Compositional Engineering of Polyelectrolyte Blend Capsules

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Received June 20, 2007; Revised Manuscript Received July 24, 2007

ABSTRACT: This study demonstrates the feasibility of using weak−strong polyelectrolyte (PE) blend systems for controlling the composition and thickness of core−shell particles and PE blend capsules. PE blend capsules were prepared from silica sphere templates via the stepwise adsorption of poly(allylamine hydrochloride) at pH 7.5, in alternation with a varying composition of weak−strong blended PE solutions of poly(acrylic acid) (PAA) and poly(styrene sulfonate) (PSS) at pH 3.5, followed by removal of the silica particles. Confocal laser scanning microscopy was used to confirm that the particle coatings contain all three polymers, and the relative amount of each component was determined by using flow cytometry. Transmission electron microscopy images show that stable PE blend capsules are prepared, in which PSS adds structural integrity. Investigation of the thickness of the capsules via atomic force microscopy indicates that thicker films are obtained when the proportion of PAA in the blend adsorption solution increases. A thickness of ∼12 nm per bilayer is observed for 10% PAA blends, and this increases to ∼20 nm per bilayer for 90% PAA blends. The addition of salt in the adsorption solution also results in thicker multilayers. Blend capsules are expected to find application in the therapeutic and diagnostic fields.

Introduction

The surface modification of particles via the layer-by-layer (LbL) method has gained significant popularity since its inception in the late 1990s.[1−3] The prominent driving force for this approach is the sequential electrostatic adsorption of oppositely charged species onto charged substrates.[4] Under appropriate conditions, charge overcompensation and charge reversal is achieved with the adsorption of each layer,[5] thereby enabling the adsorption of subsequent layers. In the case where particles are used as substrates, the particles can be removed to produce hollow capsules. Selection of particle size, type of adsorbing material, total number of layers deposited, and post-assembly treatment conditions enables the fabrication of core−shell particles and capsules that have tunable dimensions,[6,7] functionalities,[8−11] and shell thicknesses.[12,13] These core−shell particles and capsules have subsequently found use in a wide range of applications, including in catalysis and photonics,[14−16] as microreactors,[9,17−19] as biosensors,[20−22] and as encapsulation and delivery vehicles.[23−25]

The development of the LbL field has seen the use of an increasingly wide range of interactions and species in multilayer buildup.[26−34] Although electrostatics, hydrogen bonding, and covalent bonding have been used to assemble multilayer films, the electrostatic assembly of oppositely charged polymers (polyelectrolytes, PEs) remains the prevalent method used for LbL film construction. A popular combination of PEs are poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH). PSS is a strong PE that remains charged over a wide range of pH conditions. In the absence of other ionic species, it assumes an extended conformation due to the strong intrapolymer chain repulsion between charged groups. Although PAH is a weak PE (i.e., it has pH-dependent ionization[35]), it complexes strongly with PSS. The resulting PSS/PAH multilayers are relatively thin, compact, and stable.[36] This multilayer system has been extensively characterized on both planar and colloidal supports.[37−48]

The multilayer combination of poly(acrylic acid) (PAA) and PAH has been used extensively by Rubner and co-workers.[35,49−53] PAA is a weak PE, hence its degree of ionization varies with the pH of the surrounding solution. At low pH, excess protons in solution protonate the carboxylic groups on the PAA chain. This reduces repulsion between charged sites on the polymer backbone, and the PE assumes a coiled conformation. When a PAA molecule is adsorbed with such a conformation, a thick and “hairy” layer results.[51] Importantly, the protonated charged sites that are not involved in the multilayer complex can then be deprotonated and thus recharged, post-assembly.[35] The thick multilayers typically formed using weak PEs may allow for a higher degree of control over the rate of diffusion through the multilayer films. For this reason, the system is promising for applications such as encapsulation and confined microreactors.[52,53]

We previously investigated the feasibility of assembling PAA/PAH multilayers onto particles.[54] It was demonstrated that irreversible particle aggregation occurs after four layers when PAA is adsorbed under conditions of low ionization (pH 3.5). Particle aggregation can be avoided when the species are adsorbed under conditions of high ionization. However, the layer thickness in this case is comparable to the thinner PSS/PAH system due to the stretched conformation that PAA assumes. It has also been shown that the morphology of PAA/PAH multilayers can be relatively rough and inhomogeneous, depending on the adsorption conditions chosen.[54] Such uneven surface coverage limits the suitability of these core−shell particles for producing colloidally and structurally stable capsules.

One approach to overcome the limitations in colloidal stability, and enhance the control over the thickness and multilayer composition of the PSS/PAH system, is via the use of PE blend solutions. Although the simultaneous adsorption of chemically distinct species has been widely studied,[55−58] the application of this approach to multilayer film assembly is a recent development.[59−67] In previous work, we demonstrated the use of a weak/strong PE blend solution of PAA and PSS to

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10.1021/ma071372w CCC: $37.00

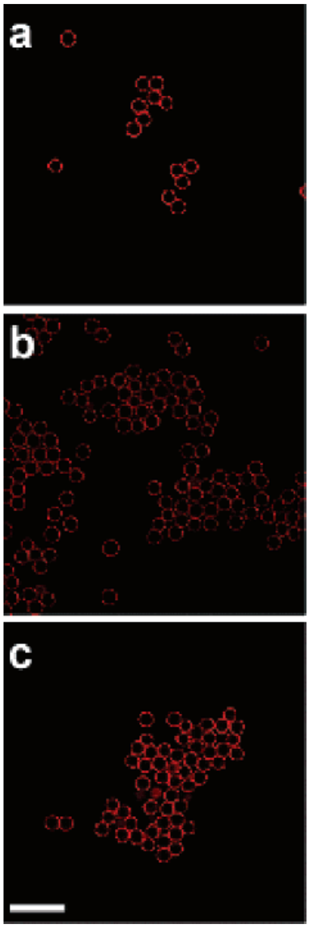

Figure 1. CLSM images of 5.3 μm diameter silica particles coated with eight PE layers, showing the presence of each PE in the multilayer coating. The layers were formed from blend (PAA/PSS) and PAH, deposited from adsorption solutions at pH 3.5 and 7.5, respectively. The PAA/PSS blend composition used was 90:10 wt %. In each case, only one of the three components is fluorescently labeled: (a) RITC-PAA; (b) Rh-PSS; and (c) RITC-PAH. All adsorption solutions contained 0.5 M NaCl. Scale bar represents 20 μm and corresponds to all images shown.

assemble multilayer films.[61] The blend layers of PAA and PSS were adsorbed in alternation with PAH on planar substrates. It was found that the thickness and composition of the multilayer films could be controlled via the proportion of PAA in the blend adsorption solution. Further, increasing the proportion of PAA in the blend adsorption solution led to an increase in the absolute amounts of PAA and PSS in the multilayers, as well as the ratio of PAA to PSS in the films.

