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Drastic Morphological Modification of Polyelectrolyte Microcapsules Induced by High Temperature

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ABSTRACT: Polyelectrolyte multilayer microcapsules of two different sizes consisting of poly(allylamine hydrochloride) and poly(styrenesulfonate) assembled on melamine formaldehyde cores were investigated by means of scanning (SEM) and transmission electron microscopy (TEM), confocal laser scanning microscopy (CLSM), and scanning force microscopy (SFM) regarding their stability at temperatures above 100 °C. A pronounced shrinking of the capsules accompanied by a wall thickness increase by more than 10 times was observed after incubating the capsule suspensions in an autoclave at 120 °C for 20 min. An estimation of the capsule wall volume revealed a densification of the polyelectrolyte layers and an exclusion of intercalated water. The gain of entropy resulting from a more coiled and interdigitated state of the polyions as well as from the great decrease of the polyelectrolyte/water interface is considered to be the driving force of this rearrangement process.

Introduction

Multilayers prepared by the alternate adsorption of oppositely charged polyelectrolytes onto charged surfaces utilizing the electrostatic attraction and complex formation between polyanions and polycations represent a large field of research.[1,2] The diversity of applicable compounds[3−5] for this layer-by-layer technique (LbL) enables the fabrication of multilayer films with varied properties having potential application in different areas such as optics,[6] electronics,[7] and sensor technology.[8] Until now, most studies have focused on polyelectrolyte multilayers assembled on flat substrates. Besides that, polyelectrolyte microcapsules are particularly promising due to their potential use as sensing elements,[9] carrier systems,[10] or microreaction chambers.[11] They are prepared by applying the layer-by-layer technique on colloidal templates with a size ranging from 100 nm to several micrometers followed by subsequent core dissolution.[12,13] The shell thickness can be tuned with a precision of nanometers. The properties of these capsules have been investigated with regard to surface charge,[13] morphology,[14] elasticity,[15] conductance,[16] and permeability.[17] Furthermore, their properties can be adjusted by exposing them to higher temperatures,[18] different pH values if they contain a weak polyion,[17] solvents of different polarities,[19] and different ionic strength.[20,21] In all of those cases the strength of the intermolecular interaction between the oppositely charged polyelectrolytes changes drastically, resulting in a denser or looser arrangement of the layers. Understanding these rearrangement processes yields insight into the structural parameters of the two-dimensional stratified layers, which grow step by step into the third dimension as compared to the bulk polyelectrolyte complexes.[22]

A basic understanding of the multilayer structure and its control during layer formation in order to tailor specific properties is required for all potential applications. However, since LbL films represent ordered nonequilibrium arrangements, it should be possible to overcome the kinetic energy barrier and to reach an energetically more favored state by input of thermal energy. In contrast to polyelectrolyte films assembled on flat substrates, capsules consist of a free multilayer film not attached to a supporting material, thus having enough space to rearrange in all three dimensions. It was already shown that incubating capsules consisting of poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) for 2 h at 70 °C leads to a slight diameter decrease accompanied by an increase of wall thickness.[23] The same shrinkage effect with increasing temperature was recently reported for capsules containing thermosensitive polyelectrolytes.[24] Besides the size decrease, a drastic reduction of the permeability coefficient for low-molecular-weight dyes was observed after heat treatment.[18,24] On the other hand, Gao et al. observed that MF-templated shells consisting of poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) swell at elevated temperature and are even unstable at 70 °C.[25] This indicates that the problem of polyelectrolyte shell rearrangement at elevated temperatures is still not clear, and more efforts are required to understand the processes occurring in the capsule shell during heating. Moreover, thermal modification of the capsule properties can lead to the formation of a new type of polyelectrolyte microcontainers, whose properties, such as stability, wall density, and permeability, are modified. In addition, heating above 100 °C is an efficient process of sterilization necessary for many biomedical applications. In the present work we studied the stability and morphological changes of PSS/PAH capsules templated on melamine formaldehyde (MF) cores at temperatures above 100 °C.

