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Young's Modulus of Polyelectrolyte Multilayers from Microcapsule Swelling

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ABSTRACT: We measure Young's modulus of a free polyelectrolyte multilayer film by studying osmotically induced swelling of polyelectrolyte multilayer microcapsules filled with the polyelectrolyte solution. Different filling techniques and core templates were used for the capsule preparation. Varying the concentration of the polyelectrolyte inside the capsule, its radius and the shell thickness yielded an estimate of Young's modulus of the order of 100 MPa. This corresponds to an elastomer and reflects strong interactions between polyanions and polycations in the multilayer.

Introduction

Molecularly thin polyelectrolyte multilayer films are composed of alternating layers of oppositely charged polyions and are important for a variety of potential applications.[1,2] Supported multilayer films are normally produced via layer-by-layer (LbL) adsorption of polyanions and polycations on a planar[1] or spherical[3] charged solid surface. In the latter case, the colloidal template can be dissolved to give so-called polyelectrolyte microcapsules.[4] The shell of such microcapsules is nothing more than a free-standing multilayer film. The free thin film geometry allows investigation of properties not accessible in the bulk or in supported films and helps to gain a better understanding of polyelectrolytes in general.

There have been a number of recent experimental studies of mechanical properties of thin multilayer films. First, by studying osmotically induced buckling of "hollow" (water inside) capsules immersed in a polyelectrolyte solution,[5] the Young's modulus was found to be above 1000 MPa, close to the elasticity of the *bulk plastics*.[6] The second, more recent, approach is based on measuring the deformation of microcapsules under applied load using an atomic force microscope (AFM).[7−9] This method yielded an estimate of Young's modulus of the order of 1−100 MPa, depending on the template and solvent used for its dissolution, which corresponds to an *elastomer*.[6] One reason for such a discrepancy between two experiments might be connected to the different chemical treatment of the shells.[7] Another might be hidden in the assumptions of the models used to explain experimental data. The first model assumes that the shell is highly permeable for water, even on short time scales of the relaxation of buckling deformation. The second approach treats the shell as impermeable for water on short time scales, relying on the conservation of capsule volume for small deformations. The accuracy of existing experimental results does not allow to conclude which approach is more realistic.

In this paper we propose an alternative way to probe the elastic properties of a polyelectrolyte multilayer. The method is based on studying the swelling of microcapsules filled with a solution of a strong polyelectrolyte. The size of a swollen capsule depends on the Young's modulus of the capsule shell. Fitting the experimental data to the prediction of a simple model yields Young's modulus of the polyelectrolyte multilayer of the order of 100 MPa. Taken together with recent AFM observations,[7] this result leads to the conclusion that the mechanical behavior of a polyelectrolyte multilayer is that of an *elastomer*.

Theoretical Model

We consider a "filled" (polyelectrolyte solution inside) capsule immersed in a low molecular weight solvent (water in our case). The capsule swells due to excess osmotic pressure of the inner solution. The osmotic pressure of polyelectrolyte solutions is the sum of polymer and counterion contributions. However, in a salt-free solution the latter exceeds the osmotic pressure due to polymer itself by several orders of magnitude.[10−12] The capsule shell is permeable to the solvent (on time scales larger than the characteristic diffusion time) but impermeable to the encapsulated polymer of high molecular weight. Then the solvent diffuses into the capsule until the elastic force of the stretched shell balances the osmotic pressure. We assume that the inner polyelectrolyte solution remains electroneutral; i.e., all counterions due to polyelectrolyte dissociation remain in the capsule interior.[5]

A general model describing the swelling of capsules might be rather involved if plastic deformations come into play.[13] Here we assume that, for small relative deformations, the response of the capsule shell is elastic. A similar assumption was made in refs 5 and 7 and was confirmed by observations of a complete reversibility of deformation of the slightly stretched shells.[7] If the capsule swells from the initial radius r_0 to the final radius r, the energy of stretching of the shell is given

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by the elastic theory of membranes[14]

$$G = 4\pi \frac{E}{1-\nu} h (r - r_0)^2 \tag{1}$$

where E is Young's modulus, ν is Poisson's ratio ($\nu \approx {}^1/_2$), and h is the shell thickness ($h \ll r_0$).

For a dilute solution of the inner polyelectrolyte or, alternatively, small concentration $n = N/V$ of counterions in the capsule, the osmotic pressure induced by the counterions reads

$$\Pi = \varphi \frac{N}{V} k_B T \tag{2}$$

Here N is the number of counterions and $\varphi \leq 1$ is the osmotic coefficient, defined as a ratio of experimentally measured osmotic pressure Π to the ideal osmotic pressure of all counterions. The difference between these two values is due to a fraction of condensed counterions being bound to the polyelectrolyte chain and not contributing to the osmotic pressure.[15-17]

The work done by the osmotic pressure Π to swell the capsule from radius r_0 to r then reads

$$A = \int_{V_0}^{V} \Pi \, dV = -3\varphi N k_B T \ln \frac{r}{r_0} \tag{3}$$

The equilibrium radius of the capsule is given by the minimum of the total energy $F = G + A$, $\partial F/\partial r = 0$

$$r = \frac{1}{2} r_0 \left(1 + \sqrt{1 + \frac{3}{2}\frac{(1-\nu)\varphi N k_B T}{E h {r_0}^2}}\right) \tag{4}$$