More recently, we extended this PAA/PSS and PAH system to coat poly(styrene) particles.[67] The introduction of PSS into the adsorption solution improved both the colloidal stability and the surface smoothness of the resulting core−shell particles,[67] as compared to particles coated with PAA/PAH multilayers.[34] In comparison to the PSS/PAH multilayer films, thicker multilayer films were obtained when blend adsorption solutions were used. The number of layers at which irreversible particle aggregation occurred also increased with an increasing proportion of PSS in the adsorption solution. That study[34] showed that the combination of a weak−strong PE solution provides a simple but effective means to tailor the composition, thickness, and colloidal stability of core−shell particles. It also allows weak PE-based coatings to be formed under conditions where they would not readily be attainable in conventional two-component systems.

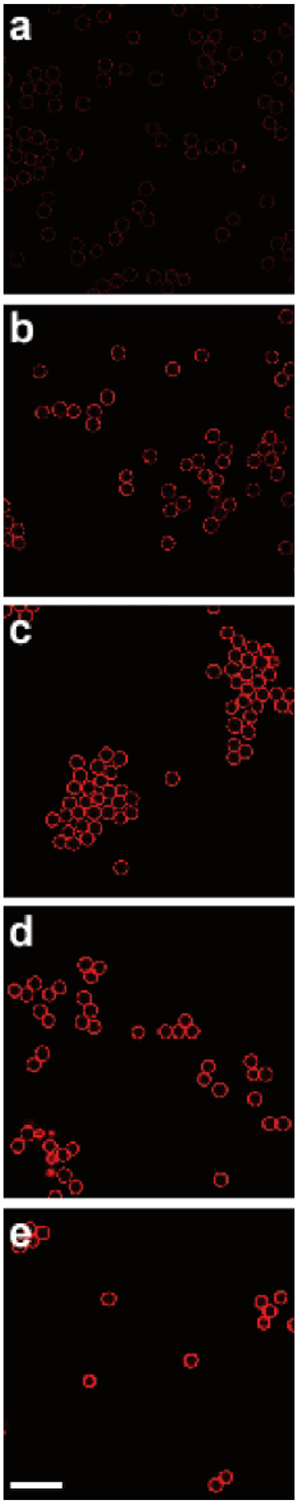

Figure 2. CLSM images of 5.3 μm diameter silica particles coated with eight PE layers, showing an increase in fluorescence with increasing proportion of PAA-RITC in the adsorption solution. The layers were formed from blend (PAA-RITC/PSS) and PAH adsorption solutions at pH 3.5 and 7.5, respectively. RITC-PAA/PSS blend compositions are (a) 10:90 wt %, (b) 25:75 wt %, (c) 50:50 wt %, (d) 75:25 wt %, and (e) 90:10 wt %. Blend and PAH adsorption solutions contained 0 and 0.5 M NaCl, respectively. Scale bar represents 20 μm and corresponds to all images shown.

In the current paper, we investigate the effect of adsorption solution composition and ionic strength on the relative adsorbed amounts for all three blend multilayer components, PAA, PSS, and PAH. This is achieved by measuring the fluorescence of eight-layer core−shell particles assembled with fluorescently

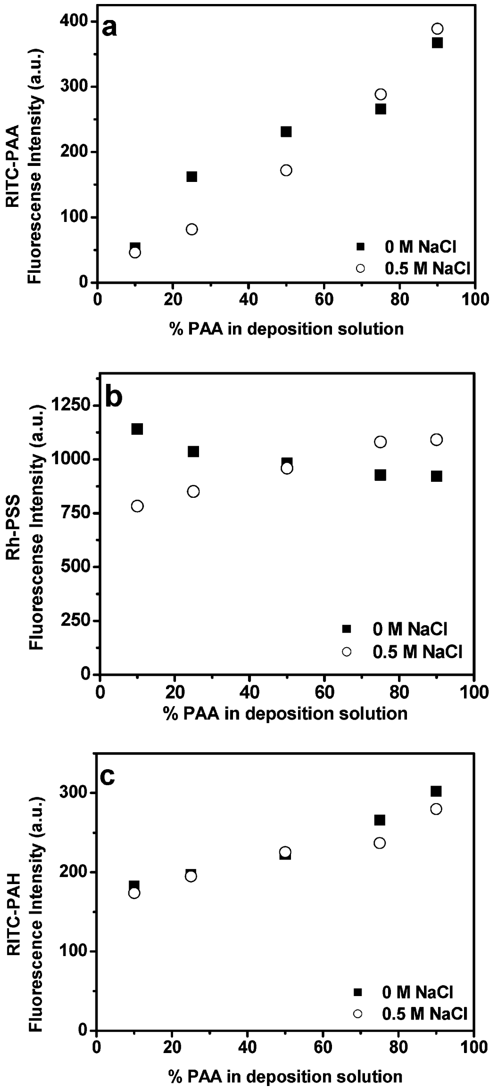

Figure 3. Fluorescence intensity measured using flow cytometry of 5.3 μm diameter silica particles with eight PE layers of blend (PAA/PSS) and PAH, deposited from adsorption solutions at pH 3.5 and 7.5, respectively. In each case, only one of the three components is fluorescently labeled: (a) RITC-PAA, (b) Rh-PSS, and (c) RITC-PAH. All PAH and RITC-PAH adsorption solutions contained 0.5 M NaCl. Blend adsorption solutions contained 0 M or 0.5 M NaCl.

