Thin Multilayer Films of Weak Polyelectrolytes on Colloid Particles

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ABSTRACT: We report the formation of poly(acrylic acid) (sodium salt) (PAA) and poly(allylamine hydrochloride) (PAH) multilayers on polystyrene (PS) and melamine formaldehyde (MF) colloid particles by the layer-by-layer (LbL) assembly technique. The use of different solution processing conditions (e.g., pH and ionic strength) was found to have a pronounced effect on film growth, with the degree of dissociation of both polyelectrolytes (PEs) playing an important role for regular PAA/PAH multilayer growth. To retain colloidal stability during the sequential adsorption of PEs, it was essential to deposit the PE layers from adsorption solutions where the PEs are in a highly charged state, the degree of which was regulated by varying the pH. Thicker PAA/PAH coatings were obtained when the pH value of the PAA deposition solution was close to the pK_a value of PAA in solution. The presence of salt in the deposition and rinsing solutions also promoted the formation of thicker PAA/PAH coatings. The ζ-potential of the particles, measured at different pH values, allowed estimation of the isoelectric point (pI) of the adsorbed layers. The pI values of the coatings showed a dependence on the nature of the underlying layers and particle surface, particularly when PAA formed the outermost layer. A pI of 5.5 was observed for PAA adsorbed on bare MF particles, compared with a pI of 2.5 for (PAA/PAH)$_2$-coated PS spheres. The formation of hollow PAA/PAH capsules, achieved by removal of the core from the PAA/PAH-coated colloids, further confirmed the deposition of PAA and PAH multilayers. The techniques of microelectrophoresis, fluorescence spectroscopy, and transmission electron microscopy were used to characterize the layer buildup and film morphology. The formation of PAA/PAH multilayers on colloids highlights the potential of weak PEs for exploitation in colloid surface modification and encapsulation technologies.

Introduction

During the past decade, the layer-by-layer (LbL) deposition technique[1−3] has been one of the most frequently utilized wet processes for assembling organic or organic/inorganic hybrid thin films. In the LbL method, when a charged substrate is immersed into an aqueous solution of an oppositely charged polyelectrolyte (PE), a thin PE layer forms on the solid support, with its adsorption driven mainly by electrostatic interactions. This adsorption leads to overcompensation of the charge and in turn to a reversal in the net surface charge of the support,[1] thus allowing the subsequent sequential deposition of polycations and polyanions and the formation of multilayered films. By utilizing the LbL technique, multilayers of well-defined thickness, composition, and structure can be prepared on a variety of supports.[1−3] The thickness of the multilayer films can be controlled with nanoscale (<1 nm) precision.[1−3] Films can comprise, for example, alternating layers of PEs, or proteins,[4] nanoparticles,[5] or dye molecules[6] interspersed with PEs. Various types of LbL assembled multilayer films have been employed as light-emitting diodes,[7] nonlinear optical[8] and electrochromic[9] devices, and sensors.[10,11] The versatility of the LbL strategy lies not only in the wide range of suitable layer components that can be used and the control that can be exerted over the film thickness and structure, but also in the applicability of a wide range of substrates that can be used as supports to deposit the thin multilayer films.[12] This has enabled adaptation of the LbL method to coat colloid particles of different shape, size, and composition, including polymer microspheres,[13] metal nanorods[14] and nanoparticles,[15] and enzyme microcrystals.[16] Subsequent removal of the templated core particles yields hollow capsules of various compositions that are attractive for applications in drug delivery, catalysis, and separations.[13a,b,14,15a,b,16a,b]

To date, mostly combinations with at least one strong PE (i.e., a PE with a degree of dissociation that is essentially constant over a wide pH range) have been used for the preparation of thin films via LbL assembly.[1−3] Recently, however, weak PEs (polymers with degrees of dissociation that depend strongly on pH) have attracted considerable interest for constructing multilayered films with novel properties because of their rich and controllable pH-dependent properties. Fundamental and detailed investigations have been performed on the formation of weak PE (e.g., poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH)) multilayers on planar supports, providing insight into their assembly and film properties such as morphology and degree of ionization.[17−20] For example, Rubner and co-workers have shown that the thickness of adsorbed multilayers of PAA and PAH depends sensitively on the pH of the adsorption solution; a variation between 0.1 and 10 nm per layer was found with a sharp maximum at intermediate pH values.[17−19] This effect is considerably stronger than the dependence of the layer thickness on the ionic strength of adsorption solutions of PEs, where the screening effect of salt ions is used to change the polymer conformation and thus the thickness of the assembled layers from typically about 0.5 to 3 nm.[21] Additionally, PAA/PAH multilayers formed under certain pH and ionic strength conditions can undergo morphological changes to form micro- and nanoporous films, simply by their post-preparation dipping into water at low pH[22] or water containing no added salt.[23] It has also been shown that weak PE multilayer films can be prepared with accessible reactive sites, which act as nanoreactors by complexing ions from solution

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that can in turn be converted to semiconductor or metal nanoparticles inside the films.[24] By monitoring the IR vibration characteristics of the protonated carboxylic acid groups (−COOH) and the carboxylate groups (−COO$^-$), Xie and Granick investigated the ionization ratio of a layer of the weak polyacid, poly(methacrylic acid) (PMA), beneath multilayers of strong PEs.[20] The fraction of charged groups in the PMA layer was found to oscillate between ca. 30% and 85% to compensate for the additional charge introduced by the presence of polycation or polyanion uppermost layers. This variation in PMA ionization occurred even if the strong PE layers were separated from the acidic groups of PMA by a distance longer than the Debye length (>8 nm). The earlier studies[17−24] involving weak PE pairs (e.g., PAA and PAH) for LbL film formation have utilized planar supports for multilayer growth.

