

Thermal Behavior of Polyelectrolyte Multilayer Microcapsules. 1. The Effect of Odd and Even Layer Number

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Received: April 28, 2005; In Final Form: August 3, 2005

The temperature-dependent behavior of hollow polyelectrolyte multilayer capsules consisting of poly-(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) with a different number of layers was investigated in aqueous media using confocal laser scanning microscopy, scanning and transmission electron microscopy, atomic force microscopy, and elemental analysis. Capsules with an even number of layers exhibited a pronounced shrinking at elevated temperature resulting in a transition to a dense sphere, whereas capsules with an odd number of layers swelled during heating to 5-fold of their initial size followed by their rupture. This effect increases for odd layer numbers and decreases for even layer numbers with increasing layer number. According to elemental analysis, an excess of PDADMAC monomers exists within the multilayers of capsules with an odd number of layers leading to a repulsion between the positive charges, whereas shells with an even number of layers have a balanced ratio between the oppositely charged polyions, so that the temperature-dependent behavior is controlled by the different interactions between polyelectrolytes and the bulk water. At a certain temperature, the polyelectrolyte material softens thus facilitating any rearrangement. Besides incubation temperature, the duration of heating has an influence on the restructuring of the multilayers.

Introduction

Complexes of two oppositely charged macromolecules, mainly polyelectrolytes, have been intensively studied over the last two decades.^{1–3} Interest to investigate the formation and properties of inter-polyelectrolyte complexes (IPECs) emanates from both fundamental and applied aspects. First, complexes between charged macromolecules often occur in nature, for instance, charged DNA is complexed by oppositely charged proteins. Second, IPECs have attracted the attention of scientists due to the variety of possible applications, including functional coatings, selective membranes, sensor materials, microreaction chambers, and carrier systems. The behavior of IPECs is mainly governed by the electrostatic interaction between the segments of the oppositely charged polyions and thus drastically differs from the behavior of the single components. IPECs can be affected by pH and salt, since these factors influence charge interactions. Temperature has also been reported to affect the solubility⁴ and substitution phenomena⁵ of polyelectrolyte complexes formed in bulk solutions.

Besides the simplest approach to form IPECs by mixing the aqueous solutions of oppositely charged polymers, the surface-mediated complex formation of polyelectrolytes introduced in the early 1990s to fabricate defined so-called layer-by-layer (LbL) assemblies of charged macromolecules onto solid substrates is well-developed.^{6–8} Since these polyelectrolyte multilayers present two-dimensionally stratified but strongly interpenetrated layers, their behavior is dominated by internal interactions, thus differing from the corresponding volume material.⁹

All potential applications require a basic understanding of the film structure and its control during layer deposition, in particular for possible postassembly treatments. Previous studies have shown that similar to bulk IPECs the resulting layer structure is affected during the deposition process by external parameters such as ionic strength^{10–12} and the type of salt of the deposition solution,^{10,13} polymer charge density, varied either by charge dilution in copolymers^{12,14–16} or by changing the pH of weak polyion solutions,^{17,18} type of solvent,^{10,19} deposition time,^{10,20} polymer concentration,¹⁰ and temperature.^{21,22} These factors mainly influence the amount of adsorbed material and thus the layer thickness. But also after multilayer formation, the film properties can be changed by varying the external conditions. In addition to the fundamental understanding of the internal layer structure, this is of special interest for a number of practical applications, such as in controlled release or separation technology which require controllable and tunable properties. A previous study concentrated on the response of multilayers to the degree of humidity,^{23,24} addition of salt,^{25–29} pH changes,^{30–32} and solvent quality,^{33,34} whereas only little is known about the thermal behavior of polyelectrolyte multilayers. Most heating studies concentrated on the temperature response of films containing a thermosensitive polymer.^{35,36} Since LbL films represent kinetically stabilized structures, one may expect that a temperature increase can provide enough thermal energy to surmount the energy barrier and to induce polyion rearrangements. Multilayers assembled on flat substrates show some annealing effects but only negligible changes in thickness when heated to elevated temperatures in an aqueous environment,^{36,37} whereas when heated at 100% humidity, they shrink distinctly indicating mainly water desorption.³⁷

By the assembly of a LbL film on spherical charged substrates and the subsequent dissolution of the colloid template, poly-

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electrolyte microcapsules can be obtained.^{38,39} In contrast to supported films, such capsules consist of a free multilayer film not attached to a substrate and thus have enough space to rearrange in all three dimensions. This enables the investigation of multilayer properties not accessible in the bulk or in supported films and can lead to a better understanding of the different interactions, for example, between oppositely charged polyelectrolytes and between water and polyelectrolytes. Thus, capsules are an optimal sample system to study the temperature-dependent behavior of pure polyelectrolyte multilayers.

We have previously shown that incubating an aqueous suspension of capsules consisting of five bilayers poly(styrene-sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) at 120 °C for 20 min leads to a capsule shrinkage to less than one-third of their initial size accompanied by a dramatic increase of their wall thickness.⁴⁰ Similar results with only a slight diameter decrease after heating the capsules for 2 h at 70 °C were reported by Leporatti et al.⁴¹ Besides the size decrease, a drastic reduction of the permeability coefficient for low-molecular-weight dyes was observed after heat treatment.⁴² On the other hand, it was found that shells composed of five bilayers of PSS and poly(diallyldimethylammonium chloride) (PDADMAC) multilayers swell at elevated temperatures.⁴³ It was assumed that this opposed behavior can be attributed to uncoupled charges due to a looser interconnection within the PSS/PDADMAC multilayer because of the nonmatching charge distances in the system, whereas PAH and PSS have the same charge distances leading to a denser network within the multilayer which finally results in the previously described shrinkage upon heating. Herein we show that the difference in charge distance for the oppositely charged polyelectrolytes is not the crucial criteria for swelling or shrinking at elevated temperatures.

For these studies it is important to make use of capsules that contain no residues of the core material, because these could influence the temperature-dependent behavior of the free multilayers. Until recently, all research in this field was done with capsules templated on weakly cross-linked melamine formaldehyde (MF) cores which leave behind MF oligomers in the capsule wall and interior upon dissolution.^{40,41,43}

In the present study, we provide a detailed analysis of the temperature-dependent behavior of PDADMAC/PSS capsules with a different number of layers, which were assembled on completely dissolvable silica particles. For this system, the core material and its dissolution have a negligible influence on the multilayers and the electrostatic interactions are better defined since both polyelectrolytes are strong ones. Besides the aspects of the basic understanding of the polyelectrolyte mobility, thermal modification of capsule properties can lead to a wide field of possible applications, for example, use as controlled release devices or microreaction chambers, since knowing capsule behavior at high temperatures is important to control reactions generally performed at high temperatures as the polymerase chain reaction.

