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Mechanical Properties of Polyelectrolyte-Filled Multilayer Microcapsules Studied by Atomic Force and Confocal Microscopy

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By using a combination of atomic force and confocal microscopy, we explore the deformation properties of multilayer microcapsules filled with a solution of strong polyelectrolyte. Encapsulation of polyelectrolyte was performed by regulation of the multilayer shell permeability in water–acetone solutions. The “filled” capsules prepared by this method were found to be stiffer than “hollow” ones, which reflects the contribution of the excess osmotic pressure to the capsule stiffness. The force-deformation curves contain three distinct regimes of reversible, partially reversible, and irreversible deformations depending on the degree of compression. The analysis of the shape of compressed capsules and of the inner polyelectrolyte spacial distribution allowed one to relate the deformation regimes to the permeability of the multilayer shells for water and inner polyelectrolyte at different stage of compression.

1. Introduction

Recently, there has been much interest in studying polyelectrolyte multilayer microcapsules.¹ These capsules are made by the alternating physisorption of oppositely charged polyelectrolytes on a charged spherical solid surface (the so-called layer-by-layer (LbL) or electrostatic self-assembly (ESA) method^{2–4}), with the subsequent removal of the latter, and represent a convenient system for basic and applied studies. Such “hollow” capsules can be filled with neutral or charged polymer solutions to give so-called “filled” capsules.^{5–10} The “filled” capsules represent a novel type of composite microstructures and are potentially important for a variety of applications. They could serve, for example, as new materials with controlled stiffness¹⁰ and allow one to mimic the advanced systems containing biopolymers.¹¹

A novel and promising area of research is connected with the investigation of mechanical properties of such

microstructures (for a recent review see ref 12). There have been several recent attempts to study the mechanical behavior of polyelectrolyte multilayer microcapsules, and several techniques have been proposed. The developed methods involve observing osmotically induced buckling of capsules immersed in a polyelectrolyte solution,¹³ studying swelling of capsules filled with polyelectrolyte,¹⁴ and measuring the deformation of microcapsules under applied load using atomic force microscope (AFM).¹⁰ The advantages of the AFM technique are its accuracy, the possibility of studying a wider range of systems, and richer experimental information.

The rich experimental information provided by the AFM method is not the last due to a combination of the force measuring setups with the optical signal. The optical schemes of the AFM setups are developing rapidly, providing many new opportunities. Thus, within the first year since the publication of the first paper on the subject,¹⁰ which has employed a simple illumination scheme, the progress in optical part included (in chronological order): fluorescence microscopy,⁹ reflection interference contrast microscopy (RICM),¹⁵ confocal microscopy,¹⁶ and a special confocal scheme, which allows the performance of a confocal scanning of deformed capsules in the vertical and horizontal directions.¹⁷ The latter development represented a major step forward. This type of optical signal combined with the AFM allows (i) simultaneous measurements of the capsule shape during the compression, (ii) working with very small capsules (radius of the order of μm), and (iii) monitoring the volume and permeability of capsules during the compression experiment. The

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approach based on a combination of AFM and confocal microscopy was applied before only to investigate the mechanical properties of “hollow” capsules.^{16–18} In this paper, we extend and develop it into studying the capsules filled with polyelectrolyte solutions. A new development concerns both the system and the method itself.

The AFM deformation experiment was performed before mostly with “hollow” capsules.^{10,15–17} There have been two recent reports^{10,20} on mechanical properties of capsules filled with polyelectrolyte by so-called “controlled precipitation”,^{8,19} i.e., by an assembly of the inner layer of polyelectrolyte shell by means of multivalent ions, with the consequent extraction of these ions and charged polymer release into the capsule interior. These capsules were found to be much stiffer than “hollow” ones,¹⁰ which reflects mostly the fact that the multivalent ions and the fragments of the original templates remain inside the capsules, forming a hydrogel-like structure.^{10,20} Clearly, to judge the role of the shell itself and/or encapsulated polyelectrolyte in determining the “filled” capsule stiffness, a comparison with the capsules prepared by a different technique is required. The alternative, so-called “permeability regulation” technique^{5,7} might be treated as that free of the mentioned above peculiarities of the “controlled precipitation” method. The “permeability regulation” technique takes advantage of the fact that the multilayer shell becomes permeable for polymer molecules in water–acetone^{9,14} mixtures. This technique was used to encapsulate a neutral polymer⁹ for an AFM mechanical experiment and to encapsulate polyelectrolytes for experiment on microcapsule swelling.^{14,21} To our knowledge, there have been no attempts to study polyelectrolyte-filled microcapsules prepared by the “permeability regulation” method in the AFM compression experiment.

