

Thermal Behavior of Polyelectrolyte Multilayer Microcapsules: 2. Insight into Molecular Mechanisms for the PDADMAC/PSS System

Karen Köhler,^{*,†} Helmuth Möhwald,[†] and Gleb B. Sukhorukov^{†,‡}

Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany and Department of Materials, Queen Mary University of London, E1 4NS, London, United Kingdom

Received: May 11, 2006; In Final Form: September 17, 2006

Polyelectrolyte multilayer capsules consisting of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) were used as a model system to study the temperature-dependent behavior of polyelectrolyte multilayer films in aqueous media. Shells terminated with PSS shrink upon heating, whereas PDADMAC-terminated ones swell, independent of the nature of the first layer, as measured by means of confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM). Elemental analysis shows that the initial exponential layer growth of the film leads to a nearly neutral overall charge in the first case or a high positive excess charge in the latter. Depending on this overall charge either surface tension, due to an unfavorable polymer–solvent interaction, or electrostatics dominates, resulting in a shrinkage or expansion of capsules, respectively. Thus, it is possible to swell temperature-shrunk capsules by coating them with an additional PDADMAC layer. Micro-DSC measurements prove that polyelectrolyte multilayers undergo a glass transition in water at which the wall material softens, allowing the rearrangements to occur. It is found that the thermal history has an influence on the temperature behavior of capsules, especially on those ones terminated with PDADMAC. Also, the molecular weight of the polyelectrolytes affects the rearrangement of capsules. The lower the molecular weight and thus the smaller the entanglement of chains, the easier polyelectrolytes can rearrange.

Introduction

Polyelectrolyte multilayers assembled by the alternate deposition of polycations and polyanions on solid surfaces (layer-by-layer technique) have been extensively studied during the past decade.^{1–4} The ease of preparation, variety of potential layer constituents, and possibility to tune the thickness in the nanometer range give rise to a vast area of potential applications of multilayers. However, the internal structure as well as the response of these films to external stimuli influencing the interaction between the oppositely charged polyelectrolytes still remains to be fully comprehended. In particular, the similarities between the effect of temperature and salt on the built-up process and completed film are currently debated.⁵ For example, both an increase of salt concentration^{6–9} and an increase of temperature^{10–13} of the polyelectrolyte solution during coating results in an increased layer thickness. Another common feature is that an increased temperature as well as an increased ionic strength smoothen polyelectrolyte films.^{14,15} Salt leads to dissociation of individual polycation/polyanion binding sites by screening the electrostatic forces that bind the film together and thus promotes a greater fluidity of the film. Temperature on the other hand is expected to break ionic bonds and increase conformational dynamics within the film by providing the energy necessary to surmount these barriers. Whereas the influence of salt has been studied intensively, there are only a few studies describing how temperature affects multilayers not containing a thermosensitive polymer like, for example, poly-

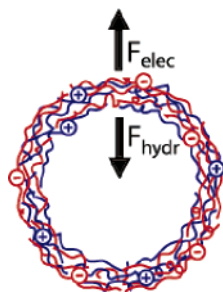
(*N*-isopropylacrylamide) (PNIPAM).^{16,17} Reflectivity measurements on flat multilayers indicate that polymer rearrangements occur but show only negligible changes in thickness when heated to elevated temperatures in an aqueous environment.^{15,18}

Suitable systems for studying the effect of temperature are polyelectrolyte multilayer microcapsules^{19–21} since they consist of a free multilayer film not attached to a substrate and thus have enough space to rearrange in all three dimensions as a reaction to an external stimulus. These capsules, which themselves have a broad field of potential application,²² e.g., as drug carriers or microreaction containers, are prepared by deposition of a polyelectrolyte multilayer on charged spherical particles and subsequent core dissolution. For fundamental investigations shells assembled on silica templates proved to be the optimal system.²³ We have shown previously that capsules consisting of the strong polyelectrolytes poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS) with PDADMAC being the first layer exhibit a quite interesting temperature-dependent behavior.²³ Shells with an even number of layers, i.e., (PDADMAC/PSS)_x ($x = 1, 2, 3, \dots$), shrink upon heating accompanied by a wall thickness increase until they form a solid sphere, whereas those ones with an odd number of layers, i.e., (PDADMAC/PSS)_xPDADMAC, swell up to 5-fold of their initial size before they rupture above 55 °C. We explained this unexpected behavior by the different ratio between oppositely charged monomers and the resultant different balance between two competing forces (Scheme 1). (PDADMAC/PSS)_x capsules have more or less a 1:1 ratio of PDADMAC and PSS monomers, so that reduction of the polymer/water interface, which is energetically unfavorable due to hydrophobic interactions (F_{hydr}), is the main driving force for shrinkage. (PDADMAC/PSS)_xPDADMAC shells, however,

* To whom correspondence should be addressed. Phone: +49 331 5679447. Fax: +49 331 5679202. E-mail: karen.koehler@mpikg.mpg.de.

[†] Max Planck Institute of Colloids and Interfaces.

[‡] Queen Mary University of London.

SCHEME 1: Two Competing Forces Determine the Thermal Behavior of Capsules^a


^a The electrostatic force F_{elec} due to a net charge of the shell is always expansive, whereas the hydrophobic force F_{hydr} due to an unfavorable polymer–water interaction always leads to the shrinkage of capsules.

contain a distinct excess of positive charges. In this case, the tendency to reduce the polymer/water interface is exceeded by electrostatic forces (F_{elec}) that lead to a repulsion between the like charges, resulting in capsule swelling. Increased polymer mobility at higher temperature provides the prerequisite for both of these rearrangements since the polyelectrolyte multilayer is frozen in a glassy state at room temperature. We could show by means of AFM force spectroscopy that the stiffness of (PDADMAC/PSS)₄ capsules undergoes a drastic decrease above 35 °C and the Young's modulus is decreased by 2 orders of magnitude between room temperature and 70 °C.²⁴

According to Scheme 1, the thermal behavior of PDADMAC/PSS capsules results from an interplay of the hydrophobic effect and electrostatics.²⁵ Hence, to further quantify and understand this phenomenon we manipulated these surfaces and provide more information on the inner film structure. We report the influence of different parameters on the heat-induced rearrangement (i.e., molecular weight of the polyelectrolytes, diameter of capsules, sequence of layering, and coating of shrunk capsules with PDADMAC), all pointing to the unusual properties of PDADMAC as capping layer. In addition, based on microcalorimetry measurements we provide further evidence that the PDADMAC/PSS system undergoes a glass transition in aqueous environment.

Materials and Methods

Materials. Sodium poly(styrene sulfonate) (PSS, M_w = 6.8, 13, and 70 kDa), poly(diallyldimethylammonium chloride) (PDADMAC, M_w = 5–20 and 200–350 kDa), poly(ethyleneimine) (PEI, M_w ≈ 750 kDa), sodium chloride, hydrofluoric acid, 3-(aminopropyl)triethoxysilane (APTES), toluene, methanol, rhodamine 6G, and 6-carboxyfluorescein were purchased from Sigma-Aldrich (Germany). All chemicals were used without further purification except for PSS 70 kDa, which was dialyzed against Milli-Q water (M_w cutoff 20 kDa) and lyophilized. Monodisperse silica particles with diameters of 4.5 and 1 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 MΩ·cm.