Of particular recent interest has been the LbL coating of colloids with PE multilayers.[12] The use of particles as supports for multilayer buildup would not only provide further insight into the deposition and layer properties of weak PEs, but will also afford a new class of coated colloids with the coating layer properties (morphology, ionization degree, etc.) and hence colloid stability controllable by small variations in pH. However, coating particles with weak PEs have a number of additional restrictions when compared to coating planar supports. The main issue is that the particles need to remain colloidally stable during and after deposition of the layers. As electrostatics plays a major role in stabilization of colloidal systems, particles coated with weak PEs can display vastly different colloidal properties because the charge density of the adsorbed polymers, which govern to a large extent their colloidal stability, can be (at the two extremes), either low or high, depending on the pH conditions employed. Another important aspect is drying between the individual PE adsorption steps, as is typically performed for films prepared on planar supports. Drying between layer depositions on planar supports is known to enhance the growth of the multilayers.[25] For particles, such drying steps often promote undesirable particle aggregation.

In the present work, the LbL assembly method is applied to coat PS and MF colloid particles with PAA and PAH. The influence of pH and ionic strength on the formation and stability of PAA/PAH multilayers deposited onto colloids is investigated in detail to determine suitable parameters that permit the uniform coating of particles with the weak PE multilayers. The PAA/PAH film buildup and coating morphology were characterized by microelectrophoresis, fluorescence spectroscopy, and transmission electron microscopy (TEM). The MF particles were primarily used because of their pH dissolution characteristics, thus allowing the formation of hollow capsules of PAA and PAH. Complementary quartz crystal microbalance (QCM) and Fourier transform infrared reflection−absorption spectroscopy (FTIR−RAS) experiments were also conducted on PAA/PAH multilayers prepared on planar supports.

Experimental Section

Materials. A 40 wt % aqueous solution of poly(acrylic acid) (sodium salt) (PAA) (M_w = 30 000) and powders of poly(allylamine hydrochloride) (PAH) (M_w = 70 000) and poly(ethylenimine) (PEI) (M_w = 25 000) were obtained from Aldrich and were used without further purification. Fluorescein isothiocyanate-labeled PAH (PAH−FITC) (M_w = 15 000) was synthesized as described elsewhere.[16b] All PEs were adsorbed from aqueous solutions with a concentration of 1 mg mL^{-1}. Millipore water (pH 6.0−7.0, resistivity >18 MΩ cm) was used for the preparation of all aqueous solutions. The pH of the solutions was adjusted by adding either HCl or NaOH. NaCl was used to modify the ionic strength of the solutions. Sulfate-stabilized polystyrene (PS) spheres (diameters of 925 and 640 nm) and melamine formaldehyde (MF) particles (diameters of 2.3, 1.9, and 1.0 μm) were purchased from Microparticles GmbH. The 2.3 μm diameter MF particles were not cross-linked and are therefore decomposable in water at a pH of 1.0. The quartz crystal microbalance (QCM) gold electrodes with a resonance frequency of ≈9 MHz were obtained from Kyushu Dentsu (Nagasaki, Japan). The quartz substrates for FTIR−RAS measurements were purchased from Hellma (Jena, Germany).

LbL Coating of Colloid Particles. For PE adsorption, approximately 2 mL of the aqueous PS or MF particle dispersion (∼1 wt %) in an Eppendorf tube was centrifuged, and the supernatant was removed. The particles were then redispersed in 1.5 mL of the PE adsorption solution by immediate shaking and sonication (less than 30 s), after which the PE was allowed to adsorb onto the particles for 20 min. The dispersions were then centrifuged, the supernatant was replaced by water, and the particles were redispersed. This washing procedure was repeated three times before the next PE layer of opposite charge was adsorbed. As PS particles possess a negatively charged surface and MF particles a positively charged one, the first layers adsorbed on the PS and MF particles were PAH (or FITC−PAH) and PAA, respectively. The duration and force of the centrifugation required to sediment the PS and MF particles mainly depend on the particle size of the spheres, as the densities of the particles are similar. For the polymer particles with a diameter of ca. 500 nm, centrifugation conditions of 10 min at 4500*g* were used, whereas particles of ca. 1 μm diameter were centrifuged for 15 min at 1500*g*. Particle aggregation as a result of LbL coating was monitored by dark-field optical microscopy.

Removal of Core Particles. To obtain hollow capsules, decomposable MF particles (diameter 2.3 μm) were used. After PAA/PAH coating, the MF particle dispersion was centrifuged, the supernatant was removed, the particles were redispersed in a droplet of water, and then 1 mL of an aqueous solution adjusted with HCl to pH 1.0 was added. Approximately 5 min was allowed for MF dissolution by HCl. The dispersions became transparent within a few seconds due to dissolution of the MF cores at low pH. Three centrifugation (10 000*g* for 5 min) and Millipore water washing cycles were conducted to remove the dissolved MF.

Microelectrophoresis. The ζ-potentials of coated particles were determined with a Malvern Zetasizer 4 by taking the average of three successive measurements.[13] To change the pH, the particle dispersions were centrifuged, the supernatants were removed, and the sediments were then dispersed in pH-adjusted water (the volume fraction of the sediment and pH-adjusted water was more than 1:1000) and diluted for measurement. The suspensions were injected into the measurement cell with a time gap between dilution and measurement shorter than 3 min.