Materials and Methods

Materials. Sodium poly(styrene sulfonate) (PSS, $M_w \sim 70$ kDa), poly(diallyldimethylammonium chloride) (PDADMAC, $M_w \sim 200$ –350), rhodamine 6G, 6-carboxyfluorescein, hydrofluoric acid, sodium chloride, ethanol, methyl methacrylate, 2,2'-azobis(2-methylpropionitrile) (AIBN), and poly(ethyleneimine) (PEI, $M_w \sim 750$ kDa) were purchased from Sigma-Aldrich (Germany). All chemicals were used without further purification except for PSS, which was dialyzed against Milli-Q water (M_w cutoff 20 kDa) and lyophilized. Monodisperse silica particles

with diameters of 4.55 μm and 0.997 μm were obtained from Microparticles GmbH (Berlin, Germany).

The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18 $\text{M}\Omega\cdot\text{cm}$.

Capsule Preparation. Hollow polyelectrolyte capsules were fabricated using the LbL technique as described previously.³⁹ The alternating adsorption of PDADMAC and PSS onto the surface of silica particles was carried out from 2 $\text{mg}\cdot\text{mL}^{-1}$ polyelectrolyte solutions containing 0.5 M NaCl, starting with PDADMAC since the silica particles are negatively charged within the used pH range of 4–6. After 15 min of adsorption, the particles were washed three times with water to remove nonadsorbed polyelectrolyte molecules using centrifugation. After deposition of the desired number of layers, the silica cores were dissolved in 0.1 M hydrofluoric acid. The resulting hollow capsules were washed again twice with 0.1 M HF to remove the remaining SiF_6^{2-} ions without shifting the equilibrium reaction to the starting materials by addition of pure water. Afterward, the hollow shells were thoroughly washed with water until the pH reached a value of 6.

Temperature Treatment. For heating, 100 μL of the aqueous capsule suspensions was incubated at the respective temperature in a Lauda Ecoline RE 112 thermostat for a certain time period.

Confocal Laser Scanning Microscopy (CLSM). Optical images of polyelectrolyte capsules in water were obtained using a Leica TCS SP confocal scanning system (Leica, Germany) equipped with a 100 \times /1.4–0.7 oil immersion objective. To visualize the polyelectrolyte shells, rhodamine 6G and 6-carboxyfluorescein were used as electrostatically bound fluorescent labels for capsules with a negative or positive surface charge, respectively, by mixing the sample suspension with the dye.⁴¹ For the determination of the capsule diameter, the fluorescence profiles of at least 50 capsules were analyzed and their diameters were averaged. The error bars shown in the capsule diameter diagrams correspond to the standard deviations of the averaging.

Scanning Electron Microscopy (SEM). SEM measurements were conducted with a Gemini Leo 1550 instrument at an operation voltage of 3 keV. Therefore, a drop of the sample solution was placed onto a glass wafer, dried at room temperature, and sputtered with gold.

Energy-Dispersive X-ray Analysis (EDX). EDX analysis was made on a Zeiss DSM 940 scanning electron microscope.

Transmission Electron Microscopy (TEM). Polyelectrolyte shells were incubated for 3 h in a 1% (w/w) OsO_4 solution, washed with water three times, and transferred into ethanolic medium by washing them with solutions of increasing ethanol content (30%, 70%, and 96%). Afterward, the sample was embedded into methyl methacrylate containing a small amount of the radical starter 2,2'-azobis(2-methylpropionitrile) (AIBN), degassed, and stored at 60 °C overnight in order to polymerize the matrix. Slices of 50–100 nm in thickness were prepared using a Leica ultracut UCT ultramicrotome. Afterward, the ultrathin sections were transferred onto a carbon film coated copper grid and investigated by means of a Zeiss EM 912 Omega transmission electron microscope.

Atomic Force Microscopy (AFM). AFM measurements were performed in air at room temperature using a Nanoscope III Multimode AFM (Digital Instruments Inc., USA) operating in tapping mode. The samples were prepared by placing a drop of the sample solution onto a freshly cleaved mica substrate and drying it at room temperature. For capsules with a negatively charged outer surface, the mica was precoated with PEI. The wall thickness was measured from the flat regions in the capsule

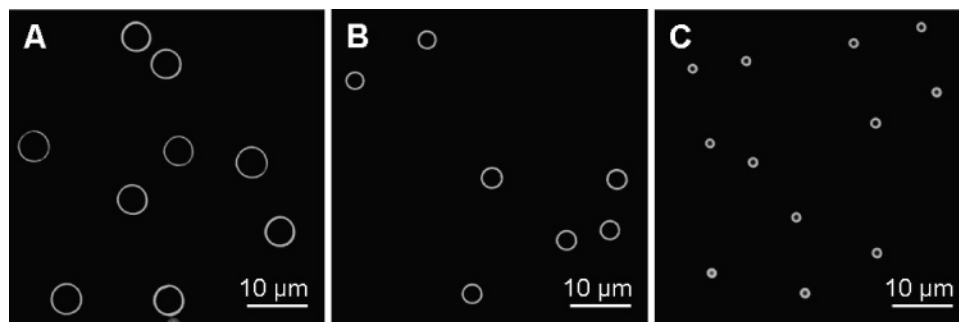


Figure 1. Confocal laser scanning microscopy images of (PDADMAC/PSS)₄ polyelectrolyte capsules made on 4.55 μm silica cores before (A) and after incubation for 20 min at 50 $^{\circ}\text{C}$ (B) and 70 $^{\circ}\text{C}$ (C).

profiles. At least 20 profiles of different capsules were analyzed, and the mean thickness differences between the mica surface and the lowest region of the shells were averaged.

Elemental Analysis. The ratio between the monomeric units of PDADMAC and PSS within the capsules was derived from the N:S ratio obtained from elemental analyses of at least 2 mg of dried shells. The measurements were performed using a Vario EL universal CHNOS analyzer (Elementar Analysensysteme GmbH Hanau, Germany).