Capsule Preparation. Hollow polyelectrolyte capsules were fabricated using the layer-by-layer (LbL) technique as described previously.²⁰ The alternating adsorption of PDADMAC and PSS onto silica particles was carried out from 2 mg·mL⁻¹ polyelectrolyte solutions containing 0.5 M NaCl, starting with PDADMAC or PSS, respectively, depending on the surface charge of the silica particles. If not stated otherwise, 200–350

TABLE 1: Ratio between the Oppositely Charged Polymeric Units in PSS/PDADMAC Capsules (PSS is the first layer) with Different Layer Numbers As Determined from the S:N Ratio Measured by Means of Elemental Analysis^a

no. of layers	PSS/ PDADMAC ratio	% PSS	% PDADMAC	% uncompensated charges ^b
8	0.67	40.2	59.8	+33
9	1.13	53.1	46.9	-12
14	0.75	42.9	57.1	+25
15	1.09	52.2	47.8	-8

^a The errors in the PSS/PDADMAC ratio are below 5%. ^b On the basis of the total amount of the excess polyelectrolyte).

kDa PDADMAC and 70 kDa PSS were used. After 15 min of polyelectrolyte adsorption, the particles were washed three times with water in order 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 SiF₆²⁻ ions. This prevents a shift of the equilibrium reaction to the starting materials by addition of water. Afterward, the hollow shells were thoroughly washed with pure water until the pH reached a value of 6.

Coating of Shrunk Capsules with PDADMAC. A 5 mL amount of a solution containing 2 mg·mL⁻¹ PDADMAC either in water or 0.5 M NaCl was added slowly to 1 mL suspension of shrunk capsules (~10⁷ capsules/mL) under stirring in a filtration cell.²⁶ A cellulose acetate filter membrane with a pore size of 0.8 μm was used. After 15 min of incubation the excess PDADMAC was removed by rinsing at least 6 times with pure water.

Preparation of Positively Charged Silica Particles. A 250 mg amount of 4.5 μm silica particles was transferred from water to toluene by washing them twice with methanol and afterward with toluene. The particles were then dispersed in 10 mL of toluene while stirring, and 1 mL of the aminosilane APTES was added dropwise under nitrogen atmosphere. The mixture was stirred for 1 h at room temperature. To remove excess APTES and transfer the silica particles back into an aqueous environment, they were washed three times with toluene, methanol, and water consecutively.^{27,28}

Temperature Treatment. For heating, 100 μL of the aqueous capsule suspensions were incubated at the respective temperature in a Lauda Ecoline RE 112 thermostatic bath for 20 min. The diameter of the shells was measured afterward by CLSM.

Confocal Laser Scanning Microscopy (CLSM). Optical images of polyelectrolyte capsules in water were obtained at room temperature using a Leica TCS SP confocal scanning system (Leica, Germany) equipped with a 100×/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.^{29,30} The sample suspension was mixed 1:1 with a 10⁻⁶ M dye solution after heat treatment. Since the highly swollen PDADMAC-terminated capsules shrink already at low ionic strengths due to electrostatic screening they were measured in 10⁻⁷ M fluorescein 6G.²³ For the determination of the capsule diameter the fluorescence profiles of at least 50 capsules were analyzed and their diameters averaged. The error bars shown in the capsule diameter diagrams correspond to the standard deviations of the averaging.

Scanning Electron Microscopy (SEM). A drop of the sample solution was placed onto a glass wafer, dried at room

SCHEME 2: Schematic Representation of How Temperature-Shrunk Capsules with PSS as the Outermost Layer Could Be Swollen again by Coating with an Additional PDADMAC Layer and Subsequent Heating



temperature, and sputtered with gold. Afterward, SEM measurements were conducted at a Gemini Leo 1550 instrument at an operation voltage of 3 keV.

Atomic Force Microscopy (AFM). A drop of the sample solution was placed onto a freshly cleaved mica substrate and dried in air. For capsules with a negatively charged outer surface the mica surface was precoated with poly(ethylene imine) (PEI). The measurements were performed in air at room temperature using a Nanoscope III Multimode AFM (Digital Instruments Inc.) operating in tapping mode. The wall thickness was measured from the flat regions in the capsule profiles. At least 20 profiles of different capsules were analyzed: the mean thickness differences between the mica surface and the lowest region of the shells were averaged and divided by 2.

ζ -Potential Measurements. ζ -Potential measurements of particles and capsules were performed in pure water using a Zetasizer Nano (Malvern Instruments, Germany). The values of five measurement cycles each containing 30 single measurements were averaged.

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

Microdifferential Scanning Calorimetry (Micro-DSC). DSC measurements were performed using a MicroCal VP-DSC differential scanning calorimeter (MicroCal Inc., Northampton, MA). Before the measurements the sample solutions (capsule suspension or pure water) as well as the water for the reference cell were degassed under vacuum while stirring. Temperature scans were recorded in the range from 2 to 90 °C with a heating rate of 0.5 K min⁻¹ after 10 min of equilibration at the starting temperature. For data analysis the thermogram of the water–water baseline was subtracted from the thermograms of the sample suspension. The heat flow difference between sample suspension and pure water was then converted into a heat capacity difference per volume of capsule sediment.

Results and Discussion

Supplementary Adsorbed Layers. In our previous paper²³ we reported that (PDADMAC/PSS)_x ($x = 1, 2, 3, \dots$) capsules shrink upon heating whereas (PDADMAC/PSS)_xPDADMAC shells swell. Since the difference between swelling and shrinking with temperature consists of only one layer, it should be possible to swell a temperature-shrunk PDADMAC/PSS capsule with an even number of layers by simply coating it with one supplementary PDADMAC layer and heating it afterward again (Scheme 2). To check this, 4.5 μm (PDADMAC/PSS)₄ shells were first heated for 20 min at 50 °C so that they shrunk to a size of around 3 μm (Figure 1). Then they were incubated for 15 min in 2 mg/mL PDADMAC solution without salt at room temperature and washed thoroughly. The ζ -potential of these

capsules increased from -46 to $+9$ mV, proving that some PDADMAC was adsorbed onto the capsule surface. The size of the capsules still remained at 3 μm . Afterward, the capsules were heated for 20 min at 70 °C to see whether the shrinkage could be reset or even changed into a swelling. The confocal micrographs in Figure 1 show that this is not possible. Instead, the capsules even shrunk further to 1.3 μm . Thus, the adsorbed amount of PDADMAC was probably not sufficient to induce a positive excess charge. In a next trial the adsorbed amount of the polycation was increased by incubating the shrunk 3 μm (PDADMAC/PSS)₄ capsules in a PDADMAC solution containing 0.5 M NaCl. This salt concentration corresponds to the salt concentration used during capsule assembly on the silica cores. After washing ζ -potential measurements revealed a highly positive value of $+45$ mV, indeed pointing to a thicker PDADMAC surface layer. Confocal micrographs indicate that these capsules swell already after washing without additional heating, whereas they still had a size of 3 μm in the saline polyelectrolyte solution (Figure 1). The high ionic strength suppresses the swelling by screening the positive excess charges. When these swollen (PDADMAC/PSS)₄+PDADMAC capsules were heated for 20 min at 50 °C they swelled further to a size of approximately 14 μm . While heating at 70 °C the shells

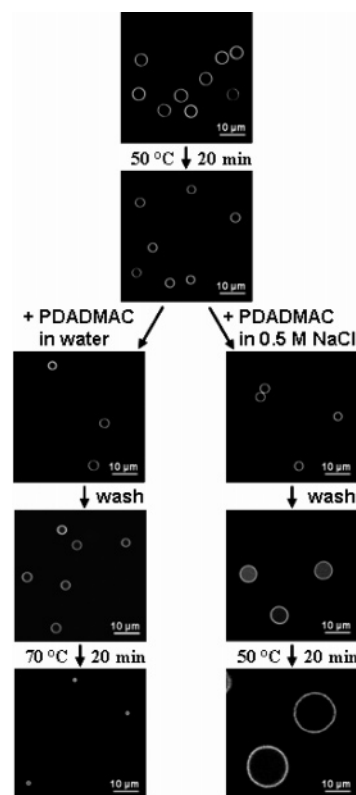


Figure 1. Confocal micrographs showing the effect of temperature treatment after coating shrunk (PDADMAC/PSS)₄ capsules with an additional PDADMAC layer in water (left) and 0.5 M NaCl (right).