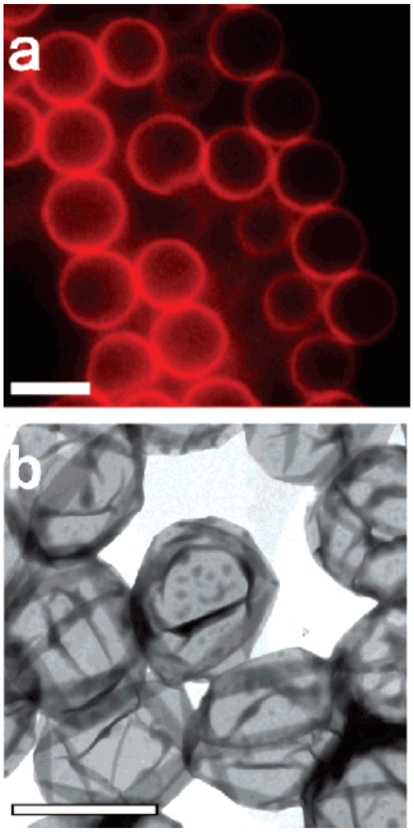

Figure 4. (a) Fluorescence microscopy and (b) TEM images of PE blend capsules obtained from 5.3 μm diameter silica particles coated with eight layers of (a) (PAA/PSS)/RITC-PAH and (b) (PAA/PSS)/PAH, deposited from adsorption solutions at pH 3.5 and 7.5, respectively. PAA/PSS blend compositions are (a) 10:90 wt % and (b) 25:75 wt %. All adsorption solutions contained 0.5 M NaCl. Scale bars represent 5 μm.

labeled polymers. The feasibility of using a blended system to form stable PE blend capsules is also examined, with particular emphasis on the role of PSS in achieving structural integrity. The thickness of the capsules after the assembly of eight layers is investigated, with reference to the influence of different adsorption solution compositions and ionic strengths. The growth of these capsules, from two to eight layers, is followed using atomic force microscopy (AFM) height profiling to examine their respective growth behavior. Further capsule characterization was performed via transmission electron microscopy (TEM) and AFM. Such blended multilayers are important because they can allow the properties of multiple, chemically distinct species to be imparted into the final film. This can lead to remarkable control over the stability, responsiveness, thickness, and morphology of interfaces and particles, which is important in applications as diverse as drug delivery, sensing, optics, catalysis, and biomaterials.

Experimental Procedures

Materials. Silica particles (5.3 μm diameter) were obtained from Microparticles GmbH. Poly(acrylic acid, sodium salt) ($M_w = 30\,000$ g mol^{-1}), poly(styrene sulfonate, sodium salt) ($M_w = 70\,000$ g mol^{-1}), poly(allylamine hydrochloride) ($M_w = 70\,000$ g mol^{-1}), and polyethyleneimine ($M_w = 25\,000$ g mol^{-1}) were obtained from Sigma-Aldrich and used as received. Fluorescently labeled polymers were synthesized according to methods described elsewhere for rhodamine isothiocyanate-labeled PAA (RITC-PAA),[26] rhodamine B-labeled PSS (Rh-PSS),[6] and RITC-PAH.[18] Sodium chloride was obtained from Merck and hydrochloric acid from BDH. High purity water was obtained from a two-stage Millipore RiOs/Synergy water purification system and had a resistivity greater than 18.2 MΩ cm.

Solutions were prepared with a total polymer concentration of 1 mg mL^{-1}. Five mass compositions of PAA and PSS were studied: PAA/PSS = 10:90, 25:75, 50:50, 75:25, and 90:10. Experiments were conducted using blend solutions containing both 0 and 0.5 M NaCl, with the pH adjusted to 3.5 using HCl. The PAH solution used contained 0.5 M NaCl, and the pH was adjusted to 7.5 using NaOH.

Particle Coating. Silica particles were dispersed in a small quantity of water (50 μL) using ultrasound and vortex mixing. The adsorption solution was then added (1 mL, PAH or PAA/PSS blend), and the mixture was agitated for 15 min during adsorption. To remove excess PE, the dispersion was either centrifuged or left to sediment, after which the supernatant was removed and replaced by water. Centrifugation conditions were optimized to prevent particle aggregation, and ranged from 27*g* to 400*g* at different stages of PE adsorption and washing. In general, the centrifugation speed was decreased as more layers were deposited to prevent particle aggregation. The particles were redispersed after washing via vortex mixing. Ultrasonication was used intermittently to aid dispersion of the particles. The rinsing process was repeated twice to ensure removal of the PE, after which the next PE solution was added to the dispersion. As the silica particles used have a negative charge,

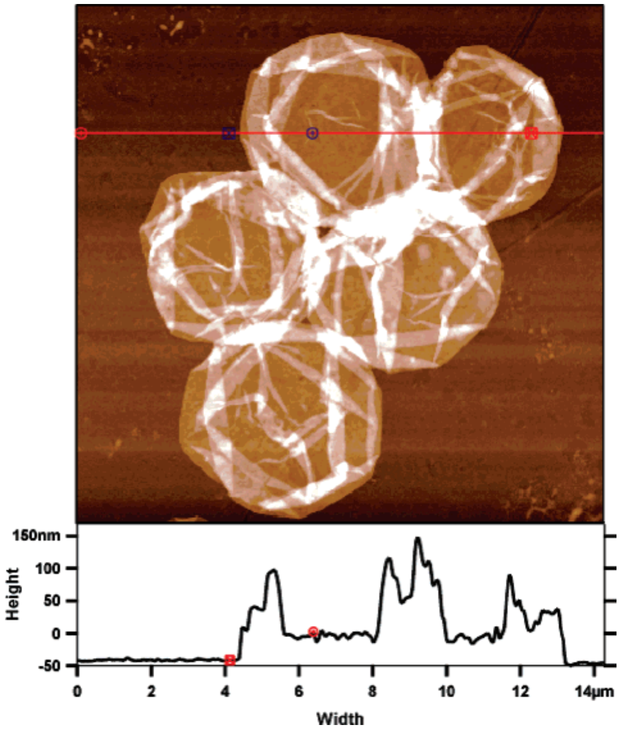

Figure 5. AFM image of PE blend capsules obtained from a template of 5.3 μm diameter silica particles coated with six layers using blend (PAA/PSS) and PAH adsorption solutions at pH 3.5 and 7.5, respectively. PAA/PSS blend composition is 90:10 wt %. Both PAH and blend solutions contained 0.5 M NaCl.

the first layer adsorbed was PAH, followed by the PAA/PSS blend layer. The process was continued until the desired layer number was attained.