Single-Particle Light Scattering. Measurements to determine the thickness of polyelectrolyte multilayers adsorbed on 1 μm silica particles were performed on a home-built photometer equipped with a Nd:YVO₄ laser (Verdi V-2, Coherent). The dilute suspension is passed through a capillary with a 0.1 mm diameter orifice at the end. Then, the particle stream is narrowed by use of hydrodynamic focusing. The light scattered by one particle at a given time is collected in the angular region of 5–10 $^{\circ}$ in the forward direction. The intensity is recorded by a multichannel analyzer. Repeating this process yields a histogram of particle number vs scattering intensity. The Raleigh–Debye–Gans theory was used to compute the thickness of the adsorbed multilayer assuming a refractive index of 1.47.⁴⁴

Results

Intact not aggregated PDADMAC/PSS capsules with a different number of layers can be prepared on negatively charged silica cores by starting with the positively charged polyelectrolyte PDADMAC (see Materials and Methods). In contrast to PDADMAC/PSS capsules assembled on MF particles,^{45,46} no rupture of the multilayer shell occurs after core dissolution even for 16 layers. This is due to a faster permeation of the smaller core degradation product SiF₆²⁻ through the capsule wall compared to the bigger MF oligomers, which thus generate a much higher osmotic pressure difference between the bulk and the capsule interior.^{47,48} The possibility to form intact polyelectrolyte multilayer capsules on silica particles together with the template monodispersity and the absence of core remains after dissolution as proved by EDX measurements make these SiO₂ particles a unique material for templating capsules for a number of fundamental physical and chemical investigations on pure polyelectrolyte multilayer films. But until recently, there have been only a few reports on the preparation of hollow capsules using this template.^{49–51} Previously exploited MF, poly(lactic acid) (PLA), polystyrene (PS), and carbonate cores are not suitable for such studies because of different reasons.⁵² As already mentioned above, in addition to the mechanical stress due to osmotic pressure, MF particles leave behind different amounts of residues in the capsule interior and the wall depending on the age of the batch.^{47,48} Capsules prepared on PLA cores exhibit a low monodispersity together with core

residues within the shell.⁵³ In THF, dissolvable PS lattices are monodisperse, but the swelling of PS in the organic solvent leads to a large volume increase that is responsible for capsule fracture. Furthermore, the THF changes the structure of the polyelectrolyte multilayers, as reported for PAH/PSS capsules in basic conditions.⁵⁴ Inorganic carbonate crystals, such as CaCO₃, MnCO₃, and CdCO₃, as templates are completely dissolvable but can only be prepared with low monodispersity. Moreover these cores are quite porous resulting in a polyelectrolyte complex network in the capsule interior.⁵⁵ All these disadvantages are not found for silica templated capsules.

At first we studied the temperature-dependent behavior of capsules consisting of eight layers PDADMAC/PSS in aqueous suspension. Figure 1 shows typical CLSM images of rhodamine 6G stained capsules before heat treatment and after incubation for 20 min at 50 and 70 $^{\circ}\text{C}$. After core dissolution they have the same size as the template. Upon heating, the capsules keep their spherical shape and integrity but shrink distinctly with increasing temperature. The dependence of capsule diameter on temperature after an incubation time of 20 min is plotted in Figure 2A. The graph has a sigmoidal form. At room temperature, the capsule diameter does not change; it still has the size of the 4.6 μm silica templates. At higher temperatures, the diameter decreases drastically, whereas above 70 $^{\circ}\text{C}$ it stays constant again at a size of 1.3 μm . The inflection point of the curve is found at approximately 50 $^{\circ}\text{C}$. Altogether a diameter decrease of more than 70% occurs. Besides the temperature, the incubation time has an influence on the rearrangement process as well. Figure 2B shows the size of the (PDADMAC/PSS)₄ capsules as a function of the incubation time at 50 $^{\circ}\text{C}$. An exponential decay of the diameter with time is observed. Even after 40 h at 50 $^{\circ}\text{C}$ the final diameter of the capsules is not reached. Because of this time–temperature interference any capsule size between 1.3 and 4.6 μm can be obtained at any temperature just by applying the appropriate period of time. The lower the temperature the longer it will take to get the desired capsule size. After more than half a year of storage at room temperature a perceptible decrease of the diameter was observed. From the diagrams it can be seen that, for example, incubation for 20 min at 55 $^{\circ}\text{C}$ as well as for 100 min at 50 $^{\circ}\text{C}$ shrinks the capsules to a size of 2.2 μm . The shrinkage process is irreversible, since a longer storage of shrunk capsules at 4 $^{\circ}\text{C}$ does not lead to a reswelling of the shells. This indicates that the polyion arrangement takes up a thermodynamically more stable state after heating. To investigate the changes of the capsule morphology induced by the rearrangement process during heat treatment, SEM images of dried capsules shrunk to different sizes were taken (Figure 3). The initial 4.55 μm capsules collapse during drying to a flat structure with creases and folds as observed previously on capsules of

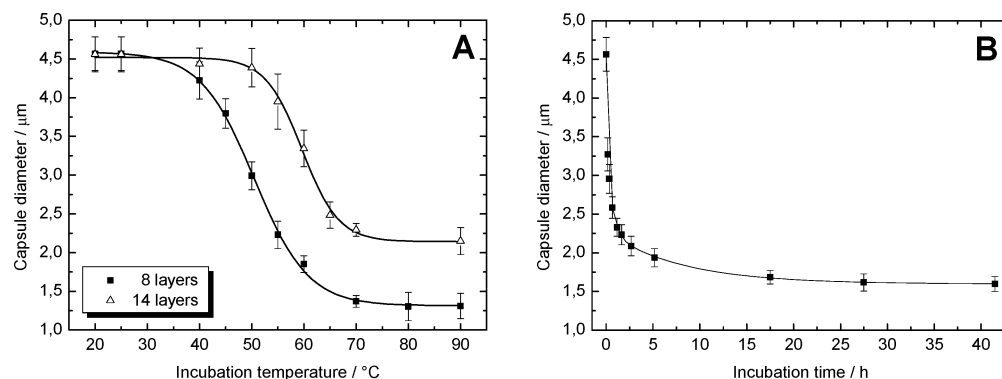


Figure 2. Quantification of the shrinkage of PDADMAC/PSS capsules with an even number of layers made on $4.55\ \mu\text{m}$ silica cores: (A) average diameter of capsules with 8 and 14 layers as a function of temperature after 20 min of incubation and (B) average diameter of capsules with 8 layers as a function of incubation time at $50\ ^{\circ}\text{C}$.