The novelty of the system inspired further development of the method. Here, we extend and develop the confocal part of our setup. So far, the combination of AFM with confocal microscopy was not employed for investigating the mechanical properties of “filled” capsules. Therefore, the issues of polyelectrolyte distribution inside the compressed capsules and of permeability of the multilayer shell of “filled” capsule for inner polyelectrolyte and water under compression were never addressed. In this paper, we, for the first time, attempt to explore the encapsulated polyelectrolyte distribution at different stages of compression. This information, taken together with the confocal measurements of the deformed capsule shape and size, allows one to conclude about water and polyelectrolyte drainage from the capsule interior depending on degree of deformation. All this led to a possibility to interpret simultaneously measured force–deformation curves and to relate the regimes of deformations found to the properties of the inner polyelectrolyte solution and of the multilayer shell.

As before, we focus on the capsules with shells composed of layers of alternating polystyrene sulfonate (PSS) and polyallylamine hydrochloride (PAH). This type of shell has been successfully used in the majority of previous studies, including those on mechanical properties.^{1,13,14,16,22} As a template for a capsule formation, we use monodis-

persed weakly cross-linked melamine formaldehyde (MF) particles, which was also intensively used before for a capsule preparation.^{1,12,20,23,24} As a polyelectrolyte for encapsulation, a strong polyelectrolyte PSS is chosen here, again to explore the correlation with the previous studies.^{14,21}

2. Experimental Section

A. Materials. The fluorescent dye Rhodamine B isothiocyanate (RBITC) and shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; $M_w \approx 70\,000$ g/mol) and poly(allylamine hydrochloride) (PAH; $M_w \approx 70\,000$ g/mol) were purchased from Sigma-Aldrich Chemie GmbH, Germany. All chemicals were of analytical purity or higher quality and were used without further purification. Suspensions of monodispersed weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of $r_0 = 1.89 \pm 0.1\ \mu\text{m}$ were purchased from Microparticles GmbH (Berlin, Germany). Water used for all experiments was purified by a commercial Milli-Q Gradient A10 system containing ion-exchange and charcoal stages and had a resistivity higher than 18 M Ω /cm.

Fluorescent PSS–RBITC for encapsulation was prepared according to a method published in refs 14 and 21. Labeled allylamine was produced, mixed with sodium styrenesulfonate (SS), and then radically copolymerized under N_2 . The allylamine was mixed with RBITC dissolved in ethanol. The mixture was stirred for 4 h at room temperature. Afterward, SS was added in an amount corresponding to about 200 monomer equivalents. Then, as initiator, 1% $K_2S_2O_8$, relative to the monomer concentration, was added to this solution for a radical polymerization. The mixture was heated to 80 °C and was stirred for 4 h in a nitrogen atmosphere. After polymerization, labeled polymer was purified by dialysis (exclusion M_w 3500 g/mol) until no more color could be observed in the wash water. The dialyzed polymer solution was freeze-dried. The weight-average molecular weight (M_w) was estimated by gel-permeation chromatography (column: TSK Gel G6000, TSK Gel G5000, TSK Gel G3000) with standard poly(ethylene oxide) as a reference using H_2O as an eluent at 23 °C. M_w and the polydispersity were found to be about 46 000 g/mol and 1.86, respectively.

B. Methods. Capsule Preparation. The original hollow polyelectrolyte multilayer microcapsules were produced at 0.5 mol/L NaCl (pH 6) by an LbL assembly of four pairs of poly(sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) on MF particles. The concentration of each polymer solution was 1 mg/mL. After each dispersion/adsorption step, the particles were thoroughly rinsed with pure water at least twice to remove excess polymers and salt. To obtain “hollow” capsules, MF particle cores coated with multilayers were dissolved in HCl solution adjusted to pH 1.2–1.6 and then produced MF oligomers and excess HCl were removed by washing with pure water until a pH of 6 was achieved, as described in ref 25.