Materials and Methods

Materials. Sodium poly(styrenesulfonate) (PSS, $M_w \sim 70$ kDa), poly(allylamine hydrochloride) (PAH, $M_w \sim 70$ kDa), rhodamine 6G, and sodium chloride were purchased from Sigma-Aldrich (Germany). Weakly cross-linked monodisperse melamine formaldehyde particles (MF particles) with a diameter of 4.6 and 1.2 μm were obtained from Microparticles GmbH (Berlin, Germany). All compounds were used without further purification except for PSS, which was dialyzed against Milli-Q water (M_w cutoff 20 kDa) and lyophilized.

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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.[13] The alternating adsorption of PSS and PAH onto the surface of MF particles was carried out from 2 mg mL^{-1} polyelectrolyte solutions containing 0.5 M NaCl starting with PSS. Each adsorption step was followed by three washing steps in order to wash out not adsorbed polyelectrolyte molecules. The particles were separated from the supernatant using centrifugation. After deposition of the desired number of layers, the melamine cores were dissolved in hydrochloric acid at pH 1.1. The resulting hollow capsules were extensively washed with water to remove the core degradation products until the pH reached a value of 6.

High-Temperature Treatment. The capsule suspensions were incubated at 120 °C for 20 min using a Fedegari autoclave from Biomedis GmbH (Germany). Therefore, the vessel containing the aqueous capsule suspension was put together with the temperature controlling sensor into a water storage jar. The maximum pressure is 2800 hPa. The whole process takes 2 h including heating and cooling.

Confocal Laser Scanning Microscopy (CLSM). Optical images of polyelectrolyte capsules in water were obtained using a Leica TCS SP confocal system (Leica, Germany) equipped with a 100×/1.4−0.7 oil immersion objective. To visualize the polyelectrolyte shells, rhodamine 6G was used as a fluorescent label by mixing the sample suspension with the dye.

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

Transmission Electron Microscopy (TEM). Polyelectrolyte shells were transferred into ethanolic medium by washing them three times with ethanol. Afterward, the sample was embedded into methyl methacrylate containing 2,2′-azobis(2-methylpropionitrile) (AIBN), degassed, and stored at 60 °C overnight in order to polymerize the matrix. Sections of 50−100 nm in thickness were prepared using a Leica ultracut UCT ultramicrotome. Afterward, the sections were transferred onto a carbon film-coated copper grid and investigated by means of a Zeiss EM 912 Omega transmission electron microscope.

Scanning Force Microscopy (SFM). SFM measurements were performed in air at room temperature using a Nanoscope III Multimode SFM (Digital Instruments Inc.) 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. The layer thickness was measured from the flat regions of the profile.

Results

The effect of high-temperature treatment on the morphology of hollow polyelectrolyte shells was studied for capsules composed of five PSS/PAH bilayers assembled on 4.6 μm melamine formaldehyde particles. The core was dissolved carefully to diminish the amount of MF oligomers remaining in the shell and the capsule interior as much as possible.[26,27] To obtain temperatures above 100 °C without changes of the solution volume, an autoclave was used to incubate the capsules at 120 °C for 20 min. Figure 1 shows a typical confocal image of rhodamine 6G stained capsules in aqueous solution before and after heat treatment. It can be seen that the capsules keep their spherical shape after heating but shrink distinctly. A reduction of the diameter from 4.6 μm to approximately 1.3 μm, namely, to less than one-third of the initial size, can be observed. However, the diameter of the shrunk capsules cannot be determined exactly by means of CLSM because of the limited resolution of the optical microscope. To measure their diameter more precisely and to study any changes of the surface morphology, scanning electron microscopy was used. SEM images of dried capsules before and after incubation at 120 °C are shown in parts A and B of Figure 2, respectively. As observed previously, the initial polyelectrolyte shells collapse on the surface during drying due to capillary interactions.[28] The thin shell is not stable enough to keep the spherical shape. Therefore, the capsules exhibit a lot of creases and folds. After heat treatment in water the capsules do not collapse anymore during drying but show a bulky spherical shape indicating a more rigid wall (Figure 2B). Their surface is very smooth, which points to a healing of defects within the wall structure. From the SEM pictures it is possible to obtain the exact diameter of the shrunk capsules. Averaging the size of 20 capsules yields a diameter of 1.40 ± 0.05 μm for the bulky shaped shells after autoclaving. This value is in good agreement with the estimated diameter derived from CLSM images. So the drying process seems to have no influence on the capsule morphology. Thus, (PSS/PAH)$_5$ capsules with an initial diameter of 4.60 ± 0.04 μm shrink by more than 70% after incubation at 120 °C for 20 min.