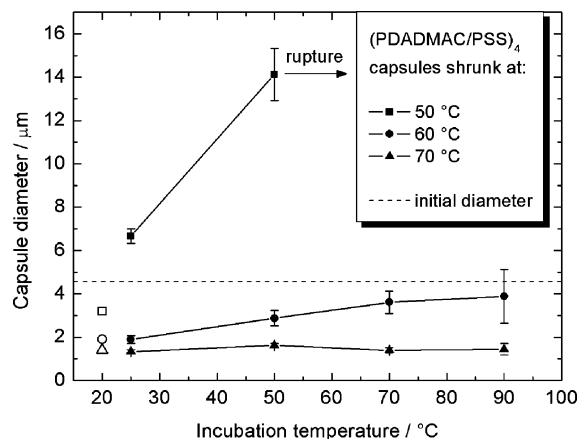


Figure 2. Average diameter of differently temperature-shrunk (PDADMAC/PSS)₄ capsules that were coated with an additional PDADMAC layer (in 0.5 M NaCl) and heated once more to induce a re-swelling as a function of incubation temperature (20 min incubation time). The dashed line corresponds to the initial size of (PDADMAC/PSS)₄ capsules before any heat treatment. The open symbols correspond to the size of (PDADMAC/PSS)₄ capsules after heating for 20 min at 50, 60, and 70 °C, respectively. The filled symbols indicate the diameter of (PDADMAC/PSS)₄+PDADMAC capsules after adding the additional PDADMAC layer and second heating.

rupture because their walls become too thin. Consequently, it is possible to reconvert temperature-shrunk capsules to swollen ones through supplying them with a sufficient amount of PDADMAC. Figure 2 indicates that the further the capsules shrunk before coating them with an additional PDADMAC layer the less is the extent of re-swelling after the second heating. (PDADMAC/PSS)₄ shells shrunk at 70 °C to a size of 1.4 μm and coated with PDADMAC in 0.5 M salt solution (ζ -potential +52 mV) did not change their size even after heating them for 20 min at 90 °C. Due to a smaller surface area and a probably smaller diffusion of PDADMAC into the densified multilayer the quantity of PDADMAC which is deposited on the negatively charged surface decreases with decreasing capsule diameter.

These experiments with varying amount of additionally adsorbed PDADMAC (varied either by salt or by extent of preshrinkage) further prove that swelling of PDADMAC/PSS capsules with temperature only occurs when an (positive) excess charge is present within the wall leading to an electrostatic repulsion.

Reverse Layering. To find out whether the observed swelling and shrinkage of capsules is really an odd–even effect or whether it is dependent on the polyelectrolyte forming the last layer, we prepared capsules with PSS as the first layer. For this purpose the surface charge of the silica templates had to be changed from negative to positive. Therefore, 4.5 μm silica particles were functionalized with 3-(aminopropyl)triethoxysilane (APTES), yielding positively charged amino groups on the surface.^{27,28} Through this reaction the ζ -potential changed from –61 to +60 mV, proving a dense coverage with amino groups. After deposition of the first layer PSS a ζ -potential of –52 mV showed that PSS was adsorbed on the positively charged particles. On these cores we prepared capsules with 8, 9, 14, and 15 layers. In contrast to the shells described before, capsules with an even number of layers have PDADMAC as capping layer whereas capsules with an odd number of layers have PSS at the outer surface. As in our previous paper,²³ we measured the capsule diameter as a function of temperature for an incubation time of 20 min by means of CLSM at room temperature (Figure 3). We expected that shells with an even number of layers have a balanced ratio between positive and

negative polyelectrolyte charges, leading to a decrease of capsule size upon heating. On the other hand, capsules with an odd number of layers (one layer more PSS than PDADMAC) should bear a negative net charge, leading to an electrostatic force which swells the capsules at higher temperatures. However, as can be seen in Figure 3, the opposite is happening. Capsules with an even number of layers, capped with PDADMAC, swell upon heating, whereas shells with an odd number of layers terminated with PSS shrink. Gao et al. found as well that (PSS/PDADMAC)₅ capsules templated on melamine formaldehyde cores swell upon heating.³¹ Thus, the properties of the polyelectrolyte forming the outermost layer control the temperature behavior of capsules consisting of the two strong polyions PSS and PDADMAC. As observed previously, PDADMAC-terminated capsules swell more with higher layer numbers, whereas the shrinkage of PSS-terminated capsules is less pronounced for thicker shells.

To find out whether this swelling is still related to a positive excess charge we measured the S/N ratio, which corresponds to the ratio between negative and positive polyelectrolyte charges (Table 1). Indeed, we found again that swelling capsules contain a high excess of positively charged monomers (25–30% based on the total amount of the excess polyelectrolyte) and shrinking ones have a more or less balanced ratio between opposite polyion charges with a slight excess of negatively charged PSS (~10%). A contribution of 2-aminoethanol, which is formed during core dissolution, to the nitrogen content of capsules can be ruled out because it is very small and will be released during the washing steps. Thus, whenever PDADMAC forms the outermost layer (independent of the charge of the first layer) the film carries a quite high positive excess charge which is (extrinsically) compensated by counterions. When PSS is deposited as the last layer, only a slightly negative excess charge is found. Since core dissolution should not change the amount of polymer deposited, the growth behavior of the PDADMAC/PSS system must be responsible for this situation. In our previous paper²³ we showed by AFM and single-particle light scattering that the film grows exponentially at least until the 10th layer, which was also found by others.^{8,9,11,13} Above that there were too few points to really prove a linear build-up regime. The alteration of the monomeric ratio of polyelectrolytes as a function of the outer layer together with the initially exponential growth of the PDADMAC/PSS multilayer points to a different adsorption behavior of the two polyelectrolytes. After deposition of PDADMAC there is always a constant high excess of this positively charged polymer, suggesting that the whole film is involved in the adsorption process. When PSS is adsorbed it neutralizes the positive excess charge, leaving behind only a slight excess of PSS monomers due to charge overcompensation at the outer surface. A model explaining the initial exponential growth of multilayers is based on the diffusion of at least one of the polyelectrolytes into the whole film.^{32–34} According to this model PDADMAC would be the penetrating polymer. Diffusion of PDADMAC through a PDADMAC/PSS film prepared at 0.5 M salt was already suggested by Miller et al. They found that multilayers capped with PDADMAC swell four times more in water compared to their PSS-terminated counterparts.³⁵ This observation can be explained by an accumulation of small counterions in the vicinity of the uncompensated PDADMAC charges, which results in a swelling of these films. We know that diffusion of PDADMAC deep into the film (at least 50 nm, corresponding to the first 10–12 exponentially growing layers) is quite speculative because there is no direct proof and PDADMAC is a quite bulky ($M_w = 200$ –

