5 \mu\text{C}/\text{cm}^2$ and the remaining charge corresponding to the zeta potential (+40 mV) was $-0.3 \mu\text{C}/\text{cm}^2$, which may be negligible in comparison with other values. Therefore, the sum of all charge densities was close to zero:

$$\sigma_{\text{Cl}^-} + \sigma_{\text{SiO}_2} + \sigma_{\text{PAH}} + \sigma_{\text{OH}^-} + \sigma_{\text{Zeta}} = 0 \quad (4)$$

The net release of H^+ (decrease in pH) was explained by the increase in ionization of the SiOH groups, due to electrostatic screening from PAH. For the same reason, the ionization of PAH certainly increased when binding with the silanol groups, causing a consumption of protons. Practically, however, the release of protons dominated the reaction. Since the charge balance was close to zero, we conclude that a negligible amount of Cl^- counterions co-adsorbed within the first PAH layer.

Conversely, in the case of the second polymer layer (adsorption of PSS on PAH-covered silica at controlled pH 9), the balance shows a large excess of negative charge. The sum of values reported in Table 2b (charge densities of the silica substrate, the adsorbed PAH, the adsorbed PSS and the additional charge of PAH calculated from the quantity of HCl to return from pH 10.5 to pH 9) amounts to $-37 \pm \mu\text{C}/\text{cm}^2$. The charge complement to produce an electrically neutral film is attributed to the co-adsorption of the PSS counterions, Na^+ .

$$\sigma_{\text{SiO}_2} + \sigma_{\text{PAH}} + \sigma_{\text{OH}^-} + \sigma_{\text{PSS}} + \sigma_{\text{H}^+} + \sigma_{\text{Zeta}} = -\sigma_{\text{Na}^+} \quad (5)$$

The charge balances for the 3rd and the 4th polymer layers are summarized in Table 2c. As stated earlier, the deposit of the 3rd layer (2nd PAH layer) caused a decrease in pH, due to an increase in the surface charge of silica ($-11.6 \mu\text{C}/\text{cm}^2$, calculated from the required addition of HCl to return to pH 9), which means that PAH still bound significantly with the silica surface. Consecutively to the adsorption of PAH, the calculation also reveals a decrease in the overall negative charge excess of the film (from -37 to $-15 \mu\text{C}/\text{cm}^2$). The explanation is that the protonated groups of the new PAH layer displaced Na^+ ions from unbound sulfonate groups of PSS. Overall, the unbound fraction of PSS groups (neutralized by Na^+ ions) decreased from 68 to 20% after PAH adsorption.

Although the sum of the polymer + surface charge was negative after adsorption of PAH, the electrokinetic potential of the film was positive. This is understandable since the negative charge of PSS within the film was neutralized by Na^+ ions; whereas the electrokinetic potential resulted from a small charge excess of the outer PAH layer which was compensated for by the charge in the adjacent diffuse layer ($<1 \mu\text{C cm}^{-2}$).

Table 2 gives the lowest value for the co-adsorption of sodium ions, since the calculation ignores the possible co-adsorption of Cl^- ions with PAH. In fact, even if part of the PAH charge

Table 2

Charge balance for the first layer (a), the first PAH/PSS bilayer (b) and calculation of the contribution of small ions in the neutralization of the film (c)

σ_{SiO^-}	$\sigma_{I_{\text{PAH}}}$	$\Delta\sigma_{\text{SiO}_2}(\text{for } I_{\text{PAH}})$	σ_{zeta}	σ_{Cl^-}	Balance	
(a)						
−8.8	29.05	−19.78	−0.3	0.47	0	
$\sigma_{\text{SiO}^-} + \Delta\sigma_{\text{SiO}_2}(\text{for } I_{\text{PAH}})$	$\sigma_{I_{\text{PAH}}}$	$\sigma_{I_{\text{PSS}}}$	$\Delta\sigma_{\text{for } I_{\text{PSS}}}$	σ_{zeta}	σ_{Na^+}	Balance
(b)						
−28.58	29.05	−53.86	+16.4	0.19	+37	0
Layer	0	1 (PAH)	2 (PSS)	3 (PAH)	4 (PSS)	
(c)						
σ_{silice}	−8.8					
$\sigma_{I_{\text{polymer}}}$	0	29.05 ± 1.5	$−53.86 \pm 2$	33.2 ± 1.5		$−58.08 \pm 2$
$\sigma_{\Delta\text{pH}}$	0	$−19.78 \pm 1.5$	16.4 ± 1.5	$−11.58 \pm 1.5$		15.4 ± 1.5
$\Sigma\sigma_i = F(I_{\text{Na}^+} - I_{\text{Cl}^-})$	8.8	0.47	−37	−15.25		+42.5
Counter-ion	100% Na	1.6% Cl^-	68% Na^+	28% Na^+		73% Na^+

All charge densities are in $\mu\text{m cm}^2$.

were neutralized by chloride ions, the co-adsorption of Na^+ ions would still be higher.