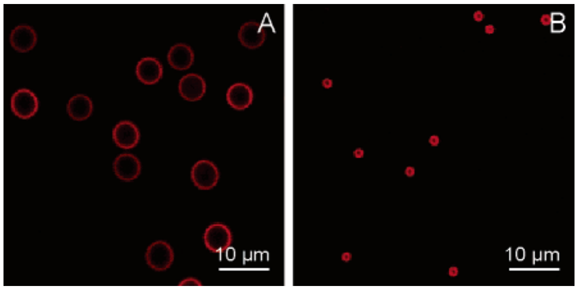

Figure 1. Confocal laser scanning microscopy images of (PSS/PAH)$_5$ polyelectrolyte capsules made on 4.6 μm MF cores before (A) and after (B) incubation at 120 °C for 20 min.

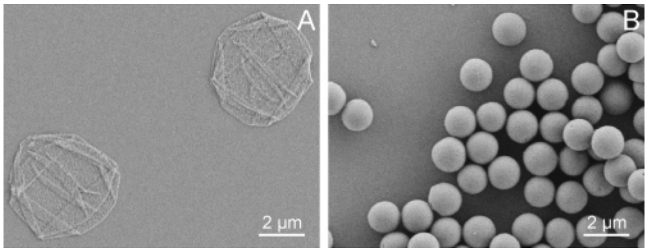

Figure 2. SEM images images of (PSS/PAH)$_5$ polyelectrolyte capsules made on 4.6 μm MF cores before (A) and after (B) incubation at 120 °C for 20 min.

(PSS/PAH)$_4$ capsules prepared on 1.2 ± 0.02 μm MF cores shrink by heating to a lesser extent of only about 50% to a final size of 0.63 ± 0.08 μm. This may be explained by the larger ratio of wall thickness to diameter and the higher curvature. One reason could be that there is an osmotic pressure caused by residual polymer inside, and this pressure may be size dependent. Already the initial shells do not collapse completely during drying because they are mechanically more stable as can be seen in Figure 3A. After heat treatment the capsules also exhibit the bulky shape with a smooth surface (Figure 3B).

To obtain further information about the heat-induced shrinking process and thus the rearrangement of the polyelectrolytes, the wall thickness of the 4.6 μm shells was determined before and after heating. The wall thickness of the initial capsules was estimated by means

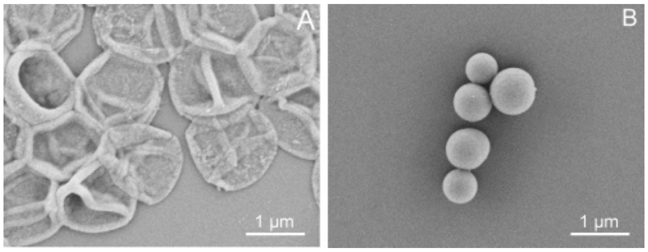

Figure 3. SEM images of (PSS/PAH)$_4$ polyelectrolyte capsules made on 1.2 μm MF cores before (A) and after (B) incubation at 120 °C for 20 min.