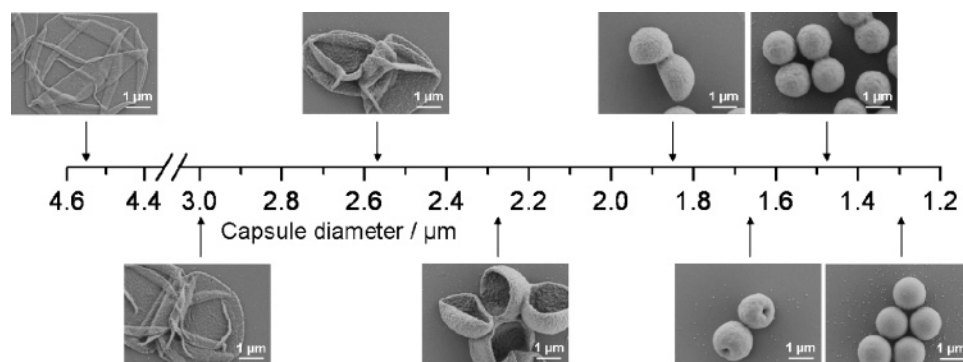


Figure 3. SEM images of (PDADMAC/PSS)₄ capsules shrunk to different sizes as a function of diameter after temperature treatment. The first image shows an initial capsule with a diameter of $4.55\ \mu\text{m}$.

similar composition.⁴⁶ The thin shell of about 20 nm is not stable enough to keep the spherical shape in the dried state. With decreasing diameter at first no significant morphological changes can be observed. Below $3\ \mu\text{m}$ the dried capsules become sturdier and show less folds. Simultaneously, the surface texture seems to become rougher according to AFM and electron microscopy images. At a size of $1.65\ \mu\text{m}$, the capsules keep their spherical shape during drying and only a small dimple points to the collapse and thus to a hollow structure. When the shells have reached their final stage of shrinkage at a size of $1.3\ \mu\text{m}$, which is in accordance with the CLSM measurements, their surface is smooth again and no dimples or deformations indicating a collapse are observed, only regular bulky spherical structures. From these electron microscopy images it seems to be obvious that the increasing stability against collapse of the capsules with decreasing diameter is due to a steadily increasing wall thickness. To verify this hypothesis, the shell thickness was measured for capsules incubated at different temperatures by means of AFM. This is done by measuring the average thickness difference between the mica surface and the lowest region of the dried shells, which corresponds to two superimposed capsule walls.⁵⁶ At least 20 profiles of different capsules were analyzed and averaged. The prerequisite for these measurements is that the dried capsules still have an area where the two capsule wall sides lie flat on each other, which is not fulfilled for capsules shrunk to diameters below $3\ \mu\text{m}$ as can be seen from the SEM images (Figure 3). On the top of Figure 4 a typical example for a capsule shrunk to $3\ \mu\text{m}$ and the corresponding height profile are shown. The results of all AFM measurements are presented on the bottom of Figure 4. For the initial (PDADMAC/PSS)₄ capsules a shell thickness of 21.2 nm is obtained. This value corresponds well to the previously observed thickness of four PDADMAC/PSS bilayers assembled on a planar surface using

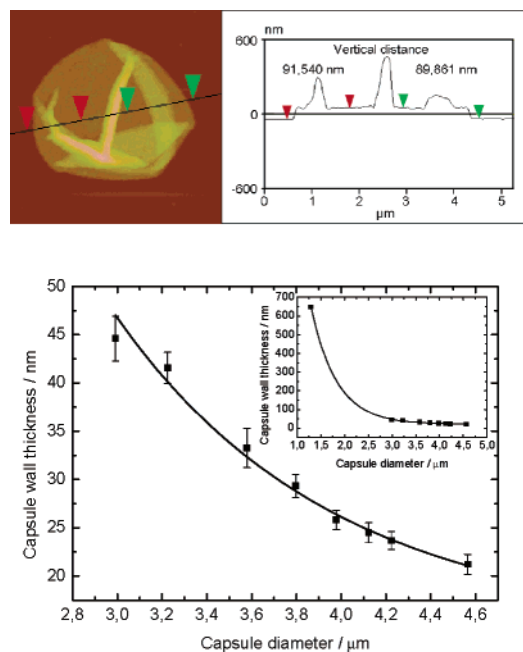


Figure 4. AFM image and cross-section profile of a (PDADMAC/PSS)₄ capsule shrunk to a diameter of $3.0\ \mu\text{m}$ after 20 min incubation at $50\ ^{\circ}\text{C}$ (top). Wall thickness of (PDADMAC/PSS)₄ capsules determined by AFM as a function of capsule diameter after heat-induced shrinkage. The inset shows the same diagram but with the wall thickness and, accordingly, the radius of the solid spheres at the endpoint of shrinkage determined by TEM (bottom).

the same salt concentration in the deposition solution.⁵⁷ As can be seen from the figure, the strong decrease in capsule diameter is accompanied by an enormous thickening of the wall, which

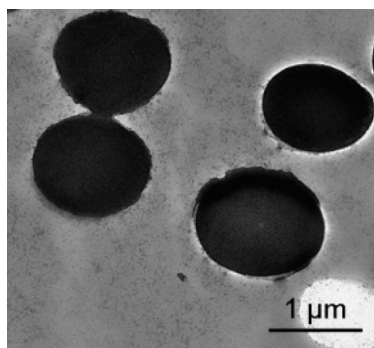


Figure 5. TEM micrograph of an ultrathin section of (PDADMAC/PSS)₄ capsules after 20 min of incubation at 80 °C.

leads to an increased mechanical stability of the shells preventing them from collapsing in the dried state. A similar stabilization of polyelectrolyte multilayer microcapsules against collapsing is observed when inorganic particles are incorporated within the layers.⁵⁸ In our case the mechanical stabilization is achieved although the shells contain only organic material. To gain a general insight into the interior of the noncollapsing, ball-shaped 1.3 μm capsules at the final stage of shrinkage, they were embedded into a polymer matrix and ultrathin sections of the sample were analyzed by means of TEM (Figure 5). It can be seen that the initially hollow shells are transformed into apparently filled spherical particles after heat treatment. But one has to keep in mind that under the conditions of preparation all dissolved polyelectrolytes would precipitate. If a small amount of polymer from the innermost layers dissolves during heating in the capsule interior, then its concentration will increase while shrinkage occurs and might pretend to be a completely filled structure after staining, although there might be a small hole inside.

The diameter of the spheres corresponds well to the diameter measured by SEM. The corresponding wall thickness of these solid spheres, which is equivalent to their average radius, is added to the diameter wall thickness diagram in the inset of Figure 4. With these values, it is possible to estimate the volume occupied by polyelectrolyte material and thus to get information about possible changes of the polyelectrolyte density during the heat-induced rearrangement process by using these equations for the wall volume of capsules V_w and the volume of the full particles at the final state of shrinkage V_p , respectively

$$V_w = 4/3\pi[(d/2)^3 - (d/2 - h)^3] \quad (\text{I})$$

$$V_p = 4/3\pi(d/2)^3 \quad (\text{II})$$

Therein d is the diameter of the corresponding capsule and h the capsule wall thickness. For the initial (PDADMAC/PSS)₄ capsules, one obtains a wall volume of $1.38 \pm 0.20 \mu\text{m}^3$, and for the 1.3 μm particles, a volume of $1.13 \pm 0.15 \mu\text{m}^3$ is obtained. At first view, the decrease of shell volume seems to indicate a densification of the polyelectrolyte shell but the errors are quite large due to the cube of the radius, and in addition, we found a small amount of PSS in the supernatant by UV-vis spectroscopy after heating at 90 °C for 40 min, confirming a partial dissolution of the polyelectrolyte shell, which amounts to 10% of capsule mass at most. Therefore, the evidence for a densification of the polyelectrolyte complex during heating accompanied by a lowering of the water content within the multilayers has to be taken with some care and is at least below 20%.