Fluorescence Spectroscopy. For fluorescence measurements, 1.9 μm MF particles were coated with PAA/PAH−FITC multilayers. The fluorescence spectra of the suspensions were measured with a Spex Fluorolog-2 (FL-2T2) spectrofluorimeter (ISA, Olching, Germany). For evaluation, the fluorescence intensity of PAH-FITC at 525 nm was used.

TEM Imaging. Approximately 3 μL of the diluted particle suspensions was dried on carbon-coated copper grids. TEM images were then taken with a Zeiss EM 912 Omega microscope at an acceleration voltage of 120 kV.

LbL Deposition on Planar Gold Substrates. LbL films were deposited onto gold QCM electrodes and onto gold-coated quartz slides for the FTIR-RAS measurements. (Details of the substrate cleaning and preparation methods can be found elsewhere.[26]) To form a uniform and densely charged surface, PEI was deposited on the gold substrates by dipping the supports into an aqueous solution of 1 mg mL^{-1} PEI containing

0.5 M NaCl for 20 min, followed by water washing the substrates with Millipore for 1 min. After deposition of this priming layer, PAA and PAH were sequentially deposited using the same conditions as described above for the particles. To keep the deposition conditions the same for the films formed on the particles and the planar supports, drying of the films after deposition of each layer was avoided.

QCM. A QCM setup using a frequency counter (HP 53131A) and a home-built oscillator for 9 MHz QCM electrodes was used for QCM experiments. Five PAA/PAH bilayers (i.e., 10 layers total) were assembled onto the QCM electrodes and blown dry with nitrogen gas before recording the frequency. The resonant frequency differences between the uncoated and coated QCMs were used to calculate the film thickness using the Sauerbrey equation.[27a] The PAA/PAH film density was assumed to be 1.2×10^6 g/m^3.[27b]

FTIR-RAS. For the FTIR-RAS measurements, five PAA/PAH bilayers were adsorbed onto quartz slides precoated with evaporated gold of thickness 150 nm, followed by drying with a gentle stream of nitrogen. A Bruker Equinox 55/S FTIR spectrometer (reflection mode) was used with a modified reflection attachment (Harrick Co.). The incident angle was 84° to the normal of the film. Before each measurement, nitrogen gas was used to dry the sample and purge the chamber.

Results and Discussion

PAA/PAH Multilayer Formation. To follow the LbL growth of PAA and PAH on particles, we monitored the stepwise adsorption process by microelectrophoresis to determine the ζ-potentials of the colloids. PS spheres (640 nm diameter) were coated using the adsorption solutions adjusted to pH 9.0 for PAA and pH 5.0 for PAH. The adsorption solutions and the water used to remove excess PE (washing solution) contained 0.2 M and 2.0 mM NaCl, respectively. The pH values of the deposition solutions used were initially chosen because PAA and PAH are highly dissociated under these conditions (pK_a of PAA = 4.5[28] and pK_a of PAH = 8.5[29]). The salt concentrations were chosen according to our previous work on the formation of PAA/PAH multilayers on planar substrates.[23] Prior to the microelectrophoresis measurements, the particles were redispersed in water with no added salt. The ζ-potential of the particles as a function of the number of PE layers deposited is shown in Figure 1a. The odd and even layer numbers correspond to the PAH and PAA adsorption steps, respectively. The ζ-potential of the PE-coated particles alternated between ca. +20 mV and −40 mV when PAH and PAA formed the outer layers, respectively. These data are consistent with the adsorbed PAH and PAA layers being dissociated under the measurement conditions used (pH ~5−6). Such alternating reversals in the sign of the ζ-potential are characteristic for the LbL formation of PE multilayers on particles,[16] suggesting stepwise layer growth of PAA and PAH on the PS spheres.

To examine the stepwise PAA/PAH layer growth on the MF particles, we followed the sequential adsorption of PAA and PAH-FITC (i.e., fluorescently labeled PAH) by fluorescence spectroscopy (Figure 1b). The layers were assembled at pH 6.5/6.5 from aqueous solutions containing 0.2 M NaCl, and the washing solution was water containing 2.0 mM NaCl. (As with the pH 9.0/5.0 combination, under these conditions both the PAA and PAH are in a highly dissociated state.) The fluorescence intensity of the suspension was normalized for particle concentration, which was determined from single particle light scattering measurements.[30] The fluorescence intensity increases with the number of PAA/PAH-FITC bilayers deposited, indicating that multilayer growth occurs. This is in agreement with our previous work where we reported an increase in fluorescence intensity with the consecutive deposition of PSS/PAH-FITC multilayers on PS spheres by using fluorescence microscopy imaging of individual particles.[31]