Core Dissolution. The core silica particles were dissolved by exposure to 1 M HF/4 M NH_4F.[68] Briefly, 10 μL of 5 wt % core−shell particles (with a negatively charged blend outermost layer) was adsorbed to a gold surface coated with a monolayer of polyethyleneimine (PEI) and dried in air. The cores were then dissolved by exposure to 10 μL of 1 M HF/4 M NH_4F for 30 s. The PEI-coated substrate with adhered PE blend capsules was then washed 3 times by dipping in deionized water (30 s each) and dried in air. In some cases, where dispersed PE blend capsules were needed, 20 μL of 5 wt % core−shell particles was mixed with 20 μL of 2 M HF/8 M NH_4F and exposed for 30 s. The PE blend capsules were then collected after 6 water washing and centrifugation (27*g* for 5 min) cycles. It is noted that all the multilayer coatings contained significant amounts of weak PE (PAA and PAH), which are susceptible to rearrangement and desorption under certain conditions. An optimum condition for core dissolution was thus vital to ensure that the capsules were not affected. It was found that 1 M HF/4 M NH_4F (high ionic strength) buffered to near neutral pH is preferable to 1 M HF (high acidity).

Confocal Laser Scanning Microscopy (CLSM). CLSM images were taken using a Lecia TCS-SP2 confocal laser scanning microscope with a Picoquant 405 nm pulsed diode laser as the excitation source. The PE-coated particles were imaged in $x-y$ mode with a 63X planapochromatic oil immersion objective using a PMT gain of 550 V, a digital zoom of 2×, a line frequency of 400 Hz, and 4× line averaging in 12-bit acquisition mode.

Fluorescence Microscopy. An inverted Olympus IX71 microscope equipped with a 60× objective lens (Olympus UPLFL20/0.5 NA, W.D. 1.6) was used to view the PE blend capsules. A CCD camera (Cool SNAP fx, Photometrics) was mounted on the left-hand port of the microscope. The fluorescence images were illuminated with a Hg arc lap, using a UF1032 filter cube.

Flow Cytometry. Flow cytometry was performed on a Becton Dickson FACSCalibur flow cytometer using an excitation wavelength of 488 nm. The silica particles were analyzed with a FL2 filter set (570−610 nm) with a PMT voltage of 600 V. The signal was normalized by measuring the fluorescence intensity of eight peak Spherotech rainbow calibration particles.

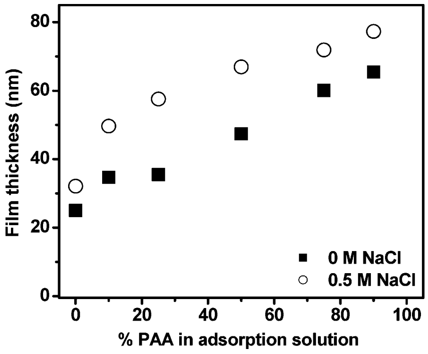

Figure 6. AFM thicknesses of PE blend capsules obtained from 5.3 μm diameter silica particles coated with eight layers (four bilayers) using blend (PAA/PSS) and PAH adsorption solutions at pH 3.5 and 7.5, respectively. All PAH solutions contained 0.5 M NaCl. Blend solutions contained 0 or 0.5 M NaCl.

TEM. TEM images were taken using a Philips CM 120 BioTWIN microscope operated at 120 kV. Copper grids coated with Pioloform film were first exposed to PEI (1 mg mL^{-1}, 0.5 M NaCl) for 15 min, followed by 3 washes in deionized water (30 s each), after which they were air-dried. A total of 10 μL of the core−shell dispersion was evaporated onto the film before core dissolution (see Core Dissolution). In some cases, TEM samples were prepared by evaporating a droplet of the PE blend capsule dispersion on a copper grid coated with a Pioloform film.

AFM. The thickness and morphology of the capsules were examined with an MFP-3D Asylum Research instrument operated in AC mode. PEI (1 mg mL^{-1}, 0.5 M NaCl) was deposited onto gold-coated silicon wafer substrates with a 15 min exposure time, followed by 3 washes in deionized water (30 s each). A total of 10 μL of the core−shell dispersion was then evaporated before undergoing further dissolution, as described previously. The air-dried samples were then imaged in air with BS-Tap300 cantilevers.

Results and Discussion

Investigation of the PEs in Blend Multilayers. Fluorescently labeled PEs were used to demonstrate the inclusion of each component into the blend multilayers on particles. This was performed by assembling three sets of eight-layered core−shell particles in parallel, each with a single labeled PE. Fluorescence was evident for core−shell particles assembled with RITC-PAA (Figure 1a), Rh-PSS (Figure 1b), or RITC-PAH (Figure 1c), proving that the multilayers formed contain all three PEs. The fluorescence of the core−shell particles was apparent in the early stages of the multilayer buildup, confirming that all three components were incorporated into the multilayer from the first bilayer. In Figure 2, the presence of RITC-PAA in eight-layered coatings assembled on silica particles across a range of different PE compositions is shown by CLSM. CLSM intensity analysis shows that a qualitative, systematic increase in the fluorescence intensity of RITC-PAA is observed with increasing proportions of RITC-PAA in the blend adsorption solution, suggesting the inclusion of more PAA in the film.