In Figure 2, the temperature dependence of the capsule diameter for shells with 14 layers after 20 min of incubation is plotted. These capsules with an initial shell thickness of 80 nm, as determined by AFM, show a heat-induced shrinkage as well but need higher temperatures to shrink to the same size compared to (PDADMAC/PSS)₄ shells. The inflection point of this curve is found at 59 °C which is about 10 °C higher than that of the capsules with eight layers. Furthermore, at the endpoint of shrinkage, the (PDADMAC/PSS)₇ shells reach a final diameter of still 2.15 μm because they contain more polyelectrolyte material resulting in a bigger size of the full particles. Estimates of the volume occupied by polyelectrolyte material before and after heating again give no clear indication on a densification of the multilayers.

Since Leporatti et al. found a difference in the degree of shrinkage in dependence on the charge of the outermost layer for MF-templated PSS/PAH capsules,⁴¹ we studied also the temperature-dependent behavior of PDADMAC/PSS capsules with an odd number of layers and, consequently, a positive surface charge. Figure 6A shows a CLSM image of initial (PDADMAC/PSS)₄PDADMAC shells stained with the negatively charged dye 6-carboxyfluorescein after core dissolution. As expected, these capsules have the same size as their 4.55 μm templates directly after core dissolution. Contrary to the capsules with an even layer number, they swell during heating (Figure 6). The corresponding diagram showing the shell diameter as a function of temperature after an incubation time of 20 min is plotted in Figure 7A. The capsules swell up to more than 5-fold of their initial size before they rupture at temperatures above 55 °C. As in the case of the shells with an even number of layers, the swelling depends not only on the incubation temperature but also on the duration of heating as can be seen in Figure 7B. For an incubation time longer than 20 min, the capsules break already at temperatures below 55 °C. While taking the CLSM pictures it was observed that the capsules adhering to the oppositely charged glass slide show an increased contact area with the substrate, whereas capsules with an even number do not deform once they are in direct contact to a positively charged surface.⁵⁹ SEM and AFM images of dried (PDADMAC/PSS)₄PDADMAC capsules show that depending on the surface charge of the slide material they collapse differently with varying formation of folds and therefore different diameter. But it can be seen that the swelling is accompanied by a wall thickness decrease and a strong increase of surface roughness (Figure 8). For shells swollen to more than 15 μm only a circular arrangement of polyelectrolyte material can be observed after drying (Figure 8). It is not yet evident whether the increased surface roughness is a consequence of the swelling in solution or of the strong adhesion to the surface during drying, which would affect most the shells with the thinnest walls. However, because of the strong surface adhesion and the increasing roughness, the wall thickness cannot be determined by means of AFM. Assuming a constant amount and density of the polyelectrolyte complex in the wall of the capsules swollen to 20 μm, this stretching would reduce the wall thickness from 23.7 to 1.2 nm, which corresponds approximately to the cross-section of one polymer molecule and is therefore difficult to visualize. The wall is probably much thicker but consists of a netlike structure with large pores as seen in the AFM and SEM images.

We found a fluorescence signal of small intensity also from the interior (Figure 6) by analyzing the fluorescence profiles of the nine layer capsules stained with the negatively charged fluorescence dye 6-carboxyfluorescein. This could be an

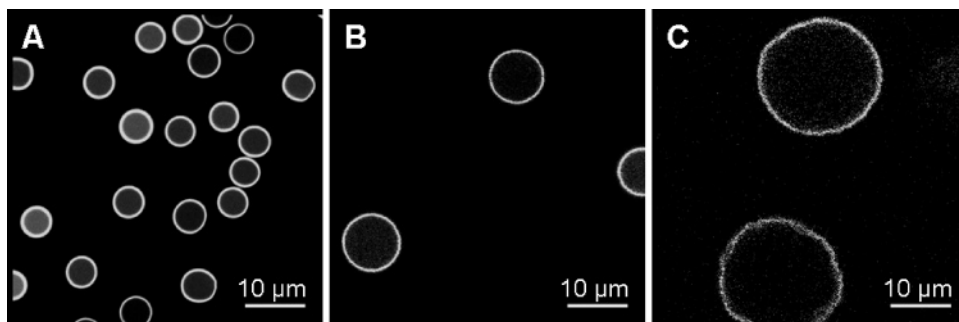


Figure 6. Confocal laser scanning microscopy images of (PDADMAC/PSS)₄PDADMAC polyelectrolyte capsules made on 4.55 μm silica cores before (A) and after incubation for 20 min at 45 $^{\circ}\text{C}$ (B) and 55 $^{\circ}\text{C}$ (C).

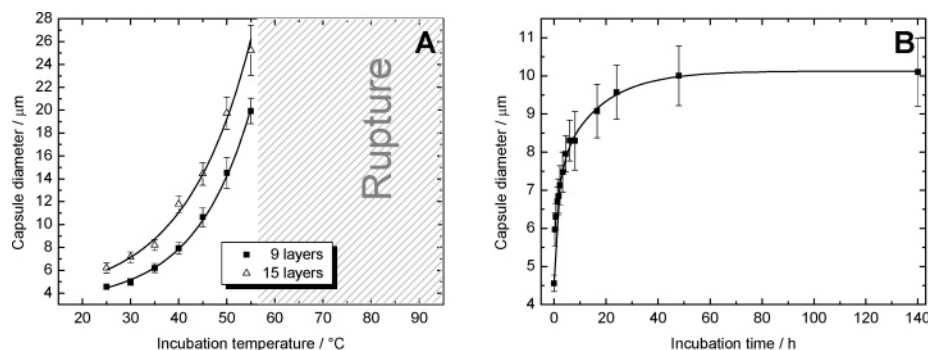


Figure 7. Quantification of the shrinkage of PDADMAC/PSS capsules with an odd number of layers made on 4.55 μm silica cores: (A) average diameter of capsules with 9 and 15 layers as a function of temperature after 20 min of incubation and (B) average diameter of capsules with 9 layers as a function of incubation time at 35 $^{\circ}\text{C}$.