The “filled” capsules were made from preformed “hollow” capsules. The encapsulation of polyelectrolyte was performed by treating “hollow” capsules with organic solvent, acetone, to make the multilayer shell permeable for polymer molecules. Briefly, the original “hollow” capsules were exposed to an acetone–water mixture (1:1),¹⁴ and then RBITC-labeled PSS molecules were added to the mixtures. During the encapsulation process, the PSS concentration was increased gradually to avoid an osmotic collapse of the microcapsules.¹³ The initial RBITC–PSS concentration was 2 mg/mL (~ 0.01 mol/L) and was doubled every hour. When the required concentration was reached, the mixture was diluted with pure water after further incubation for 30 min at room temperature, and the multilayer shells were assumed to return to an impermeable state. The “filled” capsules were separated from the PSS in the bulk solution by centrifugation.

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Afterward, washing cycles with pure water were carefully carried out at least twice to remove the excess PSS molecules. The PSS concentration inside “filled” capsules was estimated from the fluorescence cross-section intensity coming from the interior of the PSS-containing capsules. In this case, we assumed that fluorescence is directly proportional to PSS concentration and used a calibration curve of fluorescence intensity of polymer in the bulk solution. The measured concentration was then recalculated to the initial concentration inside unswollen capsules.

Since the used method of “filled” capsule preparation includes the treatment with acetone, before all measurements, we have performed a post-modification of “hollow” capsules in the same water–acetone mixture for the same amount of time. We believe that this treatment with water–acetone mixtures not only allows one to make the shells of all capsules used here uniform but also facilitates the removal of the remaining, if any, tiny rests of the MF templates. Indeed, the investigation of morphology of the shells of both “hollow” and “filled” capsules, performed with high magnification scanning and transmission electron microscopy, has not given any indication of the presence of the rest of template particles (not shown).

Atomic Force and Confocal Microscopy. The experimental setup was described before.^{10,16,17} Load (force) vs deformation curves were measured with the Molecular Force Probe device (MFP) 1D (Asylum Co., Santa Barbara, USA), which has a nanopositioning sensor. This sensor can correct piezo ceramic hysteresis and creep of the AFM piezotranslator. For force measurement, we used V-shaped cantilevers (Micromash, Estonia, spring constants $k = 3.0$ N/m). The spring constant of the cantilever was estimated from the resonance frequency calibration plot (Cantilevers catalog, Micromash, Estonia). Glass spheres were glued onto the apex of cantilevers with epoxy glue (UHU Plus, Germany). The capsule deformation experiment has been described before.¹⁶ Here, we performed the measurements in two modes. First, as before, we used the dynamic regime of the AFM force measurements, where the piezotranslator is moving at a constant speed. In this case, the intervals of piezotranslator speed varied from 0.2 to 20 $\mu\text{m/s}$. Second, we have performed the force measurements in the so-called stepped regime. In this case, the movable glass surface was driven toward the other glass surface in a series of steps and the time interval between consequent steps was roughly equal to the time required for confocal scanning of the capsule shape (1–2 s depending on the speed of scanning). The result of measurement represents the deflection, Δ , vs the position of the piezo translator at a single approach. The load force, F , was determined from the cantilever deflection, $F = k\Delta$. As before, we assume that the zero of separation is at the point of the first measurable force.¹⁰ Then, the deformation is calculated as the difference between the position of the piezo translator and cantilever deflection. The diameter of the capsule was determined optically with an accuracy of 0.2 μm and from the AFM load vs deformation curves (like in ref 10). The relative deformation, ϵ , of the capsule was then calculated as $\epsilon = 1 - H/(2r)$, where H is the minimum sphere/substrate separation^{10,16} and r is the equilibrium radius of a “filled” capsule. In the case of “hollow” capsules, $r = r_0$.

The MFP was used together with a commercial confocal microscope unit FV300 (Olympus, Japan) and an inverted fluorescence microscope Olympus IX70 especially adjusted to our experiment (two micrometric tables, sample lifting device, etc). To make confocal images of uncompressed and compressed capsules the high-resolution ($60\times$) bright ($\text{NA} = 1.45$) immersion oil objective was used. The excitation wavelength was chosen according to the label Rhodamine (543 nm). The confocal images of capsules at different steps of deformation were made together with the force measurements performed at the stepped regime, namely, during the time intervals between consequent steps of piezotranslator motion (1–2 s). The fluorescence intensity profiles were measured along the lines at the equatorial plane (distance $\approx H/2$ from the glass plate). The change in fluorescent intensity at the time scale of such an experiment was not significant, and the variability in the brightness of the multiscanned confocal images was always less than 5%.