Compositional Engineering of the Blend Multilayers. Flow cytometry experiments were conducted to examine the relative amount of PE adsorbed for each blend solution composition at a fixed layer number (eight layers). Figure 3a shows the fluorescence intensity of adsorbed RITC-PAA after the assembly of blend multilayers with varying composition on silica particles. The fluorescence intensity of the particles increases as the proportion of PAA in the blend adsorption solution increases, indicating that more PAA is incorporated into the multilayer

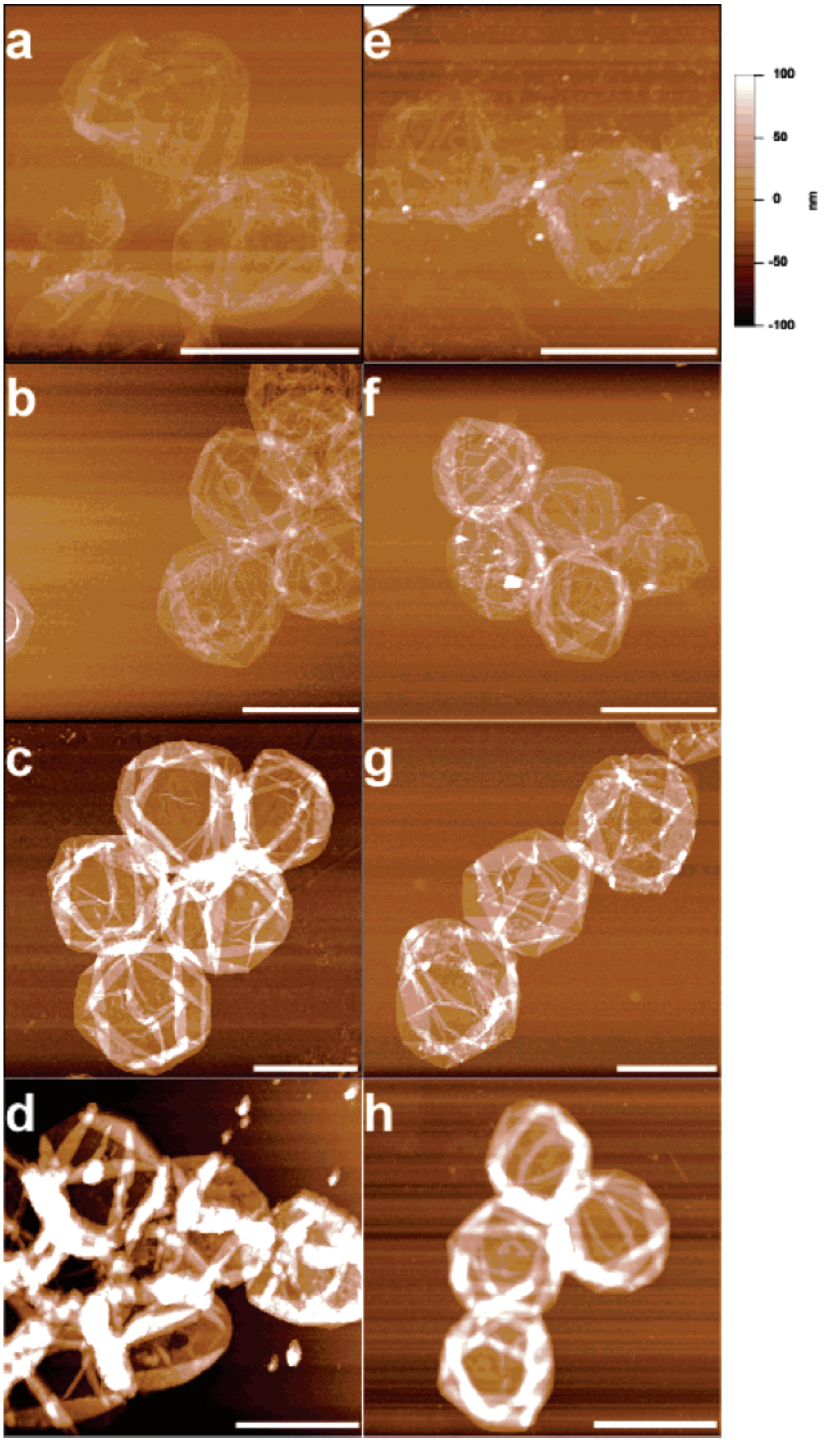

Figure 7. AFM images of PE blend capsules obtained from 5.3 μm diameter silica particles. The capsules ((a and e) two layers, (b and f) four layers, (c and g) six layers, and (d and h) eight layers) were prepared from (PAA/PSS) and PAH adsorption solutions at pH 3.5 and 7.5, respectively. PAA/PSS blend compositions are (a−d) 90:10 wt % and (e−h) 10:90 wt %. All blend and PAH solutions contained 0.5 M NaCl. Scale bars represent 5 μm.

coating. These data are in agreement with the CLSM data of Figure 2. Recently, we reported that the thickness of the blend (PAA/PSS)/PAH multilayers assembled on a planar substrate increases with increasing proportion of PAA in the blend adsorption solution.[61] The thicker multilayer film formed in this system (as compared to conventional PAH/PSS films) is a consequence of the increasing amount of PAA in the multilayer, which influences the layer properties via the formation of loops and tails. The increase in fluorescence intensity in Figure 3a agrees well with this observation.