of SFM (Figure 4). At the right side of Figure 4 a typical height profile of a dried 4.6 μm capsule is shown. At least 20 profiles of different capsules were analyzed, and the mean thickness difference between the mica surface and the lowest region of the shells was averaged. Divided by 2, a value of 14.4 ± 1.4 nm for the wall thickness of the initial capsules is obtained. This value corresponds to the observed shell thickness of PSS/PAH capsules consisting of 10 layers.[28] Since it is not possible to determine the wall thickness of the annealed capsules using SFM because they do not collapse during drying, transmission electron microscopy was used. For that purpose the heat treated capsules were embedded into a polymer matrix, and thin sections of the sample were analyzed (Figure 5). From TEM images one can see hollow capsules with a very thick shell, which makes up nearly one-fourth of the capsule radius. The elliptical shape of the capsules is due to the ultramicrotoming process. In Figure 5 one capsule shows a crack in the wall. This break can be attributed to the core dissolution process. It is known that at the final stage of core decomposition the MF residue separates from the shell which can leave behind a pore within the wall.[29] These defects do not heal up during temperature treatment. The determination of the wall thickness from the TEM images yields a mean value of 160 ± 12 nm for the heat-treated capsules, which is more than 10 times the initial shell thickness. That means that the strong decrease in capsule diameter is accompanied by an enormous thickening of the wall, which leads to an increased mechanical stability of the shells preventing them from collapsing in the dried state.

By knowing the diameter d and the wall thickness h, it is possible to calculate the capsule wall volume V_w and to derive from that a possible change of the polyelectrolyte density during the rearrangement process:

$$V_w = {}^4/_3\pi[(d/2)^3 - (d/2 - h)^3]$$

By using this equation, one obtains a wall volume of $0.95 \pm 0.11\ \mu m^3$ for the initial capsules with a diameter of 4.6 μm and $0.78 \pm 0.11\ \mu m^3$ for the same capsules after heating. This calculated decrease in shell volume can be explained either by residues of MF oligomers in the capsule interior, which would only contribute to the thickness measured by SFM and not to that determined by TEM, or just by a densification of the polyelectrolyte film during rearrangement. However, since one can assume that most of the remaining core material is located within the multilayers or at the inner surface of the shells[26] and, therefore, included in both thickness measurements, the latter explanation seems to be the more valid one. Moreover, the determined thickness per layer of 1.4 nm is lower as compared to other SFM measurements for PSS/PAH capsules templated on MF cores,[23] thus referring to a negligible amount of encapsulated MF oligomers.

Table 1 summarizes the parameters of the capsules before and after heating and quantifies the extent of shrinkage. The large decreases of the inner volume and the outer surface area, which are reduced by a factor of 76 and 11, respectively, are particularly noticeable. The rearrangement of the polyelectrolytes during capsule shrinkage is irreversible. Longer storage of the annealed capsules in water at 4 °C does not change the morphology and size of the shells, indicating that the polyion arrangement is at a state of lower free energy as compared to their state after preparation.

Discussion

It is known from previous studies that during multilayer formation the polyelectrolyte chains adsorb irreversibly onto the surface retaining their solution conformation, which depends on the ionic strength of the solution.[30] The complexation of a large number of polyion charges with an oppositely charged surface leads to a kinetic entrapment of the polyelectrolyte coils. Neutron reflectivity measurements show that there is a large overlap between the segments of adjacent layers,[31−33] resulting in a constant monomer density along the layer normal for both polyelectrolytes.[34] Altogether, the chain structure can be considered equilibrated only on a shorter length scale whereas on a length scale exceeding some nanometers nonequilibrium conditions are predominant. There is still a remaining 2D stratification of macromolecular chains.[22] Heating provides thermal energy to overcome the electrostatic attraction between oppositely charged groups, leading to a temporary breakage of ion pairs. As a consequence, the polyelectrolyte chains gain an increased degree of mobility to rearrange into an energetically more favored coiled conformation. After that, the ionic groups can recombine with other oppositely charged polyelectrolyte groups in the neighborhood producing new local configurations of the film.[23] Defects like small pores and voids heal up and the surface is still very smooth even after this large conversion (Figures 2 and 3). After several months of storing the capsule suspension at room temperature, a small decrease in capsule diameter could be observed as well. That means that not only temperature increase but also time has an influence on the polyelectrolyte rearrangement. At higher temperatures more ionic bonds gain enough energy to overcome the kinetic barrier so that the opposite charges can separate from each other leading to an increased mobility of the polymer segments. Thus, the higher the temperature, the greater the probability that several adjacent ion bonds break as well so that a macroscopic change within the film can take place. The same mechanism is described for the reorientation of polyion multilayers in salt. In this case the ion contacts are broken by interactions with the charge screening salt ions.[35] In addition to the coupling and decoupling of ionic bonds, a polyelectrolyte rearrangement and densification of the macromolecules without breaking of ionic pairs might contribute to the process as well.