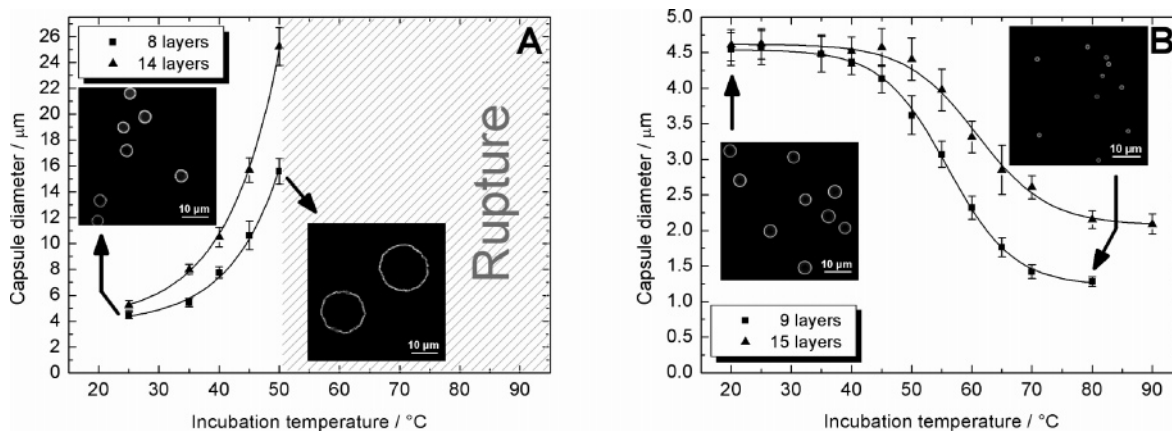


Figure 3. Average diameter of PSS/PDADMAC capsules (first layer PSS) prepared on aminosilane-functionalized $4.5\ \mu\text{m}$ silica particles with (A) 8 and 14 layers and (B) 9 and 15 layers as a function of temperature after 20 min of incubation. The insets show confocal micrographs of capsules with (A) 8 and (B) 9 layers before and after heating at the highest measured temperature, respectively.

350 kDa, rigid ring structure) and highly charged polymer. However, as polyelectrolyte adsorption is done in 0.5 M NaCl, where the Debye length ($\lambda_D = 0.43\ \text{nm}$) is comparable to the size of the monomers, charges are screened by counterions so that free polyelectrolytes behave like uncharged polymer molecules and also ionic bonds within the multilayer start to break, leading to a softening and higher permeability of the film. However, swelling and shrinkage as a function of the capping layer were also observed for capsules with 8–16 layers prepared in 0.1 M NaCl (data not shown).

NMR measurements demonstrating that PDADMAC has a higher mobility in PDADMAC-terminated multilayers compared to PSS-capped films whereas the PSS mobility does not show similar changes with layer number are in agreement with the assumption of PDADMAC as penetrating polyelectrolyte.³⁶ A higher instability of PDADMAC/PSS films with PDADMAC as the outermost layer due to the positive excess charge and the higher water content was demonstrated recently by electrokinetic measurements on flat multilayers.³⁷

Being far beyond the transition from exponential to linear layer growth should decrease the relative excess charge in PDADMAC-terminated multilayers, so that probably no swelling of capsules with temperature can be observed anymore. However, due to increased aggregation during coating and the increasing osmotic shock during core dissolution it is not possible to assemble capsules with a sufficient number of layers (>30) on silica particles.

Micro-DSC Measurements. (PDADMAC/PSS)₄ capsules undergo a glass-melt transition at around 35–40 °C, where the Young's modulus decreases significantly as determined by AFM force spectroscopy.²⁴ It is supposed that elevated temperature causes breakage of enough adjacent ionic bonds inside the film, allowing the oppositely charged polymers to rearrange. A similar softening of the multilayer is observed above a so-called glass-transition ionic strength.^{38,39} The softening by temperature leads to in the case of multilayer capsules either shrinkage or swelling of the shells depending whether hydrophobic effects or electrostatic forces dominate. Since the glass-transition temperature (T_g) of PSS (200 °C)⁴⁰ and PDADMAC (70 °C)⁴¹ are lowered significantly by the adsorption of water, it is important to work in an aqueous environment. We measured 0.5 mL of aqueous (PDADMAC/PSS)₄ capsule sediment (around $10\ \text{mg mL}^{-1}$) in a micro-DSC. In the first scan an endothermic peak with an onset at around 35 °C and a maximum at 40 °C is observed (Figure 4A). The second heating scan, which was done right after the subsequent cooling scan, does not show a similar peak.

This can be attributed to either the fact that capsules shrunk already irreversibly to dense particles during the first heating and there is no enthalpic contribution from the softening of the material or a too short annealing time at lower temperatures, since endothermic peaks (overshoots) near T_g ⁴² increase in magnitude and shift to higher temperatures as the annealing time is increased.⁴³ To check the influence of annealing we kept the sample for 24 h at 20 °C and recorded another heating scan. A peak with decreased intensity and shifted to lower temperatures (maximum at 35 °C) compared to the very first heating curve is seen (Figure 4B). Furthermore, the constant pressure heat capacity, in contrast to the first measurement in Figure 4A, shows a reproducible course for all following scans. The reason for the instabilities during the first curves is probably a slow sedimentation of material to the bottom of the cell due to a decreased effective space required by the shrunk capsules (factor 40). After the day of equilibration the sedimentation is definitely finished. From Figure 4B one can clearly see that the C_p undergoes a discrete increase up to 65 °C with an inflection point at 35 °C marking the glass-transition temperature for a heating rate of $0.5\ \text{K min}^{-1}$. The overshoots observed after longer annealing are a quantitative measure of the enthalpy relaxation that had occurred during this time.^{42,44} This physical aging occurs because at a temperature below T_g the polyelectrolyte multilayer is in a glassy, nonequilibrium state which on annealing will approach with time an equilibrium state. However, still there might be a contribution of the shrinkage of capsules to the transition enthalpy in Figure 4A. By integration of the peak as usually done for first-order phase transitions a transition enthalpy of roughly $14\ \text{J L}^{-1}$ of capsule sediment, and thus, around $1.4\ \text{kJ kg}^{-1}$ of polyelectrolyte complex is obtained. This would give a transition enthalpy per ion pair of $\Delta H(\text{IP}) \approx 0.43\ \text{kJ mol}^{-1}$. After annealing for 24 h at 20 °C the peak area (Figure 4B), which is exclusively a result of delayed enthalpy relaxation, amounts to about $0.5\ \text{kJ kg}^{-1}$ of polyelectrolyte complex.

A typical cooling scan for the (PDADMAC/PSS)₄ sample is shown in Figure 4C. All recorded cooling scans ($0.5\ \text{K min}^{-1}$) lie on top of each other because once the sample is heated above T_g its previous thermal history is eliminated. These curves also show an inflection point around 35 °C. The DSC measurements directly prove that PDADMAC/PSS multilayers undergo a glass transition in water. However, we assume that the exact glass-transition temperature of PDADMAC/PSS multilayers is a function of composition (i.e., ratio between polyelectrolytes and molecular weight) and thickness.