Additionally, we used flow cytometry to examine the effect of assembling the blend layers in the presence of a supporting electrolyte (NaCl, 0.5 M). The difference in the relative amount of PAA adsorbed due to a change in the ionic strength of the blend adsorption solutions (from 0 to 0.5 M NaCl) is negligible for blend solutions containing more than 75% PAA. These findings correlate with those reported by Cohen-Stuart and co-workers,[69] where they investigated the adsorption of weakly ionized PAA (pH = ~3.5) onto a positively charged, pH-independent surface, and concluded that the adsorbed amount

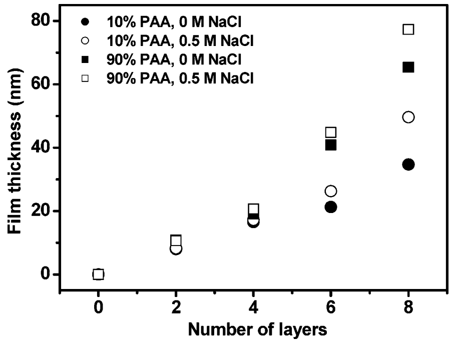

Figure 8. AFM thicknesses of PE blend capsules obtained from a template of 5.3 μm diameter silica particles. The capsules were prepared from (PAA/PSS) and PAH deposited from adsorption solutions at pH 3.5 and 7.5, respectively. All PAH solutions contained 0.5 M NaCl. Blend solutions contained 0 or 0.5 M NaCl.

showed little dependence on the ionic strength of the adsorption solution. However, in the cases where there is 50 or 25% PAA in the adsorption solution, the difference between the two ionic strength conditions becomes more pronounced. This is in keeping with the strong effect of ionic strength on highly charged PEs such as PSS,[70] which may hinder the adsorption of PAA when there is a higher proportion of PSS in the adsorption solution. Importantly, it should be noted that varying the ionic strength during the adsorption may lead to conformational differences in the adsorbed polymer, which may affect the fluorescence of the polymers. As such, direct comparison of the fluorescence for films assembled at different ionic strengths is difficult.

Since the degree of ionization of PSS is not dependent on the pH of the blend adsorption solution, a relatively acidic pH (as used in this work) should have little influence on the conformation of the PSS polymer chain. Consequently, the effect of charge shielding (via the increased ionic strength) on the conformation of PSS is expected to be more pronounced than any pH effect. Using flow cytometry, the relative amount of fluorescently labeled PSS (Rh-PSS) incorporated into the multilayer was detected for films formed from PAA blend adsorption solutions with different PAA contents. In the case of 0 M NaCl in the blend adsorption solution, Figure 3b shows that as the proportion of PAA in the blend adsorption solution increases, less PSS is adsorbed. However, when there is 0.5 M NaCl added to the blend adsorption solution, the trend is reversed; more PSS is incorporated into the multilayer with increasing proportions of PAA in the blend adsorption solution. Therefore, the addition of 0.5 M NaCl to the blend solution promotes the coadsorption of PSS and PAA; PSS assumes a less stretched conformation in the presence of salt, and the more flexible polymer chain therefore adsorbs onto the loopy surfaces and forms thicker layers. Importantly, as the proportion of PAA in the blend adsorption solution increases, the amount of PAH present on the surface also increases. This in turn requires more polymers from the blend adsorption solution to be adsorbed. Since the conditions favor the adsorption of both PAA and PSS, it follows that an increased amount of both polymers (PAA and PSS) is found within the film.

One possible explanation for the observed trends may arise from the varying surface structures formed at different adsorption conditions. For blend adsorption solutions containing 0 M NaCl, PSS adopts a more stretched conformation due to the intramolecular repulsion of charged groups in the polymer. In samples where the proportion of PAA in the blend adsorption solution is high, the increasingly "hairy" layer morphology of the film may therefore reduce the amount of PSS being adsorbed onto the multilayer surface, in an effect not dissimilar to PAA effectively reducing protein adsorption.[71] In samples where the amount of PAA in the film is low (i.e., adsorption from blend adsorption solutions with a low PAA proportion), the relatively flat layer and the high concentration of PSS in the adsorption solution may be expected to favor the adsorption of PSS onto the multilayer.

The blend multilayers prepared use PAH as a single component polycation. In all experiments, PAH is adsorbed in the presence of 0.5 M NaCl, which is added for intramolecular charge shielding on the stretched PAH chain at pH 7.5 (~75% charged[36]). The presence of 0.5 M NaCl in the PAH solution is vital. When adsorption of PAH was performed in the absence of added salt, the growth of the multilayer was limited due to incomplete surface coverage, resulting in particle aggregation (data not shown). The adsorption of PAH onto a multilayer film will also be affected by the properties of the underlying layer. RITC-PAH was employed to investigate the extent to which this is evident in the blend multilayers. Figure 3c shows that the relative amount of PAH adsorbed onto the surface increases as the proportion of PAA in the blend adsorption solution increases for the underlying polyanionic layers. We attribute this observation to the increasing amount of PAA at the contact layer. A thicker, "hairier" layer (due to an increased amount of PAA on the multilayer surface) will require the adsorption of more PAH to compensate the surface charge. This is supported by the data in Figure 3a,c: the relative amounts of both PAA and PAH increase as the proportion of PAA in the blend adsorption solution increases.

In summary, in the case where there is 0.5 M NaCl added to all adsorption solutions, the relative amount of all three components in the multilayer increases with an increasing proportion of PAA. When there is 0 M NaCl in the blend solution, the relative amounts of PAA and PAH increase, while the relative amount of PSS decreases. The difference in the adsorption behavior of PSS with ionic strength is likely to arise from the impact of ionic strength on the molecular conformation of strong PEs. These findings suggest that there will be a commensurate increase in multilayer thickness as the proportion of PAA in the adsorption solution increases, as will be demonstrated next.

PE Blend Capsules. To verify that the blend multilayer films have sufficient structural integrity and homogeneity to be potentially useful for applications in, for example, drug delivery and confined microreactor systems, we dissolved the silica core to form PE blend capsules. Further, it is important to ensure that the labeled component (and hence the corresponding PE in the original unlabeled system) does not undergo substantial desorption during the core dissolution process. Figure 4a shows the example of RITC-PAH-labeled capsules after core dissolution, and the retention of fluorescence after dissolution indicates that the capsules retain RITC-PAH in the film. Similar experiments using Rh-PSS and RITC-PAA also demonstrated that the labeled polymers remained in the film after core dissolution (data not shown). Figure 4a shows the example of PAA/PSS = 10:90, although capsules were produced across the entire range of blend compositions studied. Further, we found that the PE blend capsules are stable in solution for a period of at least 15 months (data not shown).