The driving force for the rearrangement and therewith the capsule shrinkage is assumed to be the increased entropy of the more coiled and interdigitated polymer arrangement as compared to the lower entropy state of the largely 2-dimensionally ordered layers after

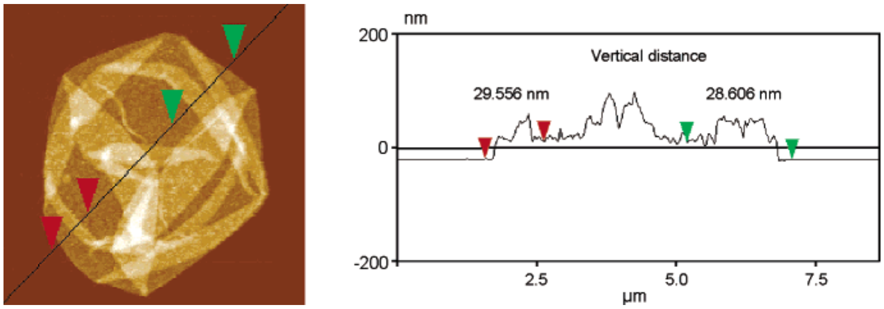

Figure 4. SFM image and cross-section profile of a $(PSS/PAH)_5$ polyelectrolyte capsule templated on 4.6 µm MF cores before thermal treatment.

Table 1. Dimensions of PSS/PAH Capsules before and after Heating to 120 °C as a Function of the Initial Shell Size[a]

	parameter	initial capsules	annealed capsules	percentage of change
$(PSS/PAH)_5$	diameter	4.60 ± 0.04 µm	1.40 ± 0.05 µm	−70%
	outer surface area	66.48 ± 1.16 µm^2	6.16 ± 0.44 µm^2	−91%
	wall thickness	14.4 ± 1.4 nm	160 ± 12 nm	+1011%
	wall volume	0.95 ± 0.11 µm^3	0.78 ± 0.11 µm^3	−18%
	inner volume	50.01 ± 1.40 µm^3	0.66 ± 0.14 µm^3	−99%
$(PSS/PAH)_4$	diameter	1.20 ± 0.02 µm	0.63 ± 0.08 µm	−48%
	outer surface area	4.52 ± 0.15 µm^2	1.25 ± 0.32 µm^2	−72%

[a] The diameter was determined by CLSM and SEM. The shell thickness was estimated by means of SFM and TEM. The other parameters were calculated out of them.

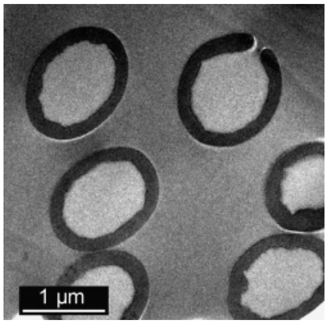

Figure 5. TEM micrograph of $(PSS/PAH)_5$ polyelectrolyte capsules templated on 4.6 µm MF cores after incubation at 120 °C for 20 min.