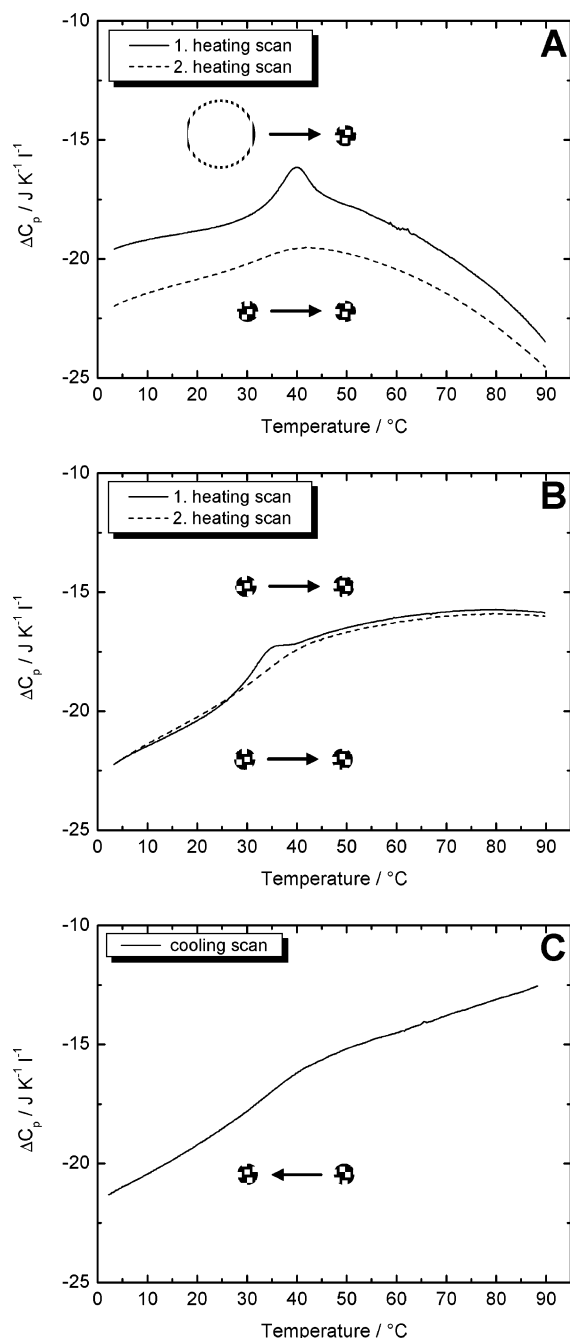


Figure 4. DSC scans at 0.5 K min^{-1} for a suspension (PDADMAC/PSS)₄ capsules in water. (A) Consecutive heating scans. During the first scan shells shrink irreversibly to solid particles. (B) Consecutive heating scans following the scans in A after an equilibration time of 24 h at 20°C . (C) Typical cooling scan between two consecutive heating scans.

Effect of Preheating on the Core. To prove that the driving forces for the rearrangement of capsules, i.e., swelling or shrinkage, are really electrostatic and surface forces and not energetically more favored conformations of the polymer chains and further investigate the influence of exceeding the glass-transition temperature before any macroscopic rearrangement, the following experiments were performed: Silica particles coated with 8 and 9 layers of PDADMAC/PSS were heated for 40 min at 90°C . This allows a relaxation of the chains within the multilayer without changing the macroscopic arrangement, i.e., the size of the polyelectrolyte shell. Afterward, the cores were dissolved and the preheated capsules incubated for 20 min at different temperatures as for the other experiments. Figure 5

shows the shell diameter as a function of incubation temperature. As can be seen from the graph in Figure 5A preheated (PDADMAC/PSS)₄ capsules also shrink at elevated temperatures until they form solid spheres. In comparison to nonpreheated capsules their diameter decreases only insignificantly faster with increasing temperature. SEM images of these capsules shrunk to different sizes are shown in Figure 6. Before shrinkage capsules look like those without preheating presented in ref 23. Furthermore, they have the same S/N ratio. AFM measurements indicate that neither the wall thickness nor the surface roughness differ from each other. However, as the diameter decreases the surface roughness increases much more for the preheated sample (Figure 6B and C). This is most pronounced when the final size is nearly reached (Figure 6C). At this stage the capsules exhibit a quite irregular shape. However, when heated at higher temperatures the capsules are converted into smooth dense particles (Figure 6D), as observed for nonpreheated (PDADMAC/PSS)_x shells.²³

For capsules consisting of 9 layers PDADMAC/PSS with PDADMAC as capping layer the influence of preheating is much more pronounced. Figure 5B shows that these capsules swell only up to $7 \mu\text{m}$ after incubation for 20 min at 55°C instead of $20 \mu\text{m}$ like their nonpreheated analogues.²³ Interestingly, they also rupture above 55°C , which indirectly indicates that the excess PDADMAC, leading to the instability of the film, was not removed completely during the pretreatment. Indeed, elemental analysis revealed that through the preheating the polycation excess within the (PDADMAC/PSS)₄PDADMAC shells is reduced from 23% to 19%. This charge excess is still sufficient to destabilize the multilayer. However, AFM investigations yielded the same thickness for capsules with and without preheating. SEM images of preheated capsules before additional heating and after incubation at 45°C do not show significant differences compared to nonpreheated (PDADMAC/PSS)₄PDADMAC capsules of the same size (Figure 6D and E).²³

These results indicate that even after preheating for 40 min at 90°C , which is well above the glass transition, the PSS-terminated capsules still undergo rearrangements, i.e., they shrink at elevated temperatures. Thus, the driving forces are not microscopic relaxations within the multilayer or a more coiled rearrangement of chains such as assumed by Leporatti et al. for the temperature-induced shrinkage of PAH/PSS shells⁴⁵ but the reduction of surface energy. PDADMAC-terminated capsules with a positive excess charge mark still an energetically unstable state and rupture. However, the annealing above T_g changes the internal structure of the multilayer (i.e., dissolution of excess PDADMAC), resulting in a smaller extent of swelling at elevated temperatures. Furthermore, for both types of capsules the preheating probably leads to a stronger intermixing of the layers.

Effect of Molecular Weight and Core Size. In our previous paper²³ we reported on the temperature-dependent behavior of capsules with different layer numbers consisting of PDADMAC with a molecular weight of 200–350 kDa (1200–2200 monomer units) and PSS having a molecular weight of 70 kDa (~ 340 monomer units). By preparing PDADMAC/PSS capsules with low molecular weight polyelectrolytes we wanted to investigate the influence of chain length on the rearrangement of these shells (i.e., shrinkage and swelling) upon heating. As low molecular weight polyelectrolytes we used 6.8 kDa PSS (LMW-PSS) with around 33 monomers per chain and PDADMAC with a molar mass of 5–20 kDa (LMW-PDADMAC) corresponding to 30–125 monomer units. Silica particles $4.5 \mu\text{m}$ in size were coated