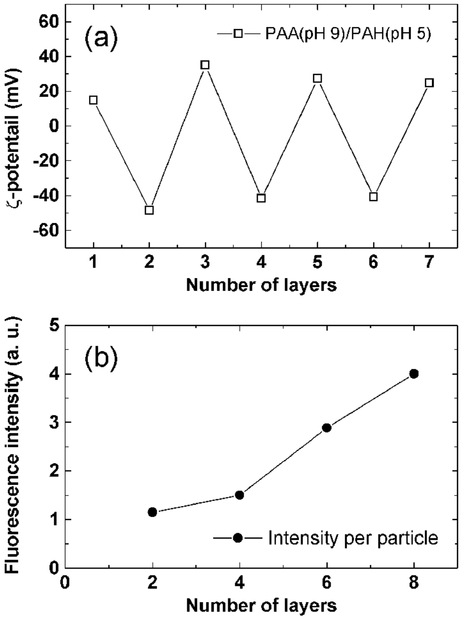

Figure 1. (a) ζ-potential of PAA/PAH-coated PS particles (640 nm diameter) as a function of layer number. The PAA/PAH layers were deposited on the particles from solutions of pH 9.0/5.0 with a salt content of 0.2 M. The salt concentration of the washing solution was 2.0 mM. (b) Fluorescence intensity of PAA/FITC-labeled PAH multilayers on MF particles with a diameter of 1.9 μm as a function of layer number. The PAA and PAH-FITC adsorption solutions used were adjusted to pH 6.5 and had a salt content of 0.2 M NaCl. 2.0 mM NaCl solutions were used for the intermediate washing steps.

We employed MF particles as colloid supports for PAA/PAH buildup because MF particles decompose upon exposure to solutions of pH <1.6. This property can be exploited to prepare hollow capsules from PE multilayer-coated colloids,[13b] the formation of which provides evidence for the formation of PE layers on particles. PAA/PAH coatings were formed on the MF particles and the core subsequently dissolved with an acidic solution of pH 1.0, leaving behind hollow PAA/PAH capsules. Figure 2 shows a representative TEM image of the hollow capsules prepared from PAA/PAH-coated MF particles prepared at pH 9.0/5.0. The fact that such capsules were obtained indicates that the PAA/PAH layers deposited also tolerated the treatment of low-pH solution for the core removal. The hollow capsules have a morphology similar to those obtained from other PEs.[13c,32]

The microelectrophoresis, fluorescence spectroscopy, and TEM data clearly indicate that PAA/PAH multilayers can be constructed on particles under conditions where both the PEs are deposited in a highly charged state. As shown in earlier studies on planar supports,[17,18] the layer buildup behavior and morphology of PAA and PAH films are highly sensitive to the pH of the adsorption solutions used. Therefore, the following sections examine the influence of the pH of the deposition solutions on PAA/PAH film growth and morphology on particles. Additionally, the effect of the ionic strength of the adsorption solutions and the washing solutions is investigated.

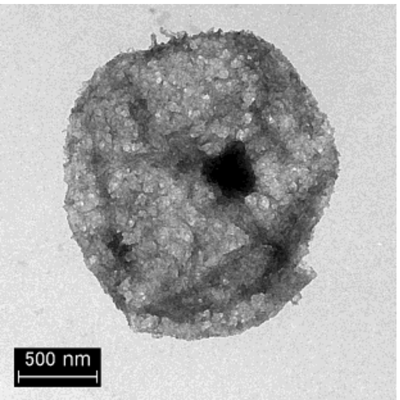

Figure 2. TEM image of a (five-bilayer) hollow PAA/PAH capsule. MF particles with a diameter of 2.3 μm were used as the dissolvable templates at pH 1.0. Numerous, similar capsules were observed by TEM, but only one is shown because the high dilution of the capsule dispersion used resulted in capsules separated by large distances (hundreds of micrometers) on the TEM grid. The PAA/PAH layers were deposited on the MF particles from solutions of pH 9.0/5.0 with a salt content of 0.2 M. The salt concentration of the washing solution was 2.0 mM.

Table 1. Influence of pH of the Adsorption Solutions on the Formation of PAA/PAH Multilayers on 925 nm Diameter PS Colloid Particles

	pH (PAH)				
pH (PAA)	3.5	4.5	5.0	7.5	9.0
3.5	2[a]	4[a]	4[a]	4[a]	3[a]
4.5	2[a]	4[a]	4[a]	4[a]	3[a]
5.0	2[a]	thick, rough[b]	4[a]	4[a]	3[a]
7.5	thin, smooth[b]	thick, smooth[b]	thin, smooth[b]	9[a]	9[a]
8.0	thin, rough[b]	thin, smooth[b]	thin, rough[b]	thin, rough[b]	7[a]

[a] The number of layers at which strong and irreversible aggregation of the particles occurs. Odd numbers correspond to PAH layers and even numbers to PAA layers. Particle aggregation could not be significantly reversed by exposing the aggregated colloids to a solution containing an oppositely charged polyelectrolyte. [b] Here the particles were successfully coated with five bilayers of PAA/PAH. The layer morphology given was derived from TEM images.

Influence of pH on PAA/PAH Multilayer Formation on Colloid Particles. An array of different pH combinations for the two PE adsorption solutions was used to examine the influence of pH on the formation of PAA/PAH multilayers on particles. Unlike the formation of PAA/PAH multilayers on planar supports,[18] the main challenge to be addressed for coating colloids is to use conditions that maintain the colloidal stability of the particles and facilitate multilayer growth. All experiments were performed with PS particles of diameter 925 nm as templates. Salt concentrations in the solutions were adjusted to 0.2 M NaCl, and Millipore water was used for the washing steps. The results obtained are summarized in Table 1. This matrix is divided into three regions. At values higher than pH 5.0 for the PAA solution and lower than pH 7.5 for the PAH solution (lower section of the table), the particles were successfully coated with five bilayers of PAA/PAH without any detectable aggregation. These conditions correspond to the region where each surface layer of PE is highly charged, as determined from the ζ-potential measurements (see later). In the region with a pH of the PAH solution at 9.0 (right column of the table), the PAH charge on the coated particles is drastically decreased, and aggregation occurs when PAH is the outermost layer (odd layer numbers). The same effect is seen in the region where the charge of the PAA layers decreases, i.e., at pH values of the PAA solution lower than about 5.0 (top part of table). Here, the aggregation occurs after an even number of layers are deposited, i.e., when the outermost layer is PAA. We also note that aggregation occurred at a different number of adsorption cycles, depending on the pH of the solutions used. This is most likely due to the different morphology of the coatings obtained under the different pH conditions. It is likely that as the coatings become thicker and in some cases rougher, enhanced interparticle entanglement occurs, leading to aggregation. Overall, the above data indicate that the PEs need to be deposited from adsorption solutions where they have a high degree of ionization in order to form PAA/PAH multilayers on colloid particles and to maintain their colloidal stability.