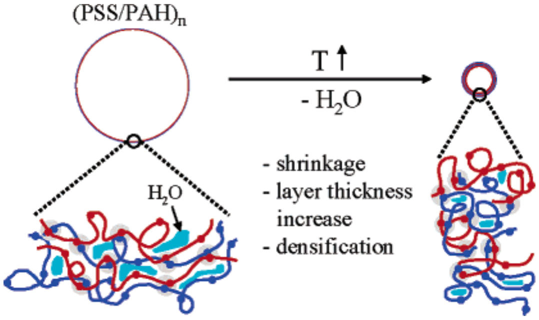

Figure 6. Scheme of the heat induced rearrangement process of PSS/PAH capsules into an entropically more favored state which is characterized by an increased coiling of the polyelectrolytes and a strongly decreased water content inside the film.

preparation.[23] To our opinion a second driving force also corresponding to an entropy increase has to be considered. Since the used polyelectrolytes (PAH and PSS) consist of a hydrophobic hydrocarbon chain as backbone, hydrophobic interactions have to be taken into account.[36] The shrinkage of the capsules during heating is accompanied by an enormous decrease of the outer and inner surface area of the capsules (Table 1) and thus the interface between water and the polyelectrolyte molecules. Also, the densification of the capsule wall can be explained by the hydrophobic effect. It is well-known that polyelectrolyte multilayers contain a substantial amount of water.[37] Small-angle neutron scattering measurements on coated latex particles showed that the water fraction in PAH/PSS layers amounts to approximately 42%, which can be subdivided into adsorbed water and water filling up the pores and small voids of the multilayer.[38] The observed densification of the polyelectrolyte film during heating results from a larger interpenetration and coiling of polyions, leading to a denser structure with fewer water-filled cavities. During temperature treatment water is expelled from the multilayers even though the capsules were heated in aqueous suspension, hence decreasing the water/polyelectrolyte interface. Figure 6 schematically summarizes the polyelectrolyte rearrangement.

Both above-discussed driving forces, the more coiled state of the polyions, and the hydrophobic effect correspond to an increase of entropy and contribute to the rearrangement process. PAH/PSS films assembled on a flat substrate and investigated in D_2O by neutron reflectometry show a decrease in roughness but not an appreciable change in thickness after temperature treatment.[39] A possible explanation is that the polyions rearrange into a more coiled conformation, but they cannot decrease their external surface because they are adsorbed on the substrate and therefore not free to spread out in all dimensions like in the case of polyelectrolyte capsules. In contrast, dried flat PAH/PSS films show a reversible decrease in thickness with increasing temperature. This change in thickness is also explained by losing water.[40]

Further investigations to get a closer insight into the mechanism of polyelectrolyte rearrangement during temperature treatment and the influence of different parameters on that effect are under way.

Conclusions

Polyelectrolyte capsules composed of PSS/PAH multilayers templated on MF cores preserve their integrity after heating at 120 °C for 20 min in aqueous solution but show a considerable decrease in size. The degree of shrinkage is dependent on the diameter of the initial capsules. 4.6 μm shells show a size decrease of 70% whereas 1.2 μm capsules shrink by less than 50%. The diameter decrease is accompanied by a strong increase of layer thickness and a smoothening of the surface. Calculations of the wall volume reveal a densification of the polyelectrolyte film. Through input of thermal energy the electrostatic attraction between oppositely charged polyelectrolyte groups is overcome, leading to a more coiled and interpenetrated arrangement of polyions and a healing of voids. Probably some water which fills up the pores of the multilayers is expelled during temperature treatment. The driving force for this polyelectrolyte rearrangement process is the entropy gain through the more coiled state of the polyions and the decreased interface between the complexed polyelectrolytes and water.

Through heating it is possible to obtain hollow polyelectrolyte capsules with a thickness comparable to more than 100 single layers, whose fabrication using the LbL technique is difficult and time-consuming. The tuning of capsule thickness and obviously permeability over a remarkable range of values is possible by heat treatment after capsule fabrication. This seems to be an elegant and perspective approach for capsule applications which in addition affords sterilization.

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