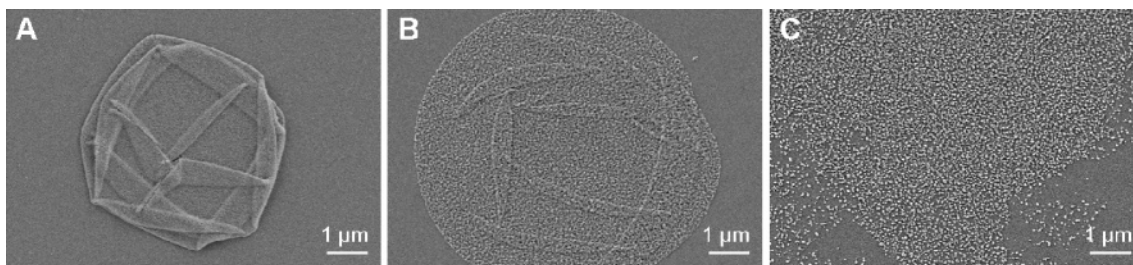


Figure 8. SEM images of (PDADMAC/PSS)₄PDADMAC made on 4.55 μm silica cores before (A) and after incubation for 20 min at 40 $^{\circ}\text{C}$ (B) and 55 $^{\circ}\text{C}$ (C).

evidence for the release of some PDADMAC from the innermost layer into the capsules interior, since the dye binds to the positively charged polymer via electrostatic interactions.⁶⁰ The polymer remains inside the shells because they are impermeable for high-molecular-weight compounds at least up to a certain size. To stain the highly swollen shells, we had to be careful with the added amount of 6-carboxyfluorescein, because already at dye concentrations of 10^{-5} M an explicit shrinking could be observed which is due to charge compensation and equivalent to salt-initiated shrinking.⁴³ Therefore, we worked with dye concentrations of 10^{-7} M.

Capsules with 15 layers as another example for shells with an odd layer number also swell with increasing temperature. From Figure 7 it can be seen that the initial shells are remarkably larger than their templates after core dissolution, which takes approximately 2 h including the following washing steps. The shells already swell during this time period. Therefore all heating experiments were performed just after these 2 h of core dissolution. By comparison with the plot of the (PDADMAC/PSS)₄PDADMAC capsules, it is obvious that capsules with 15 layers show a more pronounced swelling but rupture at the same temperature, namely, above 55 $^{\circ}\text{C}$ for an incubation time of 20 min. They reach a maximum size of 25 μm before breakage.

CLSM, AFM, and SEM measurements of these capsules show that they exhibit, like shells with nine layers, a strong adhesion to negatively charged surfaces resulting in a large contact area with the substrate and indicating a stronger electrostatic attraction to oppositely charged surfaces compared to capsules with an even number of layers. Capsules with an odd layer number have PDADMAC as the inner- and outermost layers and thereby have one layer more than PSS giving rise to an excess of the positively charged polyion at least for low total layer numbers and a constant layer growth. By storing the swollen capsules at lower temperatures after heating, one realizes that, as in the case of capsule shrinkage, the swelling of the shells is not reversible.

All these data indicate that PDADMAC/PSS capsules with an even layer number shrink during heat incubation finally resulting in dense spheres and those with an odd layer number swell with increasing temperature until they rupture. To systematically quantify this finding, PDADMAC/PSS capsules with 5–15 layers were prepared and incubated at 50 $^{\circ}\text{C}$ for 20 min. Their diameter as a function of layer number is plotted in Figure 9. As expected a well-defined odd–even effect in the temperature behavior of PDADMAC/PSS capsules with different layer numbers is seen. Furthermore, it shows that the

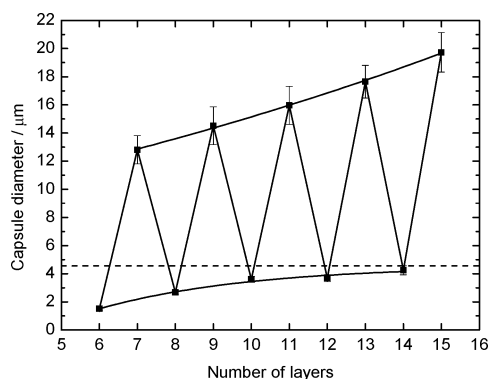


Figure 9. Average diameter of PDADMAC/PSS capsules after incubation at 50 °C for 20 min as a function of layer number. The dashed line corresponds to the diameter of the silica templates.

TABLE 1: Ratio between the Oppositely Charged Polymeric Units in PDADMAC/PSS Capsules with Different Layer Numbers As Determined from the N:S Ratio Measured by Means of Elemental Analyses

no. of layers	PSS/PDADMAC ratio	% PSS	% PDADMAC	% uncompensated charges ^a
8	1.12	52.8	47.2	−11
9	0.77	43.4	56.6	+23
14	1.08	51.9	48.1	−7
15	0.75	42.7	57.3	+25

^aOn the basis of the total amount of excess polyelectrolyte.

shrinkage of shells with an even number of layers decreases with increasing layer number, whereas the swelling for capsules with PDADMAC as the outermost layer is more pronounced with higher layer numbers.

Elemental analyses of PDADMAC/PSS capsules with 8, 9, 14, and 15 layers were performed in order to determine the ratio between the oppositely charged polyelectrolytes since we expected an influence of noncompensated charges on the rearrangement process. The ratio between PDADMAC and PSS monomer units was calculated from the nitrogen and sulfur contents of the samples. Since both polyions are strong, and thus all monomer groups are charged within a broad pH range, one derives from that value directly the ratio between positive and negative polyelectrolyte charges. The results of the measurements are summarized in Table 1. Both examples for capsules with an even number of layers show nearly a 1:1 ratio of the polyions. For 9 and 15 layers a PSS/PDADMAC ratio of about 0.8 is found which means that around 25% of the positive charges are uncompensated. Contrary to all expectations, the stoichiometry does not tend toward the 1:1 ratio of the bulk complex with an increasing number of layers. The excess of positive charges can also explain the observed strong adhesion of capsules with an odd layer number to negatively charged substrates. The determined ratio between the oppositely charged monomer units for eight and nine PDADMAC/PSS layers is consistent with the values given by Smith et al. for coating of 70–100 nm silica particles.⁶¹

Discussion

Polyelectrolyte multilayers assembled by the LbL technique are kinetically stabilized structures which would never form spontaneously by simply mixing their individual components. Any rearrangement of the film requires the simultaneous decoupling of a large number of ionic bonds which is highly improbable without an additional input of energy. The force which keeps the hollow capsule integrity is based on this

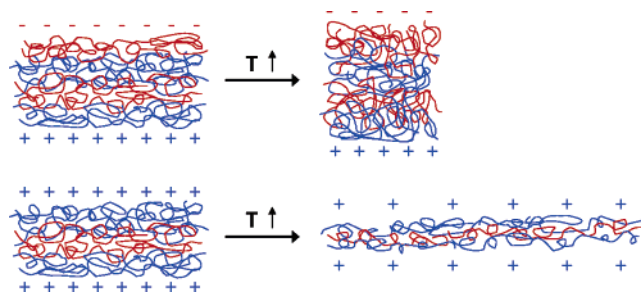


Figure 10. Schematic representation of the rearrangement of the multilayer film of PDADMAC/PSS capsules with an odd and even number of layers at elevated temperature.