PS particles coated with five bilayers of PAA/PAH were imaged by TEM (Figure 3). A decrease in the coating thickness was observed as the pH value of the PAA adsorption solution was increased. This is shown in Figure 3 for samples at the pH combinations of 5.0/4.5 (a, b), 7.5/4.5 (c, d), and 8.0/4.5 (e, f) for PAA/PAH. The polydispersity of the PS particle size (standard deviation: ±30 nm) prevents *precise* determination of the coating thickness by measuring the particle diameters from TEM. However, from the gradation from gray to black at the perimeter of the particles (e.g., Figure 3d), an approximate thickness of 2 nm per layer (or 20 nm total coating thickness) was estimated. For comparison, PAA/PAH multilayers with the combination 7.5/4.5 were also constructed on QCM electrodes under the same conditions that the particles were coated, i.e., 0.2 M NaCl in the adsorption solutions, Millipore water washing, and no drying step was employed during formation of the layers. An average thickness per layer of 2.3 nm was calculated using the Sauerbrey equation,[27a] assuming a PAA/PAH film density of 1.2×10^6 g/m^3.[27b] This value corresponds well with the estimated PAA/PAH coating thickness from TEM (Figure 3d). For the samples coated at the pH combination 5.0/4.5, inhomogeneous, "raspberry-like" coatings were obtained (see Figure 3a,b). As the pH of the PAA deposition solution approaches the pK_a value of PAA in bulk solution (4.5),[28] a transition to a rather loose and loopy polymer adsorption appears to takes place. Such a drastic increase in film roughness (and thickness) was also observed for PAA/PAH multilayers formed on planar supports when the pH of the PAA solution was changed from 5.5 to 4.5.[18] If the pH of the PAA adsorption solution is lowered even further (below 5.0), irreversible aggregation of the particles occurs. It is interesting to note that the influence of pH of the PAA solution on film formation is much stronger than that of the PAH solution in the pH range investigated. For example, when the pH combination of the PAA/PAH solutions was altered from 8.0/3.5 to 8.0/7.5, i.e., the pH of the PAH deposition solution approaches the pK_a value of PAH in bulk solution (8.5),[29] the morphology of the coatings remained almost the same: the only change observable in TEM (not shown) was the disappearance of small protuberances of about 10 nm in thickness on the surface of the particles when the pH of the PAH solution was increased.