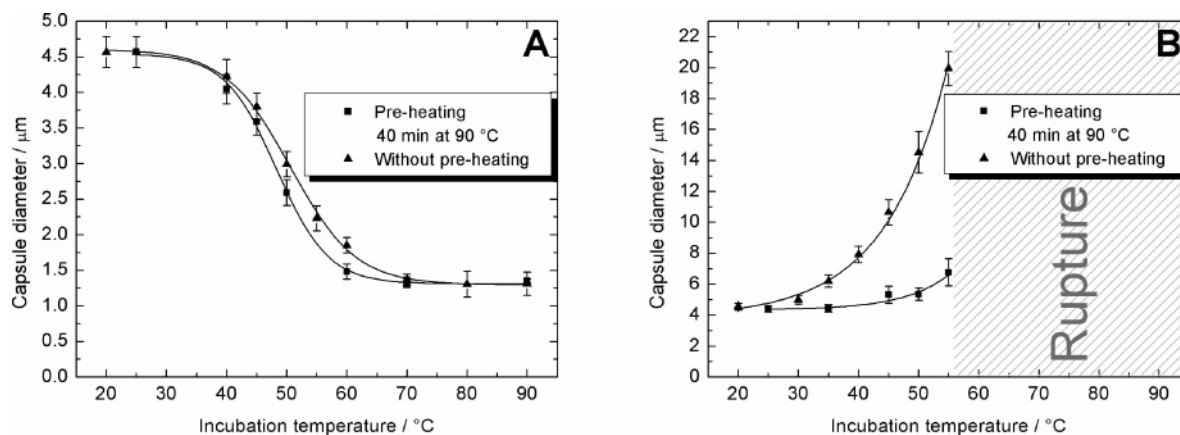


Figure 5. Effect of preheating on the temperature-dependent behavior of PDADMAC/PSS capsules. Average diameter of (A) (PDADMAC/PSS)₄ and (B) (PDADMAC/PSS)₄ PDADMAC capsules prepared on 4.5 μm silica particles as a function of temperature after 20 min of incubation. Before core dissolution the coated particles were preheated for 40 min at 90 $^{\circ}\text{C}$ in water. As a comparison the data for nonpretreated shells are included (taken from ref 23).

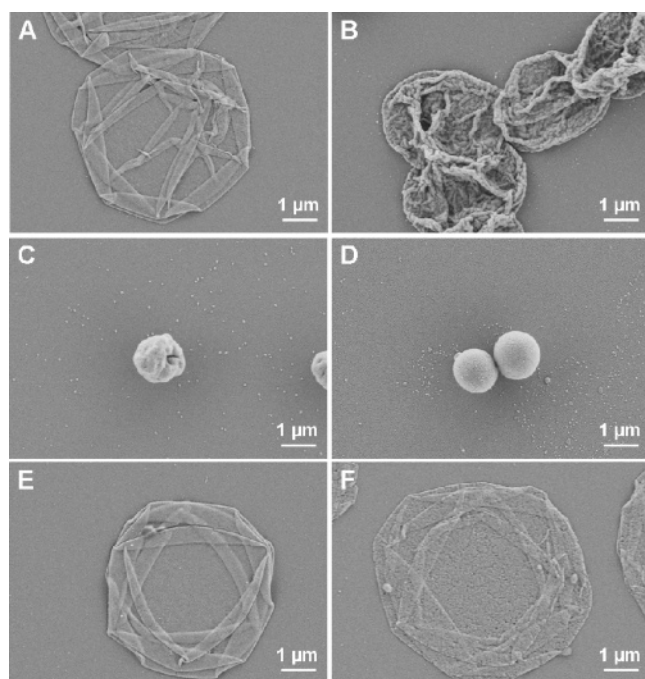


Figure 6. SEM images of dried preheated PDADMAC/PSS capsules after 20 min incubation at different temperatures. Before core dissolution the coated particles were preheated for 40 min at 90 $^{\circ}\text{C}$ in water. The micrographs show (PDADMAC/PSS)₄ capsules (A) before and after heating at (B) 50, (C) 60, and (D) 70 $^{\circ}\text{C}$ as well as (PDADMAC/PSS)₄PDADMAC shells (E) before and (F) after incubation at 45 $^{\circ}\text{C}$.

with 8 and 9 layers of either exclusively low molecular weight polyelectrolytes or with one low and one high molecular weight polymer. After core dissolution no proper capsules were obtained for all combinations containing LMW-PSS (LMW-PDADMAC/LMW-PSS as well as HMW-PDADMAC/LMW-PSS): Capsules with 8 layers already shrunk to a size of 2–3 μm after core dissolution, whereas in the case of 9 polyelectrolyte layers no capsules at all could be found after removal of the templates. Increasing the molecular weight of PSS from 6.8 to 13 kDa (~ 63 monomer units per chain) did not lead to different results. The reasons for these observations could, on one hand, be a very low film thickness compared to high molecular weight analogues because surface polyelectrolyte is stripped off by its oppositely charged partner during coating.⁴⁶ On the other hand, a higher mobility of the shorter chains, which leads to a shrinkage and rupture already at room temperature, could cause

this effect. AFM measurements of 2–3 μm (PDADMAC/LMW-PSS)₄ capsules indeed show that although they have shrunk their wall thickness in the dried state is only 13–14 nm.

Only for the sample containing LMW-PDADMAC and HMW-PSS proper capsules with 8 and 9 layers having the same size as the initial silica cores were obtained. AFM measurements of (LMW-PDADMAC/HMW-PSS)₄ capsules reveal a wall thickness of around 20 nm, which is comparable to that of capsules consisting of only high molecular weight PDADMAC and PSS (21 nm).²³ The observed differences in film thickness and thus in capsule stability between LMW-PDADMAC/HMW-PSS and HMW-PDADMAC/LMW-PSS can be explained by the different properties of the low molecular weight constituents. LMW-PDADMAC seems to stick stronger to oppositely charged polyelectrolyte. The reasons may be, first, the broader molecular weight distribution of LMW-PDADMAC compared to the LMW-PSS, probably favoring adsorption of the longer chains, and, second, the branched structure of PDADMAC.

Figure 7 compares the temperature dependences of the diameter for LMW-PDADMAC/HMW-PSS capsules with 8 and 9 layers with the respective values of HMW-PDADMAC/HMW-PSS shells.²³ Just as for 8-layered capsules consisting exclusively of high molecular weight polyelectrolytes the diameter of (LMW-PDADMAC/LMW-PSS)₄ shells decreases drastically with increasing temperature until it reaches a constant value of around 1.2 μm (Figure 7A). Above the glass-transition temperature the polyelectrolyte network softens due to breakage of ionic bonds, allowing rearrangement to a structure with less surface energy. However, as can be seen from Figure 7A, the rearrangement starts at significantly lower temperatures for the system with LMW-PDADMAC, pointing to a higher mobility of short polymer chains compared to longer ones due to less entanglement of HMW-PSS with LMW-PDADMAC.

The corresponding SEM micrographs of dried (LMW-PDADMAC/HMW-PSS)₄ capsules shrunk to different sizes can be seen in Figure 8A–E. The initial 4.5 μm capsules collapse during drying to a flat structure with many folds just as the previously investigated (HMW-PDADMAC/HMW-PSS)₄ shells and have a comparable surface roughness (Figure 8A).²³ At the endpoint of shrinkage smooth spherical dense particles are observed as well (Figure 8E). However, capsules shrunk at lower temperatures, which thus have not yet reached the final size, show a somewhat rougher surface. This is particularly obvious for the sample shrunk at 50 $^{\circ}\text{C}$ where the end size is more or less reached but the particles exhibit a quite irregular shape.