Measurements for the second deposit of PSS (4th polymer layer) were similar to those in the first deposit step, but the deficit of positive charge was still higher. The second adsorption of PSS brought about $-58 \mu\text{C/cm}^2$ (Table 2), and the corrected pH, a positive charge (increase in the protonation of the PAH groups) $+16 \mu\text{C/cm}^2$. Overall the excess in charge was $-42 \mu\text{C/cm}^2$ (i.e. about 75% of the charge of the last adsorbed PSS layer), that were compensated for by co-adsorbed Na^+ ions. The next deposits of PAH and PSS (3rd bilayer) resembled the first two, although even more protons were required to maintain the pH (2.6 mL of HCl 1 M) upon adsorption of PSS, thus indicating a strong interaction with the underlying PAH layer. Note again that the adsorption of PSS increased significantly in the 3rd bilayer, contrary that of PAH.

Thus, PAH and PSS behaved differently in the adsorption process. PAH adsorbed with an apparently negligible amount of Cl^- counterions, as opposed to the charge of PSS, which was largely compensated for with Na^+ counterions. In addition, the uptake of PAH increased only slightly in comparison with that of PSS. As suggested previously, the difference in behavior is attributed to the difference in charge densities: the protonation ratio of PAH was about 40% at pH 9 [31] whereas PSS was fully ionized. Other results in the literature suggest similar differences in the behavior of the two polymers, although the charge balance has rarely been computed explicitly. With respect to washing with water or salt solutions, the co-adsorption ratio of counterions in the polymer layers (so-called extrinsic charge compensation ratio) is an important factor in both film growth behavior and film stability. An absence of small ions in the polymer film (intrinsic charge compensation) reveals a very good matching of charge between the two polymers. This was the case for PSS with PAH at pH 5 [45] and with PDADMAC [46,47]; it was apparently associated with a linear growth of the film with the step number. However, this question remains open since a reversible exchange of salt ions was found with PAH-PSS films

in contact with solutions of different NaCl concentrations [48] and small ions were found to partially neutralize the polyions in PSS-PAH films [37,49,50].

5. A mechanism for the multilayer growth

The adsorption measurements and the AFM pictures in this investigation show that the self-assembled multilayer film did not grow as a successive superposition of interacting polymer layers, such as puff pastry. However, the principal findings in this work can be helpful in attempting to rationalize the data. Scheme 1 presents the successive deposit steps as described below.

The charge balance showed that in the first layer, PAH adsorbed up to the neutralization of the silica surface. At this point, a large part of the silica surface remained free of polymers. In the second step, the deposit of PSS took place exclusively through electrostatic interaction with the predeposited PAH molecules. In separate experiments, we found that PSS did not adsorb directly on silica. Interaction between PSS and PAH molecules on the surface formed polymer complexes that probably aggregated to form units about 200 nm wide, resembling coacervates in a solution [51]. The adsorption of PSS caused a reversal from a positive to a negative charge. In fact, as shown in Fig. 5, the surface always takes the charge sign of the last deposited polymer. In the next step, when PAH was introduced for the second time, the molecules could adsorb both on the bare silica areas and on the PAH-PSS aggregates. In our experiments, two results support this assumption: (i) the decrease in pH reveals the binding of PAH with silica (equilibrium 1) and (ii) from the charge balance, we deduce that about half of the Na^+ counterions of the sulfonate groups are displaced by the positive PAH. The presence of a 1–2 nm thick polymer layer (presumably PAH) between the bumps is also confirmed by the scratching experiments. The overall charge of the film after adsorption of PAH (deposit sequence $\text{SiO}_2/\text{PAH}/\text{PSS}/\text{PAH}$) was positive, although the charge balance showed an excess of about 30% of the nega-

Scheme 1. Scheme of multilayer deposition. First bilayer (a), second bilayer (b), third bilayer (c).