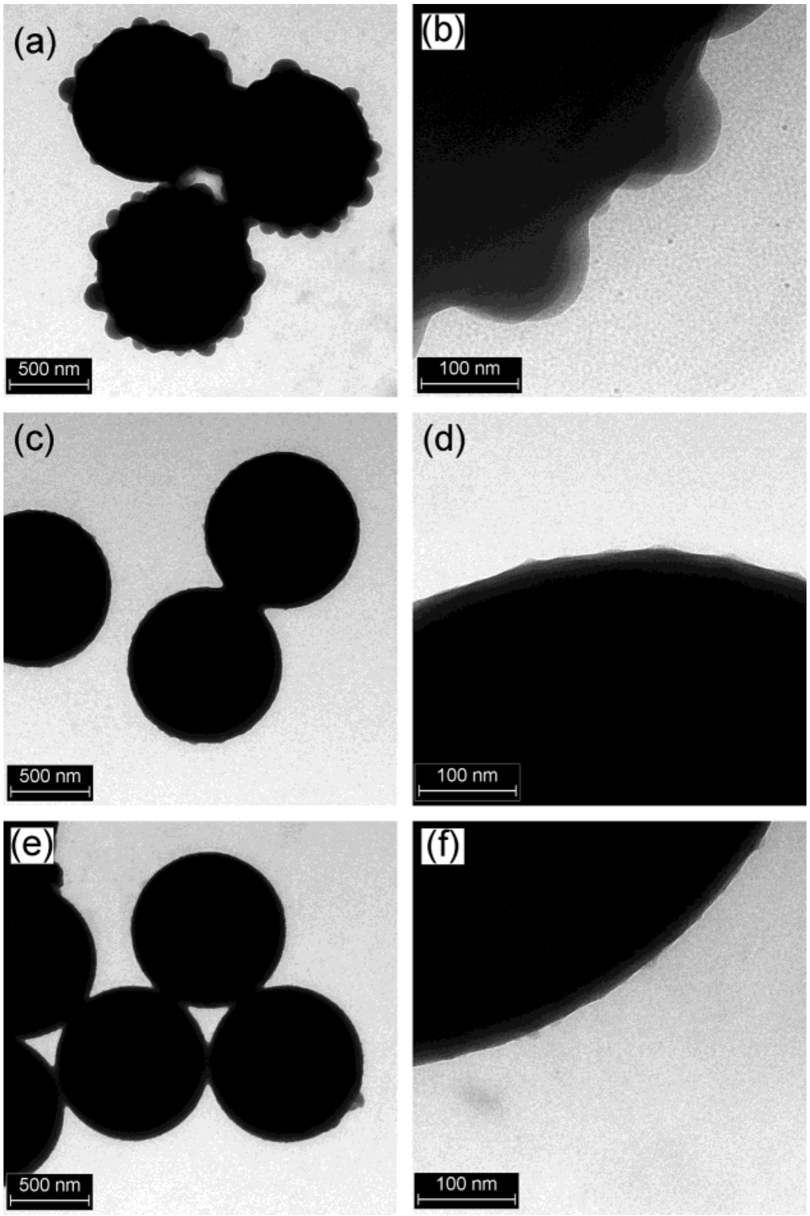

Figure 3. TEM images of 925 nm PS diameter particles coated with five PAA/PAH bilayers, prepared using PAA and PAH adsorption solutions of (a, b) pH 5.0/4.5, (c, d) pH 7.5/4.5, and (e, f) pH 8.0/4.5. The salt concentration of the adsorption solutions was 0.2 M. Millipore water was used for the washing steps.

Effect of Salt in the Adsorption Solutions. In salt-free media, electrostatic interactions should occur over a longer range than in salt-containing solutions, thus favoring colloidal stability of particles with a low charge. Thus, a similar array of samples (as earlier) was prepared by using adsorption solutions containing no added salt. The results obtained were similar to those given in Table 1. Further, we found that the p*I* of the systems remained the same when salt was used in the deposition solutions. These data indicate that the pH region for successful particle coating is not altered by the presence of salt in the deposition solutions. However, in contrast to an approximate thickness of 20 nm for the PAA/PAH multilayers adsorbed at 7.5/4.5 with 0.2 M NaCl (Figure 3c,d), the absence of salt in the deposition solutions resulted in particles with only a slightly noticeable coating (close to the detection limit). This corresponds well to the findings of Rubner and co-workers for similar adsorption conditions for PAA/PAH on planar substrates.[18] This decrease in layer thickness is due to a different conformation of the PEs; that is, the absence of salt ions in the solution results in a more rigid and linear conformation and therefore in thinner adsorbed layers, as widely reported for multilayers of strong PEs on planar and colloidal supports.[21]

Influence of Salt Concentration in Rinsing Solutions. Considering our earlier results obtained for PAA/PAH multilayer films on planar supports,[23] another series of experiments were undertaken to investigate the influence of the ionic strength of the washing (or rinsing) solution on the coating of particles. Four batches of MF particles (1.0 μm diameter) were coated by using a pH combination of the PAA/PAH solutions of 7.5/4.5, with both PE solutions containing 0.2 M NaCl, but with different washing solutions. The washing solutions contained 0, 0.002, 0.02, and 0.2 M NaCl. After the deposition of five PAA/PAH bilayers, the particles were transferred to Millipore water containing no salt for TEM imaging. The MF particles coated with PAA/PAH and washed with Millipore water (Figure 4a,b) have a similar morphology to those shown in Figure 3c,d. When salt-containing solutions were used for

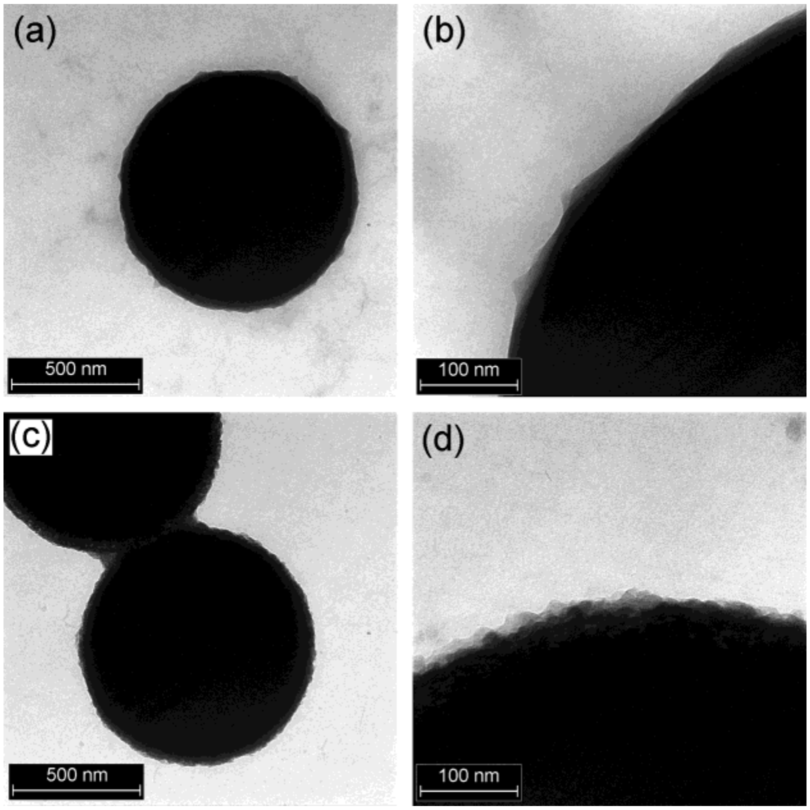

Figure 4. Lower (a, c) and higher (b, d) magnification TEM images of PAA/PAH-coated (five-bilayer) MF particles (diameter of 1.0 μm), showing the influence of salt concentration in the washing solution on layer thickness. Solutions with pH 7.5 for PAA and pH 4.5 for PAH containing 0.2 M NaCl salt were used. The washing solutions contained no added salt for (a) and (b) and 0.2 M NaCl for (c) and (d).

washing between layer depositions, an increase in the average coating film thickness was observed (Figure 4c,d). From TEM, an increase in film thickness was observed from 0.002 to 0.02 M, saturating at about 0.02 M.