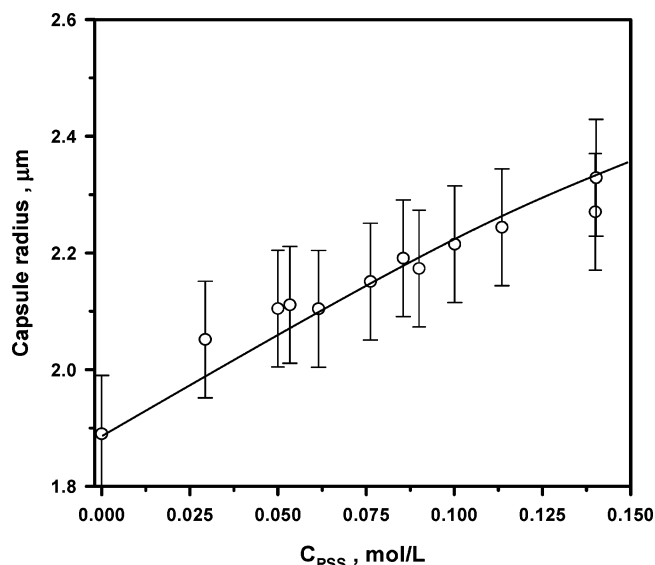


Figure 1. Equilibrium radius of the “filled” capsules as a function of polyelectrolyte concentration inside the capsule. Fitting (solid curves) corresponds to $E = 120$ MPa.

3. Results and Discussion

A. Microcapsule Swelling. Figure 1 shows the typical dependence of the equilibrium radius of “filled” capsules on the concentration of the inner polyelectrolyte (C_{PSS} , mol/L). Immediately after the preparation of “filled” capsules, the capsule sizes were close to the size of the original “hollow” capsules. The capsules swell due to excess osmotic pressure of the inner polyelectrolyte solution for at least several days before reaching their equilibrium sizes. The diameters were measured from the fluorescence intensity profiles measured along the diameter of an equatorial cross-section of the swollen “filled” capsules. Three dimensional (3D) confocal scanning showed that swollen “filled” capsules always have spherical form. The size of the swollen capsules was determined as an average of 6–10 capsules. Around 10% of the capsules were too big or too small compared to an average value, and thus were ignored in the analysis. As before,¹⁴ we have found that the radius, r , of the swollen capsules increases with the amount of encapsulated PSS. The fit of these data to the theoretical model,^{10,16} which relates the size of the swollen capsules, concentration of the inner solution, thickness of the multilayer shell (≈ 20 nm for four bilayer shells),¹⁶ and Young’s modulus, E , gives $E = 120 \pm 20$ MPa, which is consistent with previous results.^{14,16,21}

B. Force–Deformation Curves. Since it is rather difficult to encapsulate exactly the same amount of PSS, we found some variability in the force curves for similarly prepared capsules. Therefore, we have performed several series of experiments, each including the measurements of about 15–20 capsules, and we present here the average curves. The difference between force curves measured at the driving speed from 0.2 to 20 $\mu\text{m/s}$ was found to be within experimental error. The measurements of the forces were also performed using the stepped regime, described above. No difference from the value of force measured in the standard dynamic regime was found up to $\epsilon \approx 0.5$. At larger ϵ , we have observed slightly different forces and some variability in the results. All the force results reported below were obtained at driving speed of 20 $\mu\text{m/s}$.