The successful preparation of PE blend capsules was demonstrated using TEM. Eight-layered PE blend capsules were prepared from the entire range of blend ratios investigated, with Figure 4b showing the example of capsules formed from a blend solution containing a PAA/PSS ratio of 25:75. Further, for

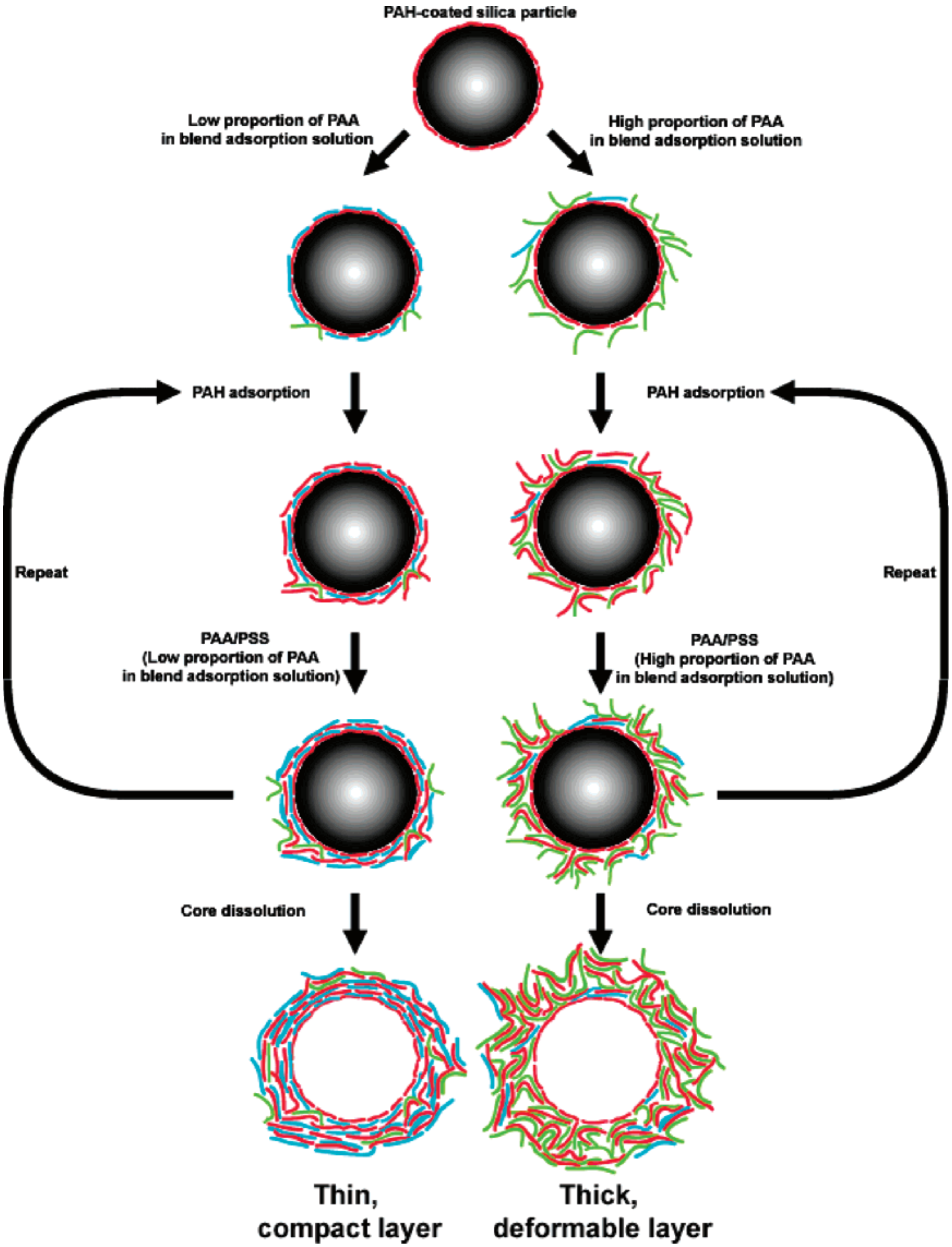

Figure 9. Schematic of the formation of core−shell particles and capsules for blend adsorption solutions containing low (left) and high (right) proportions of PAA. The schematic depicts the effect of blend adsorption solution composition on multilayer conformation.

multilayers assembled from blend adsorption solutions containing 0 M NaCl, it was observed that as the proportion of PAA in the adsorption solution increases, the resulting PE blend capsules had a highly deformable structure (data not shown). This can be attributed to a change in the multilayer composition (Figure 3). The decrease in the relative amount of PSS in the multilayer, coupled with the large increase in the relative amount of PAA incorporated, appears to significantly reduce the rigidity of the PE blend capsules, as is evident in the deformable structure observed using TEM. The outcome of this is that the capsules are thicker but less rigid. This suggests that the fully charged PSS acts to stabilize the loosely bounded components and provide rigidity to the structure of the film. We have previously observed similar phenomena in corresponding planar experiments, where an increasing proportion of PSS in the adsorption solution reduced the propensity of the layers to rearrange upon exposure to acidic conditions.[61]

To further investigate this observation, we compared PAA/PAH capsules with PE blend capsules, assembled in alternation with PAH. In both cases, all adsorption solutions contained 0.5 M NaCl; polyanion adsorption was conducted at pH 3.5 and

PAH adsorption at pH 7.5. As the PAA/PAH core−shell system undergoes irreversible aggregation after four layers,[54] four-layered capsules of PAA/PAH were compared to four-layered PE blend capsules assembled from a 90% PAA (10% PSS) blend adsorption solution. We found that it was not possible to prepare capsules that contain only PAA and PAH—the multilayer was consistently destroyed upon core dissolution. However, with 10% PSS in the adsorption solution, the stabilizing effect is sufficient to ensure that the capsules remain intact. The capsules showed no sign of deformity, even though the shell was comprised of only four layers. This result emphasizes the role of PSS for providing film integrity in the three-component nanoblended multilayer system. This demonstrates that the structural integrity of the capsule formed is a function of both the shell thickness and the composition/conformation of the shell components.