Microelectrophoresis Studies of PAA/PAH-Coated Particles. We also investigated the electrophoretic mobility of the particles coated with PAA and PAH as a function of pH of the dispersing medium. Such studies reveal the pH-dependent characteristics of the preassembled PAA/PAH layers on colloids. Four types of particles were prepared: (1) PS particles coated with PAH (PS-PAH), (2) MF particles coated with PAA (MF-PAA), (3) PS-PAH/PAA/PAH, and (4) PS-$(PAH/PAA)_2$. The diameters of the PS and MF particles were 925 nm and 1.9 μm, respectively. The layers were deposited from PAA (pH 7.5) and PAH (pH 4.5) solutions containing 0.2 M NaCl, and excess PE was removed by washing with Millipore water with no added salt. These conditions were the same as those used for preparation of the coated PS particles shown in Figure 3c,d and the coated MF particles shown in Figure 4a,b.

Figure 5 displays the measured ζ-potentials as a function of pH. The p*I* of the coated particles depends strongly on the composition of the coating and underlying substrate. For PAH adsorbed on PS particles (Figure 5a, filled circles), a p*I* of about 8.0 was obtained. This value shifted slightly to approximately 9.0 when a PAH layer was adsorbed onto PS spheres precoated with PAH/PAA (Figure 5b, filled circles). When PAA was the outermost layer, a more pronounced dependence on the underlying PE film was observed. A p*I* value of ca. 5.5 was measured for PAA coated on MF particles (Figure 5a, open circles), as compared with a p*I* of 2.5 for PAA deposited onto PAH/PAA/PAH-coated PS particles (Figure 5b, open circles). The large shift in the p*I* value in the case of PAA could be explained in terms of charge regulation of weak PEs.[33] Upon adsorption onto preformed PE multilayers containing PAH (which has a higher linear charge density than PAA within the pH range of about 2−4), the degree of ionization of PAA is higher than when assembled directly onto the MF surface, thus leading to the observed change in p*I*. Such charge regulation effects have been theoretically predicted for weak PE adsorption onto surfaces.[33] This is also consistent with the study of Xie and Granick,[20] where the ionization ratio of a layer of the weak polyacid, PMA, deposited beneath multilayers of strong PEs, was found to vary depending on the additional PE layers adsorbed. It is also noted that the underlying layer (in this case PAH) is required to explain the charge reversal seen at the low pH values (<2.5), as PAA is predominantly in the uncharged state (−COOH) at this pH, as verified by the FTIR-RAS measurements (see later). Similarly, the underlying layer(s) or substrates (i.e., particle surface) in the other systems contribute to the ζ-potential observed, making it possible for charge reversal to take place. Experimentally, we also found that changing the salt concentration to 0.2 M NaCl in the measurement chamber lowered the ζ-potential (by about 50%), as expected due to screening of the charges,[34] but no change in the measured p*I* values was observed, indicating that the layer composition remained unaltered.

It was shown earlier that PAA/PAH films might desorb from a substrate when immersed in water at pH 2.0.[22] To examine the stability of our systems at low pH, electrophoresis measurements for PS particles coated

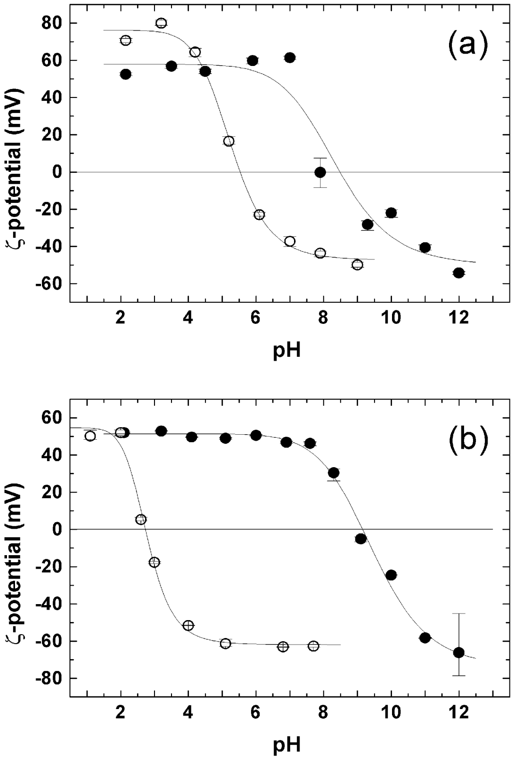

Figure 5. ζ-potential of PE-coated particles as a function of pH of the dispersing solution. (a) Solid and open symbols indicate the ζ-potential of PS particles coated with PAH (PS-PAH) and MF coated with PAA (MF-PAA), respectively. (b) Solid and open symbols indicate the ζ-potential of PS-PAH/PAA/PAH and PS-$(PAH/PAA)_2$, respectively. The curves are drawn to guide the eye. The PAA/PAH layers were deposited on the particles from solutions of pH 7.5/4.5 with a NaCl content of 0.2 M. The washing solution was Millipore water. No attempt was made to keep the ionic strength of the measuring solutions constant to compensate for the addition of HCl or NaOH.

with $(PAH/PAA)_2$ multilayers were performed first at pH 7.0, then at pH 2.0, and finally at pH 7.0 again. If significant desorption of the outermost PAA occurred at pH 2.0, the sign of the ζ-potential for the third measurement (pH 7.0) would be expected to be positive, in contrast to that observed for the first measurement. The observed ζ-potential values were −59 mV at pH 7.0, +47 mV at pH 2.0, and finally −53 mV at pH 7.0. This indicates that no significant desorption of PAA occurred at pH 2.0. Furthermore, the fact that we obtained hollow PAA/PAH multilayer shells after treatment at pH 1.0 (see Figure 2) further indicates that the PAA/PAH multilayers are relatively stable, withstanding decomposition upon short exposure (few minutes) to low-pH solutions.