The height of the capsules, or the AFM diameter,¹⁰ normally coincided with the diameter measured optically. However, in the case of capsules with a high concentration

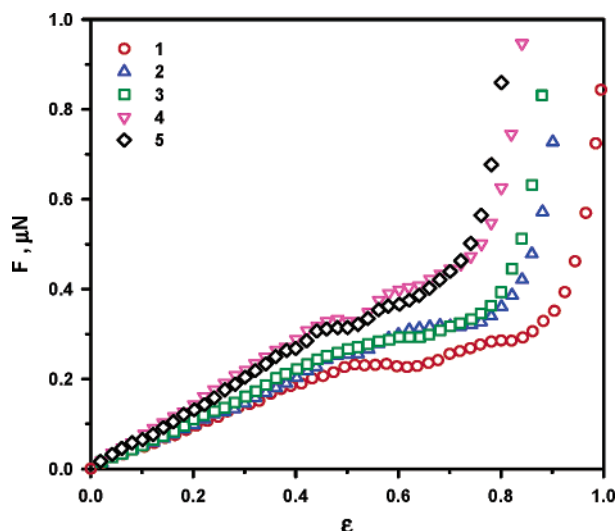


Figure 2. Typical load–deformation curves for “hollow” (1) and “filled” capsules with the concentration of inner polyelectrolyte equal to 0.08 (2), 0.10 (3), 0.11 (4), and 0.14 (5) mol/L.

of the inner PSS, it was slightly smaller. To calculate ϵ , we use the optical (confocal) diameter. Figure 2 shows typical load vs deformation curves measured for “filled” capsules with different concentrations of the inner PSS solution. The deformation profile of “hollow” capsules is also given. The essential observations are summarized below.

Our first observation concerns the stiffness of the studied capsules. The “filled” capsules explored here are 1.5–2 times stiffer than the “hollow” ones¹⁶ and the capsules filled with a neutral polymer.⁹ One can see a tendency for “filled” capsules to become slightly stiffer with the increase of the concentration of the inner PSS. This result indicates the important role of the osmotic pressure of the inner polyelectrolyte solution in determining the microcapsule stiffness. This is not surprising since the same phenomenon was responsible for the microcapsule swelling.^{14,21} At the same time, the “filled” capsules are 50–100 times softer than the capsules filled with the PSS solutions of roughly the same concentration using another encapsulation technique.^{10,20} We have shown before that the stiffness of capsules prepared by a “controlled precipitation” technique reflects a combined effect of osmotic pressure, irreversible structure changes in the highly stretched shell, and formation inside the capsules of a hydrogel-like 3D structure.¹⁰ Such a structure is created by negatively charged molecules of PSS and traces of positively charged multivalent ions and/or MF fragments of the initial templates.^{10,20} Since the “permeability regulation” encapsulation technique used here cannot introduce any positively charged species, the hydrogel formation inside the “filled” capsules studied here is impossible. One can, therefore, conclude that the pure contribution of the osmotic effect to the force–deformation curves is much weaker than that due to a formation of hydrogel-like 3D structures.

Second, the “filled” capsules show qualitatively similar deformation profiles to those previously observed for “hollow” capsules^{14,21} and capsules filled with neutral polymer.⁹ Namely, the deformation profiles always include three distinct regimes. In the *first regime*, with low applied load (ϵ up to ~ 0.2 – 0.3 for “hollow” capsules and up to 0.3 – 0.4 for “filled” ones), the deformation is completely reversible. We also note that at small deformation the “filled” capsules always react to applied loads as linear springs. In other words, the measured force depends

linearly on relative deformations. As we have shown before,¹⁷ in the case of “hollow” capsules, different situations can be observed depending on the permeability of the multilayer shells. The *second regime* ($\epsilon \approx 0.3$ – 0.8 for “hollow” and 0.4 – 0.7 for “filled” capsules) is characterized by a decrease in the slope of the load–deformation profiles, which now show a stronger dependence on concentration of the inner polymer solution, and only partial reversibility. After substantial deformation, the capsules enter the *third regime* ($\epsilon \approx 0.7$ – 1.0), in which major damage is caused by higher load and deformation is irreversible. The capsules “filled” with PSS studied here are qualitatively different from capsules filled with PSS by using the controlled precipitation technique.^{10,20}

Also, it has to be mentioned that we do not observe any detectable pull-off force, which indicates no adhesion to the glass surfaces (glass slide and sphere). The same observation was made for all types of “filled” and “hollow” capsules studied before in the AFM compression experiment.^{9,10,16}

C. Images from Confocal Scanning. The phenomena determining the deformation regimes can be better understood if we analyze the images from confocal scanning at the different stages of compression shown in Figure 3. The corresponding fluorescence intensity profiles along the diameter of the capsules measured at the indicated cross-section (the same direction for all relative deformations) are also given. Also included is the intensity of fluorescent signal in the center of capsules as a function of relative deformation.