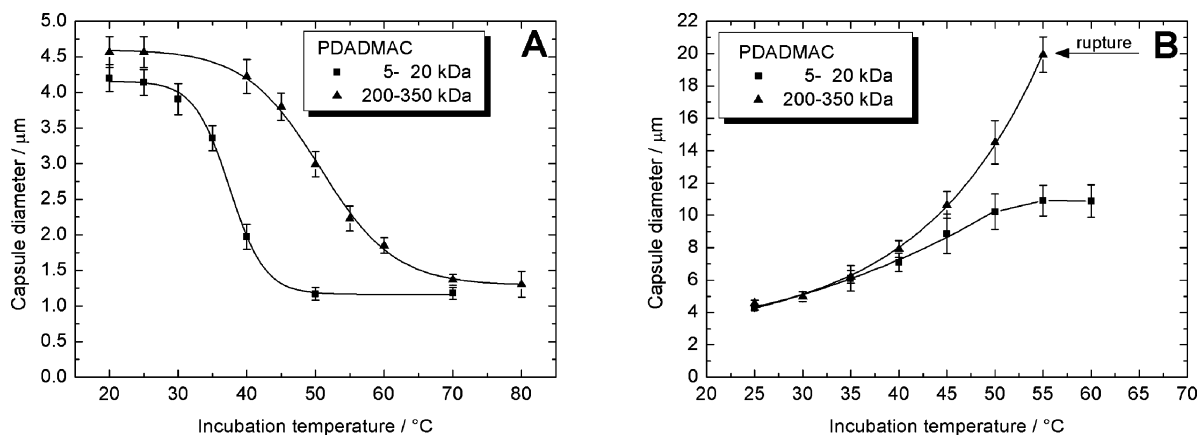


Figure 7. Average diameter of PDADMAC/PSS capsules containing low and high molecular weight PDADMAC and 70 kDa PSS as a function of temperature after 20 min of incubation. The temperature behavior of these shells depends also on the number of layers and is shown for (A) (PDADMAC/PSS)₄ and (B) (PDADMAC/PSS)₄PDADMAC capsules. (Data for high molecular weight PDADMAC were taken from ref 23).

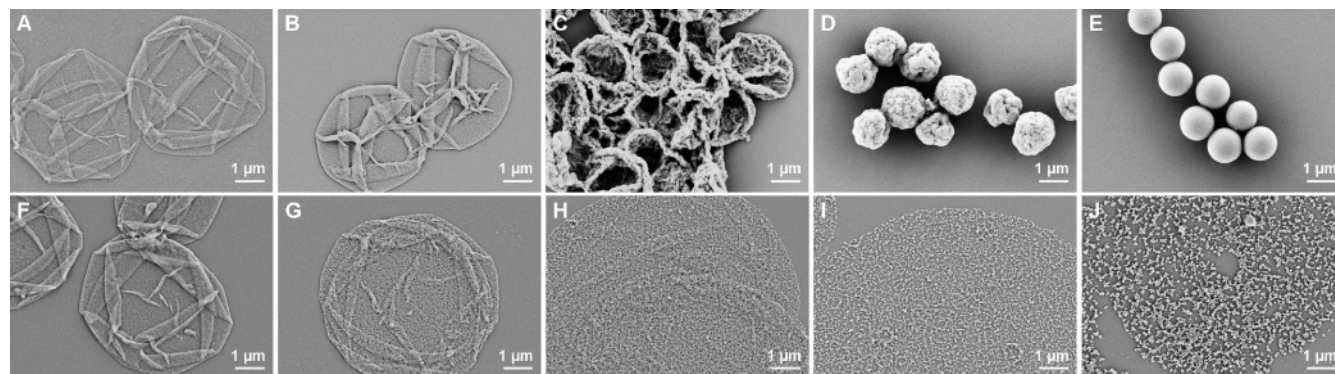


Figure 8. SEM images of dried LMW-PDADMAC/PSS capsules (5–20 kDa PDADMAC, 70 kDa PSS) after 20 min incubation at different temperatures. The first row shows (LMW-PDADMAC/HMW-PSS)₄ capsules (A) before and after heating at (B) 35, (C) 40, (D) 50, and (E) 70 °C. The second row presents (LMW-PDADMAC/HMW-PSS)₄LMW-PDADMAC capsules (F) before and after heating at (G) 35, (H) 40, (I) 55, and (J) 70 °C.

Capsules consisting of 9 layers LMW-PDADMAC/HMW-PSS also show the same behavior as their high molecular weight analogues: They swell upon heating due to a positive excess charge within the shell, which overcompensates the hydrophobic force, thus leading to an expansive force. Figure 7B depicts the change in capsule size for the two different systems. In comparison to the previously investigated PDADMAC/PSS system with 9 layers (LMW-PDADMAC/HMW-PSS)₄LMW-PDADMAC capsules swell less and do not burst because of a too thin wall above 55 °C. Instead, their diameter stays constant above that temperature but their walls become less defined and they lose more and more their spherical shape until they disintegrate. SEM micrographs of these capsules swollen at different temperatures confirm the swelling and the accompanying wall thinning together with a surface roughness increase (Figure 8F–J). By comparing Figure 8I and J the increasing disintegration of these capsules at temperatures above 55 °C with constant diameter can be seen. The behavior of these (LMW-PDADMAC/HMW-PSS)₄LMW-PDADMAC shells again confirms the weaker entanglement of chains. Probably some PDADMAC molecules detach during heating, reducing the electrostatic repulsion. However, enough PDADMAC chains still remain in the shell to destabilize the capsules. In addition, shorter chains cannot stretch out that much, also reducing the extent of swelling.

The initial size of capsules does not influence the general thermal behavior of PDADMAC/PSS shells. Temperature experiments on PDADMAC/PSS capsules that were assembled on 1 μm silica particles also showed a swelling or shrinkage

depending on the capping polyelectrolyte. (PDADMAC/PSS)₄ capsules 1 μm in size shrunk to a final size of around 435 nm. In comparison to their 4.5 μm analogues, which reach the endpoint of shrinkage at around 80 °C for 20 min of incubation, the 1 μm (PDADMAC/PSS)₄ shells form dense particles already at 60 °C because less material has to be rearranged.

Conclusions

Polyelectrolyte multilayer capsules consisting of PDADMAC and PSS as wall constituents show either a swelling or a shrinkage in water at elevated temperatures depending on the polyelectrolyte forming the outer layer but not depending on the total number of layers. The reason for this behavior is the alternating ratio between the two strong polyions with layer number as measured by elemental analysis. PDADMAC-capped capsules contain a high excess of positively charged monomers, whereas PSS-terminated capsules are nearly charge balanced. The driving force for the shrinking of the charge-balanced capsules is minimization of the water–polymer interface. In highly positively charged PDADMAC-terminated shells the tendency to reduce the surface tension is overcompensated by an electrostatic force, i.e., repulsion between the excess charges, resulting in expansion. Because of that surface-charge-dependent behavior it is possible to shrink PSS-capped capsules by heating and swell them afterward by coating with an additional layer of PDADMAC, inducing a positive excess charge. The relative amount of PDADMAC and thus the quantity of charge excess is determined by the salt concentration during deposition and

the extent of capsule shrinkage before adsorption. Multilayers rearrange easier the lower the molecular weight of the polyelectrolytes due less entanglement of the chains. The initial shell size does not influence the direction of rearrangement, i.e., shrinkage or swelling.