tive charge of the deposited PSS. We previously explained that the negative excess was neutralized by codeposited Na^+ ions (table). At the second stroke of PSS, the molecules could bind on the preformed aggregates (the bumps) and form new aggregates of PAH-PSS complexes between the bumps. The analysis of AFM pictures indeed showed a large increase in the number of bumps (8 to 20 per μm^2), although there was no significant increase in average height. The accuracy of the AFM analysis does not yet allow a reliable evaluation of a possible change in width. A detailed investigation of the growth process, currently in progress, it is not within the scope of the present report. The same mechanism was involved in the build up of the third bilayer comprised a significant binding of PAH with bare silica sites (as shown by the decrease of pH) and with the PSS covered aggregates, as revealed by the correlated displacement of Na^+ ions as well as, the adsorption of PSS molecules which formed new aggregates with PAH molecules.. Interestingly, we found a very similar description of the growth mechanism in a report by Picart et al. [52]. The polymer pair was $\text{pol}(\text{L-lisylne})/\text{hyaluronic acid}$ (PLL^+/HA^-) and the deposit was done on quartz. Using optical waveguide lightmode spectroscopy (OWLS) and a quartz microbalance, they found that the positive PLL adsorbs over the entire surface of silica, whereas the next deposit of HA formed islands of PLL/HA complexes. They also observed the coalescence of islands and the increase of surface coverage during the successive and alternate deposits of the two polymers. In their work the islands in the first bilayer were larger (a few micrometers width and height) than those we observed (200 nm). This

difference may be due to the fact that they used high molecular weight polymers (about 200×10^5 Da) and made the deposits in high ionic strength solutions (0.15 M NaCl), which is known to increase the adsorption of polyelectrolytes significantly. These authors continued the deposit up to 13 bilayers and found a new growth regime after the deposit of eight PLL/HA layers. At this stage the surface was completely covered and exhibited a continuous, homogeneous film. Very similarly to our observations, they did not measure a significant increase in the average height of aggregates, which would suggest that the increase in coverage is more likely to come from the coalescence of aggregated PAH/PSS complexes.

In addition to the general scheme of growth described above, our measurements bring some insight to the interaction mechanism between PSS and PAH. We have already shown that the change in pH and the consumption of reactant (acid or base) to restore the initial pH are indicative of the type and the extent of a binding mechanism. With respect to the binding of PAH, and as stated previously, the decrease in pH provided an unequivocal indicator measuring the direct contact between the polymer and the bare surface of the silica. As for PSS, we gave the increase in pH upon addition of PSS as evidence for the increase in the charge density of PAH (i.e. higher protonation ratio) caused by binding with this polymer. Quantitatively, it is interesting to note that the amount of acid required to return to pH 9 is far in excess of the last deposited amount of PAH. This could be a strong indication that the last PSS molecules also bound with PAH molecules deposited in earlier layers, which is reminiscent of the so-called interdigitation of the polymer molecules in succession.

6. Conclusion

The stepwise analysis of the early growth of the PAH/PSS film revealed new features relative to polymer uptake, charge balance, adsorption of counterions and pH influence.

Separate adsorption isotherms demonstrated different behavior between the strongly charged PSS and the moderately charged PAH. PSS uptake increased with the step number significantly more than PAH uptake did. PSS also showed a broadening of the intermediate part of the isotherm that was attributed to a progressive modification of the film structure. Considerable attention was paid to the change in pH consecutive to the adsorption of each polymer, which allowed identification of the binding sites and mechanism. A significant difference in uptake was found, depending on whether the pH was returned or not to the initial value at pH 9. Although the comparison was not continued to the end of the construction, we observed that not controlling the pH has a strong influence on both the depositing process and the properties of the film.

From the charge balance we deduced that PSS adsorbed with a large number of Na^+ counterions, which was not the case for Cl^- with PAH. We also found that from the amount of acid required to restore the initial pH, PSS macromolecules bound with amine groups far inside the formerly deposited PAH layers. We pointed out that the charge excess corresponding to the zeta potential of the film was quite negligible in comparison with the total ionic

charge of a polymer layer. Oppositely, PAH did not seem to diffuse inside the PSS layer to bind with sulfonate groups; this is probably a consequence of the lower charge density of the molecule. This is also an explanation to the low increase of the PAH uptake with the step number.

AFM analysis showed a bumpy film morphology. The density in the number of bumps increased with the number of bilayers (1 to 3), but the height between remained approximately 60 nm.

A schematic growth model was proposed to rationalize most of the experimental features in the study. Our model is also consistent with other results in the literature and highlights the interpenetration and the mobility of the macromolecules in the course of progressive self-assembly.

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