Generation of Carboxylic Acid Groups in Preformed PAA/PAH Films. The results obtained indicate that successful PAA/PAH multilayer growth on particles is possible when both PEs are in a highly charged state. At first sight, this condition would appear to limit one of our interests in PAA-based LbL assembled films, that is, the usage of accessible carboxylic acid groups in the films for chemical reactions.[24] However, these uncharged groups may also be introduced after the formation of the films by exposing them to low-pH water.[22] We first applied our experimental conditions used for particles to coat planar supports. The PAA/PAH films were deposited under identical conditions to those used for coating particles (pH 7.5/4.5 containing 0.2 M NaCl, washing with Millipore water), including no drying between the PE adsorption steps. To examine the influence of pH on these films, two substrates coated with five bilayers of PAA/PAH were immersed in solutions of different pH for 8 h, the first into water at pH 5.0 and the second into water at pH 2.5. The films were dried and examined by FTIR-RAS in order to confirm the generation of carboxylic acid groups in the layers. As shown in Figure 6, the film treated at pH 5.0 exhibits absorption bands at 1567 and 1402 cm^{-1}, which are attributed to the carboxylate ($-COO^-$) asymmetric and symmetric stretches.[35] The film dipped into water at pH 2.5 shows a band at 1727 cm^{-1}, originating from carboxylic acid groups (−COOH).[35] This result clearly indicates that the formation of carboxylic acid groups inside the PAA/PAH films is possible and should be directly transferable to PAA/PAH-coated particles for the preparation of, for example, PE/nanoparticle-coated colloids. To this end, we are exploiting these carboxylic acidic groups in the films for metal ion binding, thus using the multilayers as chemical nanoreactors, as has been already shown for similar systems on planar supports.[24] This is expected to open up a new synthesis route for the preparation of nanoparticle-coated (micro)particles. Further, the creation of multilayer coatings of weak PEs of defined porosity is of interest as they can potentially be used to encapsulate drug compounds and to control their release through the morphology of the coatings.[22,23]

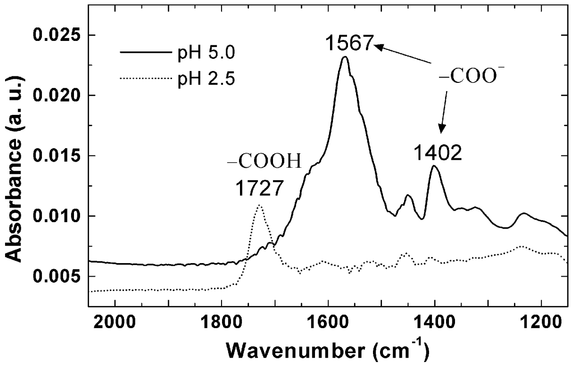

Figure 6. FTIR-RAS spectra of five-bilayer PAA/PAH films deposited on a gold-coated quartz substrate. The PAA/PAH layers were deposited on the particles from solutions of pH 7.5/4.5 with a NaCl content of 0.2 M. Millipore water was used for the washing steps. The films were dipped into water at pH 5.0 (solid spectrum) and pH 2.5 (dotted spectrum) for 8 h prior to measurement. The disappearance of the two peaks at 1567 and 1402 cm^{-1} and the emergence of the peak at 1727 cm^{-1} indicate protonation of the carboxylate groups ($-COO^-$) to give −COOH.

Conclusions

Multilayers of PAA and PAH were formed on colloid particles, and the changes that occur in film growth and layer morphology of the layers as a function of pH and ionic strength of the adsorption and washing solutions were demonstrated. Systematic variations of the pH and ionic strength of the adsorption solutions as well as the ionic strength of the washing solutions revealed that the colloidal stability of the particles during and after the coating procedure is mainly controlled by pH, with the role of the ionic strength being less important. The requirements for multilayer buildup and colloidal stability were found to be conditions of pH higher than 5.0 for the PAA adsorption solution and a pH lower than 7.5 for the PAH solution. By comparing these pH regions to the p*I* values determined, it is evident that for the stability of the coated colloids the outermost layer needs to be in a highly charged state. It was further found that both the pH and ionic strength are important factors for determining the thickness and roughness of the PE coatings. Specifically, the pH value of the PAA adsorption solution has a stronger influence than that of PAH (within the range studied). As the pH of each adsorption solution becomes closer to the pK_a value of PAA in bulk solution, thicker and rougher and even raspberry-like polymer coatings were obtained. Ionic strengths of 0.2 M for both (PAA and PAH) adsorption solutions also result in thicker coatings. Furthermore, the use of salt in the washing solutions promotes the formation of thicker coatings. By using salt-containing adsorption and washing solutions, along with pH conditions where the PEs are highly charged, PAA/PAH hollow capsules that are strong enough to withstand the core removal procedure and that do not rupture were obtained.

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