To allow any rearrangement of multilayers to occur the polyelectrolyte network has to soften so that the chains have an increased mobility because the films are in a glassy kinetically stabilized state at room temperature. Indeed, micro-DSC measurements of a concentrated suspension of (PDADMAC/PSS)₄ capsules show a glass transition at around 35 °C (0.5 K min⁻¹) with an overshoot which strongly depends on the thermal history of the sample. Heating of PDADMAC/PSS-coated particles before core dissolution above the glass-transition temperature indicates that thermal history has only a major influence on the behavior of PDADMAC-terminated shells upon heating. Furthermore, it proves that the driving force for the shrinking is not only a change in polyelectrolyte chain conformation but the overall forces on the capsule as a whole (electrostatic, hydrophobic).

Acknowledgment. The authors thank Rona Pietschke and Dr. Dmitry Shchukin for taking the SEM images, Anneliese Heilig for AFM measurements, and Silvia Pirok for elemental analyses. We acknowledge Dr. Maarten Bishevel and Dr. Radostina Georgieva for useful discussions. This work was supported in part by the EU-project "Nanocapsules for Targeted Delivery of Chemicals" STREP N001428, Sofja Kovalevskaja Program of the Alexander von Humboldt Foundation, and German Ministry of Education and Research.

References and Notes

- (1) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210*, 831.
- (2) Decher, G. *Science* **1997**, *277*, 1232.
- (3) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
- (4) Schönhoff, M. *J. Phys.: Condens. Matter* **2003**, *15*, R1781.
- (5) Jaber, J. A.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2006**, *128*, 2940.
- (6) Ladam, G.; Schaaf, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16*, 1249.
- (7) McAloney, R. A.; Sinyor, M.; Dudnik, V.; Goh, M. C. *Langmuir* **2001**, *17*, 6655.
- (8) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153.
- (9) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592.
- (10) Büscher, K.; Graf, K.; Ahrens, H.; Helm, C. A. *Langmuir* **2002**, *18*, 3585.
- (11) Tan, H. L.; McMurdo, M. J.; Pan, G. Q.; Van Patten, P. G. *Langmuir* **2003**, *19*, 9311.
- (12) Gopinadhan, M.; Ahrens, H.; Günther, J. U.; Steitz, R.; Helm, C. A. *Macromolecules* **2005**, *38*, 5228.
- (13) Salomäki, M.; Vinokurov, I. A.; Kankare, J. *Langmuir* **2005**, *21*, 11232.
- (14) Dubas, S. T.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 7725.
- (15) Ahrens, H.; Büscher, K.; Eck, D.; Förster, S.; Luap, C.; Papastavrou, G.; Schmitt, J.; Steitz, R.; Helm, C. A. *Macromol. Symp.* **2004**, *211*, 93.
- (16) Glinel, K.; Sukhorukov, G. B.; Möhwald, H.; Khrenov, V.; Tauer, K. *Macromol. Chem. Phys.* **2003**, *204*, 1784.
- (17) Jaber, J. A.; Schlenoff, J. B. *Macromolecules* **2005**, *38*, 1300.
- (18) Steitz, R.; Leiner, V.; Tauer, K.; Khrenov, V.; Von Klitzing, R. *Appl. Phys. A: Mater. Sci. Process.: Mater.* **2002**, *74*, S519.
- (19) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2202.
- (20) Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Möhwald, H. *Polym. Adv. Technol.* **1998**, *9*, 759.
- (21) Peyratout, C. S.; Dähne, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3762.
- (22) Sukhorukov, G. B.; Rogach, A. L.; Zebli, B.; Liedl, T.; Skirtach, A. G.; Köhler, K.; Antipov, A. A.; Gaponik, N.; Sussha, A. S.; Winterhalter, M.; Parak, W. J. *Small* **2005**, *1*, 194.
- (23) Köhler, K.; Shchukin, D. G.; Möhwald, H.; Sukhorukov, G. B. *J. Phys. Chem. B* **2005**, *109*, 18250.
- (24) Mueller, R.; Köhler, K.; Weinkamer, R.; Sukhorukov, G.; Fery, A. *Macromolecules* **2005**, *38*, 9766.
- (25) Köhler, K.; Biesheuvel, P. M.; Weinkamer, R.; Möhwald, H.; Sukhorukov, G. B. *Phys. Rev. Lett.*, in press.
- (26) Voigt, A.; Lichtenfeld, H.; Sukhorukov, G. B.; Zastrow, H.; Donath, E.; Bäuml, H.; Möhwald, H. *Ind. Eng. Chem. Res.* **1999**, *38*, 4037.
- (27) Badley, R. D.; Ford, W. T.; McEnroe, F. J.; Assink, R. A. *Langmuir* **1990**, *6*, 792.
- (28) Cant, N. E.; Critchley, K.; Zhang, H. L.; Evans, S. D. *Thin Solid Films* **2003**, *426*, 31.
- (29) Caruso, F.; Donath, E.; Möhwald, H.; Georgieva, R. *Macromolecules* **1998**, *31*, 7365.
- (30) Peyratout, C.; Donath, E.; Dähne, L. *J. Photochem. Photobiol. A: Chem.* **2001**, *142*, 51.
- (31) Gao, C. Y.; Leporatti, S.; Moya, S.; Donath, E.; Möhwald, H. *Chem.—Eur. J.* **2003**, *9*, 915.
- (32) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. *PNAS* **2002**, *99*, 12531.
- (33) Lavalle, P.; Picart, C.; Mutterer, J.; Gergely, C.; Reiss, H.; Voegel, J. C.; Senger, B.; Schaaf, P. *J. Phys. Chem. B* **2004**, *108*, 635.
- (34) Porcel, C.; Lavalle, P.; Ball, V.; Decher, G.; Senger, B.; Voegel, J.-C.; Schaaf, P. *Langmuir* **2006**, *22*, 4376.
- (35) Miller, M. D.; Bruening, M. L. *Chem. Mater.* **2005**, *17*, 5375.
- (36) McCormick, M.; Smith, R. N.; Graf, R.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Macromolecules* **2003**, *36*, 3616.
- (37) Köstler, S.; Ribitsch, V.; Stana-Kleinschek, K.; Jakopic, G.; Strnad, S. *Colloids Surf. A* **2005**, *270*, 107.
- (38) Kovacevic, D.; van der Burgh, S.; de Keizer, A.; Cohen Stuart, M. A. *Langmuir* **2002**, *18*, 5607.
- (39) Kovacevic, D.; van der Burgh, S.; de Keizer, A.; Stuart, M. A. C. *J. Phys. Chem. B* **2003**, *107*, 7998–8002.
- (40) M'Bareck, C. O.; Nguyen, Q. T.; Metayer, A.; Saiter, J. M.; Garda, M. R. *Polymer* **2004**, *45*, 4181.
- (41) Yeo, S. C.; Eisenberg, A. *J. Macromol. Sci. Phys.* **1977**, *B13*, 441.
- (42) Hodge, I. M. *J. Non-Cryst. Solids* **1994**, *175*, 303.
- (43) Hutchinson, J. M. *Thermochim. Acta* **1998**, *324*, 165.
- (44) Chakrabarti, D.; Bagchi, B. *J. Chem. Phys.* **2004**, *120*, 11678.
- (45) Leporatti, S.; Gao, C.; Voigt, A.; Donath, E.; Möhwald, H. *Eur. Phys. J. E* **2001**, *5*, 13.
- (46) Sui, Z. J.; Salloum, D.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 2491.