irreversible polyelectrolyte adsorption at room temperature. Especially for long molecular weight polymers any rearrangement seems to be negligible at a reasonable time scale. The results presented above clearly show that the energetically most stable state of nonsupported polyelectrolyte multilayer shells depends mainly on the balance of opposite charges and thus on the ratio between the polyelectrolyte monomeric units (Figure 10). Capsules with an even number of PDADMAC/PSS layers and a balanced ratio of opposite charges show a temperature-induced shrinking accompanied by a wall thickness increase, which finally results in a transformation to a dense sphere. In this case extrinsically compensated charges, where small counterions participate in charge neutralization, exist mainly only at the inner and outer surface of the capsule and counterbalance each other. On the contrary, the interior of the capsule wall is quite hydrophobic since the majority of the opposite charges form ionic pairs.⁶² The same is observed for polyelectrolyte complex particles, which consist of a neutralized, hydrophobic core and a shell of the excess polyion stabilizing the particles against further coagulation.⁶³ The energetically most favored state of these multilayer capsules is determined by the difference of the interaction energy between the polyelectrolyte material and water and the interaction energy within the polyelectrolyte complex itself. In view of the fact that PDADMAC and PSS with their large ring structures and the hydrocarbon chain as the backbone are quite hydrophobic, the capsules want to decrease their interface toward the water as much as possible resulting in a full sphere with the minimum surface area and the minimum surface tension. Also other authors inferred from their results the importance of hydrophobic interactions within the build-up and behavior of LbL films.^{37,64} The spontaneous polyelectrolyte complex formation between PDADMAC and PSS by simply mixing solutions of the polyions also yields nearly spherical aggregates with a size of 10–200 nm as observed by means of electron microscopy.⁶⁵ Possibly also some of the water located within the layers is expelled during the rearrangement process further decreasing the water/polymer interface. However, this could not be clearly proved, because as stated above the errors are too big and some of the polyelectrolyte material is lost upon heating. The loss of polyelectrolyte material at elevated temperatures can be attributed to the nonmatching charge distances of PDADMAC and PSS, which are 0.36⁶⁶ and 0.26 nm,⁶⁷ respectively. Besides the hydrophobic effect and a decreased surface tension, a more coiled and interdigitated polymer arrangement compared to the lower entropy state of the largely two dimensionally ordered layers after multilayer preparation might be a further driving force for the rearrangement as described in our previous paper.⁴⁰ The mechanism of shrinkage is assumed to be as follows: At room temperature, an individual polyelectrolyte molecule within the multilayer has many bonds with polyelectrolytes of adjacent

layers and thus any rearrangement is sterically hindered. Since Auch et al. determined self-diffusion constants of $<10^{-15}$ cm²/s for polyelectrolytes in LbL films,⁶⁸ which are in the same order of magnitude as found in glassy polymers in aqueous suspension, multilayers can be considered to be in a glasslike state under these conditions.^{69–71} With an increase in temperature more thermal energy is provided to overcome the electrostatic attraction between oppositely charged groups, leading to the breakage of ionic bonds. At room temperature, the Coulombic energy of two oppositely charged ions at typical distances is in the order of about $2.5k_B T$ in water.⁷² To cause a macroscopic rearrangement of the multilayer capsules, several adjacent ionic bonds have to break so that the polyelectrolyte segments gain an increased degree of mobility. This softening of the multilayers can be considered as an exceeding of a kind of melting temperature T_m of the polyelectrolyte system. From the graph in Figure 2, one may deduce that T_m of a PDADMAC/PSS complex determined from the onset of the diameter decrease is approximately 35 °C for films with 8 layers and about 50 °C for films with 14 layers. For the single dry components only glass transition temperatures are reported: For bulk PSS and PDADMAC, values of about 200⁷³ and 70 °C,⁷⁴ respectively, can be found in the literature. But both polymers are plasticized by the adsorption of water, for example, with a water content exceeding 20%, and the glass transition of PDADMAC is lowered below room temperature.⁷⁴ Because of the complex interplay of Coulombic interactions between the polyions and the influence of water, it is difficult to draw any conclusions from these values on a transition of the multilayer in an aqueous environment. Additionally, one has to consider that here the melting temperature of the multilayer is approximated from a temperature-dependent curve with an incubation time of 20 min. This value is slightly shifted to lower temperatures at longer heating times. As stated already in the Results section, the same shrinking state of a capsule can be either reached by increasing the temperature or reached by prolonging the incubation time. This principle is known as the time–temperature superposition for most physical properties of polymers.

The fact that capsules with higher even layer numbers shrink less compared to shells with a lower number of layers, and thus an increased apparent softening temperature, might be explained by more polyelectrolyte material that has to be rearranged and by a little different structure and composition of the multilayers. Besides this, the shift of T_m to higher temperatures with increasing film thickness might be influenced by the ratio between interface and bulk material, since a reduction of the glass transition temperature in thin films ($d < 100$ nm) has been observed for different neutral polymers.⁷⁵

PDADMAC/PSS capsules with an odd number of layers show a heat-induced swelling. In this case, the tendency to reduce the polymer/water interface is overcompensated by the repulsion between the positive excess charges resulting from the larger amount of PDADMAC monomers compared to the amount of negatively charged PSS monomers since both polymers are strong polyelectrolytes and thus all monomer units are charged (Figure 10). These positive excess charges lead to an increase of their mutual distance resulting in a swelling of the structure. If a constant amount of material and a constant number of uncompensated charges are assumed, a swelling from 4.6 to 20 μ m reduces the charge density per area by nearly 20 times. As in the case of capsules with an even number of polyelectrolyte layers, the increased degree of mobility of the polymer chains at higher temperatures leads to a faster rearrangement. At a certain temperature, the capsule wall becomes so thin that the

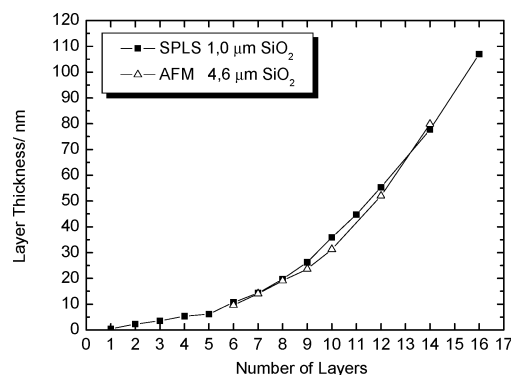


Figure 11. Layer thickness of PDADMAC/PSS multilayers measured on 1 μ m silica particles by means of single-particle light scattering and on dried 4.6 μ m capsules using AFM.

spherical structure is not stable enough to keep the shape resulting in a rupture. The addition of small amounts of salt leads to a shrinkage of the swollen capsules, pointing to the electrostatic nature of this process as well, since the positive charges get screened by the salt. The release of some PDADMAC of the innermost layer into the capsule interior could also be a consequence of the strong repulsion between the positive charges. It was previously observed that encapsulated material leads to an increased osmotic pressure of the inner solution resulting in a swelling of the capsules.⁷⁶ The osmotic pressure increases with temperature according to the van't Hoff equation, which could also yield swelling upon heating. However, the temperature range employed in this study as well as the released amount of material are too small⁷⁶ to induce osmotic changes which would explain the observed magnitude of swelling.