One can see that in the *first regime* of deformation, the free area of the “filled” capsules remains spherical. The fluorescence profiles do not depend on the scanning direction of the confocal images (Figure 4, top), suggesting the axi-symmetrical distribution of the inner polyelectrolyte. Essentially, the value of intensity of fluorescence in the center (dash-dotted line in Figure 3) remains constant up to ϵ around 0.2 – 0.3 , indicating that the PSS concentration inside does not change compared with the noncompressed capsule. This observation is crucial. It confirms that the capsule volume does not change at the initial stage of compression and water does not drain out of the shell. Here, we remark and stress that the confocal scanning was done in the stepped regime of force measurements and that the time scale of this regime of force measurements is larger than that of a standard dynamic regime. Therefore, the losses in capsule volume during fast force measurements can only be smaller than what we observe in the stepped regime but never the opposite.

The confocal images corresponding to the *second regime* of deformation are significantly different. They show the deviations of the shape of the capsules from the spherical and give nonuniform distribution of encapsulated PSS inside the shell. This concerns both the intensity of fluorescence measured along one cross-section (Figure 3) and intensities at different cross-sections/directions of scanning (Figure 4, middle). The fluorescence intensity at the center increases with relative deformation, which suggests that the capsule volume decreases but the encapsulated polymer remains inside. All these indicate some local ruptures in the shells and rapid drainage of inner water. This phenomenon is likely responsible for only partial reversibility of deformation and changes in slope in the force–deformation curves.

The fluorescence profiles corresponding to the *third regime* of deformation, suggest the total destruction of the capsules. Indeed, the fluorescent profiles show some irregularities and dramatically depend on the scanning

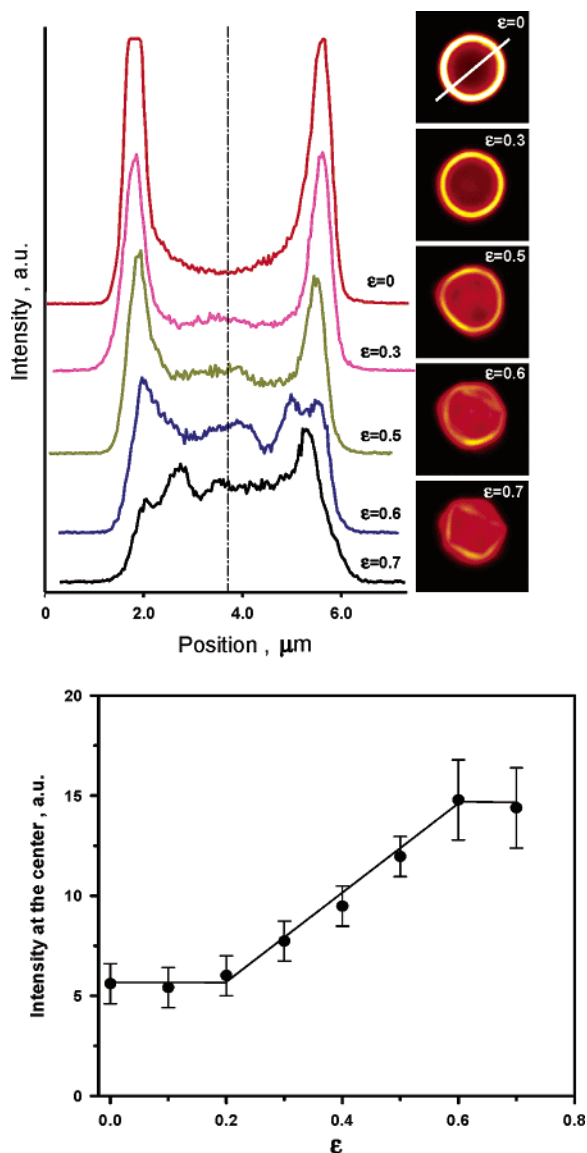


Figure 3. (top) Distribution of fluorescent intensity and images from confocal scanning of compressed “filled” capsules ($C_{\text{PSS}} \approx 0.10$ mol/L) obtained on different stages of deformation. From top to bottom, $\epsilon = 0, 0.3, 0.5, 0.6$, and 0.7 . (bottom) Relative fluorescence intensity at the center of “filled” capsule ($C_{\text{PSS}} \approx 0.10$ mol/L) on different stages of deformation.