The thickness of the capsules as a function of assembly conditions and blend solution composition was examined by AFM (Figure 5). The film thickness was calculated by examining the height profile of the capsules where they are folded only once. Figure 6 shows that the thickness of the capsules increases as the proportion of PAA in the blend adsorption solution increases. For example, 10% of PAA in the blend adsorption solution leads to more than a 25% increase in thickness when compared to capsules assembled using only PSS and PAH, regardless of whether or not salt was added to the polyanion adsorption solution. Thereafter, the thickness of the capsules increased as the proportion of PAA in both the blend adsorption solution and in the multilayer increased (see Figure 3a). It is worth noting that in the case of the blend adsorption solution with 0 M NaCl, the relative amount of PSS adsorbed decreased as the proportion of PAA in the blend adsorption solution increased (Figure 3b). Therefore, the increase in thickness observed with the increasing proportion of PAA in the blend adsorption solution suggests that the thickness of the capsule can be attributed mainly to the inclusion of additional PAA into the multilayer.

Capsules assembled from blend adsorption solutions containing 0.5 M NaCl are thicker than their respective 0 M NaCl counterparts. For instance, four-bilayer capsules assembled from solutions with PAA/PSS = 10:90 prepared with 0.5 M NaCl had a wall thickness of 50 nm, as compared to 33 nm for the case of 0 M NaCl. The percentage difference in the thickness ranged from ∼15−40% across the blend adsorption solution composition. For the blend adsorption solution containing 0.5 M NaCl, added salt may lead to the presence of extrinsically compensated carboxylate groups in the final film,[5] thereby increasing the amount of water in the final film and forming thicker layers.

We also followed the growth of the capsules with increasing layer number, as a function of assembly conditions and blend solution composition, using AFM. The capsule wall thickness was measured via the height of the collapsed capsules, as described previously. Measurements were performed only on capsules with a negatively charged outermost layer; when the outermost layer was positively charged, both the core−shell particles and the resulting capsules were considerably more aggregated.[6] Figure 7 shows the stepwise growth of these capsules with respect to the number of layers deposited. It was observed that the capsules became progressively thicker as the number of layers deposited increased. Capsules deposited from a 90% PAA blend adsorption solution (Figure 7a−d) only became noticeably thicker than capsules deposited from a 10% PAA blend adsorption solution (Figure 7e,f) after adsorption of the sixth layer (Figure 8). This is evidence that the increase in shell thickness of these capsules is nonlinear over the layer number range examined.

Figure 8 also shows that the nonlinearity is most pronounced for capsules assembled from a 90% PAA adsorption solution, which is consistent with our previous results.[61] After layers two and four, the thickness between the samples was similar; however, after layers six and eight, the difference in the thickness of the capsules becomes more obvious. This observation confirms that the difference in layer properties is amplified as the number of layers assembled increases. This is likely due to a complex interplay between the initial substrate surface, the bulk and surface properties of the multilayer, and the adsorbing species, which combine to affect the properties of the newly formed layer.

The origin of this effect is likely to lie in changes in the multilayer conformation between the two compositional extremes, as proposed in Figure 9. Importantly, the initial step in the assembly of (PAA/PSS)/PAH multilayers is the adsorption of pure PAH onto a bare silica particle. The blend layer that follows is adsorbed onto a monolayer of PAH on the silica sphere. At this stage, irrespective of the composition of the blend adsorption solution, the difference in the total amount of PAA and PSS adsorbed onto the surface of the multilayer is very small. This is evident by inspection of Figure 8—the thickness of the multilayer film is similar for all blend adsorption solutions used. As the multilayer builds up, the difference between each layer is amplified due to the presence of a weak PE pair (PAA and PAH). Under the conditions used, weak PEs have a tendency to form layers that contain loops and tails.[51] The combination of these loops and tails and the coiled conformation of an adsorbing weak PE contribute to an increasingly “hairy” surface, which leads to an increasing surface area available for adsorption of the next layer.[41] Additionally, adsorption of coiled polymers onto “hairy” surfaces produces loosely bound multilayers. This facilitates the diffusion of uncomplexed species into and out of the multilayer, which has been reported to be a significant factor in multilayer buildup.[72] In this manner, the amount of material adsorbed and hence the thickness of the newly assembled layer may increase exponentially as more layers are adsorbed.

Conclusion

The relative adsorbed amount of each species (PAA, PSS, and PAH) in blended multilayered films on particles was investigated via the use of fluorescently labeled polymers in tandem with flow cytometry and CLSM. CLSM images confirmed that the core−shell particles and the resulting capsules contained all three polymers. Flow cytometry data show that the proportion of PAA in the blend adsorption solution influences the relative adsorbed amount of all three polymers. Additionally, it was found that the effect of added salt in the adsorption solutions is more profound on the fully ionized PSS when compared to the weak PE components (PAA and PAH). PE blend capsules were prepared from the entire blend ratio investigated. The study of the thickness of the capsules as a function of the composition of the blend adsorption solution was performed with AFM. The results indicate that increasing the proportion of PAA in the adsorption solution leads to an increase in the thickness of the multilayer, while PSS serves to add both colloidal stability and structural integrity to the resulting capsules. A growth mechanism for the nanoblended multilayers was proposed based on the growth profile of the capsules, with more “hairy” layers formed from solutions containing higher proportions of weak PE (PAA). This study demonstrates the ability to control the composition, thickness, and stability of PE blend capsules using adsorption from weak−strong blend PE solutions.

Acknowledgment. Alexander N. Zelikin is gratefully acknowledged for the synthesis of fluorescently labeled polymers and Elvira Tjipto for fluorescence microscopy measurements. This work was supported by the Australian Research Council under the Federation Fellowship and Discovery Project schemes. Infrastructure support from the Particulate Fluids Processing Centre at the University of Melbourne is also acknowledged.

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MA071372W