It is difficult to explain the observed larger swelling of capsules with higher odd layer number, but possibly this is due to a denser arrangement of layers for increasing layer number. It is known that the layers at the interface have a more looplike conformation dangling in the solution leading to a less dense arrangement compared to the so-called core zone.⁷⁷ Former fluorescence studies give a value of about 10 nm for this outer zone.⁷⁸ With increasing layer number the thickness of the denser core zone increases leading to a denser arrangement of the uncompensated charges and thus a larger swelling.

For linearly growing polyelectrolyte multilayers and completely intrinsic charge compensation the ratio between the opposite polyion charges should approach the 1:1 ratio of the bulk complex with an increasing number of layers. Deviations from this behavior occur for multilayers with partially extrinsic charge compensation, where the ratio between the polyions should tend toward a certain value or for exponentially growing multilayers. It was shown previously that the thickness of polyelectrolyte films assembled from PDADMAC and PSS adopts a linear, or steady-state, dependence on layer number after approximately the first 10 layers.^{10,57} At the beginning of the multilayer build-up the increment per deposition cycle is smaller, imparting an upward curvature to the layer thickness vs the layer number curve. We measured the film thickness as a function of layer number in solution by single-particle light scattering on 1 μ m silica particles and by AFM on dried 4.6 μ m capsules (Figure 11). The graph shows exponential growth at least until the 10th layer which seems to change to a linear growth with increasing layer number, but there are too few points to really prove it on the colloid substrates.

Knowing about the great influence of the ratio between the oppositely charged monomer units on the temperature-dependent behavior of polyelectrolyte microcapsules, it is possible to

explain the previously observed swelling of (PSS/PDADMAC)₅ capsules templated on MF cores⁴³ although they have an even number of layers: In this case, PSS is the innermost and PDADMAC the outermost layer. A temperature-induced swelling takes place when the multilayer carries a sufficiently high excess charge according to our theory. It is more likely that these capsules contain an excess of positive charges, since it is known that after MF-core dissolution as much as 20% of the capsule mass can be ascribed to positively charged core degradation products located mainly at the inner surface of the capsules.⁴⁸

In our previous paper, we reported that capsules consisting of five bilayers of PAH/PSS templated on MF particles show a similar shrinking behavior like PDADMAC/PSS capsules with an even number of layers.⁴⁰ In this case a temperature of 120 °C leads to a drastic shrinkage of the shells, but they remain hollow. We did not vary the layer number and temperature for that study, therefore no definite conclusions can be drawn concerning the softening temperature of the PAH/PSS system or a comparable odd–even effect. But one can at least say that the softening temperature seems to be higher than that for the PDADMAC/PSS system investigated here, probably due to a higher cross-linking density between PAH and PSS. To really compare the two most frequently used polyelectrolyte couples, a detailed study of PAH/PSS capsules prepared on silica particles to exclude any influence of remaining core material needs to be performed. But for this purpose, the problem of aggregation after core dissolution has to be solved first.⁵² Since PAH is a weak polyelectrolyte, the effect of uncompensated charges will be different compared to multilayer films consisting of exclusively strong polyelectrolytes.

Further investigations to verify the observed effect for other inter-polyelectrolyte complexes and to prove the softening of the complexes upon heating are under way.

Conclusions

Silica particles were introduced as unique templates for fundamental physical and chemical studies on polyelectrolyte multilayer capsules. Monodisperse intact capsules consisting of the strong polyelectrolytes PDADMAC and PSS with a different number of layers have been prepared on 4.55 μm silica templates, and their temperature-dependent behavior was studied. Capsules with an even layer number and a balanced ratio between positively and negatively charged monomer units show a heat-induced shrinking accompanied by a wall thickness increase finally reaching a solid sphere for high incubation temperatures or long incubation times. Between 30 and 50 °C the polyelectrolytes gain an increased degree of mobility providing a prerequisite for the rearrangement. The driving force for the shrinkage is the decreased water/polyelectrolyte interface, since PDADMAC and PSS contain large hydrophobic ring structures. The shrinkage is less pronounced with increasing layer number due to a higher layer thickness and thus more material has to be rearranged. In contrast to this, capsules with an odd number of layers and an excess of positive charges swell with increasing temperature up to 5-fold of their initial size until they rupture above 55 °C when their wall becomes too thin to keep integrity. The driving force for this process is determined by the trend of the multilayers to increase the mutual distance between like charges. In this case, the tendency to reduce the polymer/water interface is exceeded by the unbalanced ratio between the polyelectrolytes. Both rearrangement processes, the shrinking as well as the swelling of PDADMAC/PSS capsules, are not only a function of the temperature but also dependent on the incubation time.

The ratio between the opposite charges within the multilayers plays a crucial role for the thermodynamically most stable state of these films, since they are structures kinetically stabilized during their preparation. A temperature increase can provide enough energy to overcome the kinetic barriers and to soften the polyelectrolyte material so that rearrangements are possible.

It is possible to fine-tune the layer thickness up to several hundred nanometers by heating capsules with a balanced ratio between the opposite polyelectrolyte charges. The fabrication of such capsules using the LbL technique is nearly impossible due to aggregation and core dissolution problems. In parallel to the layer thickness increase, the permeability of capsules should be decreased. This may be suitable for the encapsulation of low-molecular-weight compounds, which can be envisaged for applications in various fields.

Note Added after ASAP Publication. There was an error in the caption of Figure 7 and was changed from 8 layers to 9 layers. This paper was published ASAP on September 9, 2005. The corrected version was reposted on September 16, 2005.

Acknowledgment. The authors thank Anneliese Heilig for the AFM measurements and Silvia Pirok for the elemental analyses. This work was supported in parts by the EU-project “Nanocapsules for Targeted Delivery of Chemicals” STREP N001428 and by the Sofja Kovalevskaja Program of the Alexander von Humboldt Foundation and the German Ministry of Education and Research. D.S. acknowledges the Marie-Curie Actions of EU FP6 for the incoming international fellowship.

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