direction (Figure 4, bottom). The confocal images indicate the capsule collapse and formation of structures with the folds and creases. These optical observations are entirely consistent with the irreversibility of the force curves corresponding to this stage of deformation. The fluorescence in the center again becomes quasi-constant, which could, in principle, be caused by two limiting situations. On one hand, this could be due to simultaneous release of both water and polyelectrolyte from the capsule interior. On the other hand, an alternative scenario would be that both water and polyelectrolyte do not drain out of the capsule at the time scale of experiment. This could happen, for example, due to a dramatic decrease of the free area of the capsules at high compressions. One cannot also entirely exclude that there is some contribution to the fluorescent intensity in the center coming from the capsule shells. Unfortunately, the current status of our method does not allow to draw a more definite conclusion.

Finally, we would like to mention another typical feature of fluorescence profiles we have recorded. We remark that we have always detected some peaks at the walls, which

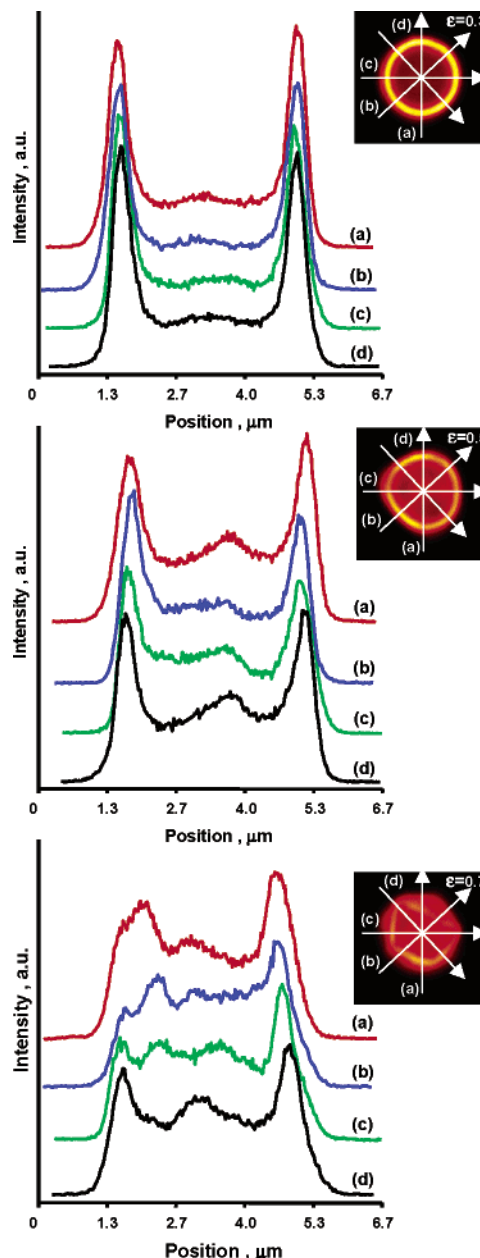


Figure 4. Confocal fluorescent profiles of compressed “filled” capsules ($C_{\text{PSS}} \approx 0.10$ mol/L) corresponding to three different regimes of deformation and measured at different directions.

can be linked to adsorption/redistribution of the inner polyelectrolyte due to the drainage of water. The comparison of the profiles obtained at different stages of deformation (Figures 3 and 4) clearly shows that with compression of these adsorption peaks are getting lower and wider. Whether this reflects the change in polymer adsorption properties or is caused by some optical errors, which are inevitable for such a thin shell, remains an open question. We will address this issue in future publications.

4. Conclusion

In summary, the experiment we have reported suggests that the encapsulation of a charged polymer, performed by the so-called “permeability regulation” method, changes the mechanical properties of polyelectrolyte microcapsules by increasing their stiffness. The increase in stiffness is likely due to the excess osmotic pressure of the inner polyelectrolyte solution. As a result, at small deformations,

the capsules are deformed at quasi-constant volume and their mechanical behavior is controlled both by the elasticity of the multilayer shells and osmotic properties of the inner PSS solution. At larger deformations, the capsule mechanics is determined by drainage of water through the shell, which leads to an only partial reversibility of deformation and to an increase in concentration of the inner polyelectrolyte (due to a decrease in capsule

volume). Further compression leads to a collapse of the capsules.

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