To relate the number of counterions to the concentration of the polymer in the solution, we need to know the degree of dissociation, i.e., the number of counterions per monomer. For a strong polyelectrolyte this number could be taken as 1, i.e., one counterion per monomer. Then

$$N = N_A c V_0 = \frac{4}{3}\pi {r_0}^3 c N_A \tag{5}$$

where c is the concentration of the polymer solution in the capsule before it swells and N_A is the Avogadro number. Substituting eq 5 into eq 4, one obtains

$$r = \frac{1}{2} r_0 \left(1 + \sqrt{1 + \frac{2\pi r_0}{h}\frac{1-\nu}{E}\varphi c R T}\right) \tag{6}$$

where $R = k_B N_A$ is the universal gas constant. Equation 6 relates the size of the swollen capsule to the concentration of the inner solution, thickness of the capsule shell, and Young's modulus.

Our model allows design of a swelling experiment. To determine Young's modulus, one can measure the deformation of the capsule as a function of concentration c and the shell thickness h and then fit the experimental data to eq 6.

Experimental Section

For an initial application of our approach we have chosen to study two types of capsules, characterized by different methods of encapsulation and templated on different cores. The first type are "filled" capsules prepared on manganese carbonate templates by a controlled precipitation,[8,18] i.e., by an assembly of the inner layer of polyelectrolyte shell by means of multivalent ions with the subsequent extraction of these ions and polymer release into the capsule interior. The second type of "filled" capsules was made from the "hollow" ones, templated on melamine formaldehyde particles, by regulating their permeability for high molecular weight polymers.[9,19]

As a polyelectrolyte for encapsulation we have chosen sodium poly(styrenesulfonate) (PSS). The behavior of this highly charged flexible polyanion in salt-free conditions has been studied both theoretically[16] and experimentally.[10,11,20,21] The value of φ for PSS was found to range from 0.2 to 1 and suggests some condensation of counterions.[16,17]

Here we study the capsules with the shells composed of layers of alternating PSS and PAH (poly(allylamine hydrochloride)). This type of shell was used in the majority of the previous studies, including those of mechanical properties.[3,5,7,22] One reason for our choice is that the PSS/PAH multilayers are stable in various chemical environments and are permeable for small polar molecules and ions but not for polymers. Another is that the mass and thickness of the PSS/PAH films grow linearly with the number of deposited bilayers, so that the multilayer presents a layered nanostructure.[23-25] All this makes PSS/PAH multilayers a convenient system for verification of our approach.

Materials. The fluorescent dye Rhodamine B isothiocyanate (RBITC), monomers allylamide and 4-styrenesulfonic acid sodium salt hydrate (SS), shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; $M_w \sim 70\,000$ g/mol) and poly(allylamine hydrochloride) (PAH; $M_w \sim 70\,000$ g/mol), and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma-Aldrich Chemie GmbH, Germany. Hydrochloric acid (HCl), acetone, and sodium chloride (NaCl) were purchased from Riedel-de Haën; Germany. The ionic initiator potassium peroxodisulfate ($K_2S_2O_8$) for the radical polymerization and $Y(NO_3)_3$ were obtained from Merck GmbH, Germany. All chemicals were of analytical purity or higher quality and were used without further purification.

To produce labeled PSS for encapsulation, we used a modification of a method published in ref 26. First, labeled allylamide was made which was afterward mixed with 4-styrenesulfonic acid sodium salt hydrate and then copolymerized radically. The allylamide was mixed with RBITC solved in ethanol. The mixture was stirred for 4 h at room temperature. Afterward, SS was added in an amount corresponding to a label grade of about 200 monomer units each. Then $K_2S_2O_8$ was added to this solution as an ionic initiator for the radical polymerization. The mixture was heated to 80 °C and was stirred for 4 h in a nitrogen atmosphere. Afterward, it was centrifuged with a membrane that filters molecules with a molecular weight of 100 000 g/mol or more, and polydispersity was found to be $M_w/M_n \sim 1.8$. The remaining PSS was chopped into small parts and washed with ethanol until no more color could be observed in the filtrate.

Suspensions of monodispersed weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of $r_0 = 2.0 \pm 0.1$ μm were purchased from Microparticles GmbH (Berlin, Germany).

The manganese carbonate template ($MnCO_3$) was prepared by a mixing method described in ref 27. Briefly, acidic manganese sulfate solution (9×10^{-3} M, pH = 4.2 adjusted by sulfuric acid) was added at 1:1 volume ratio to 2.25×10^{-3} M NH_4HCO_3. Then the stirred mixture was aged at 50 °C for 16 h. The resulting $MnCO_3$ particles had a spherical shape with a radius of 1.85 ± 0.2 and 2.5 ± 0.2 μm.

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 MΩ/cm.

Methods. *Capsule Preparation.* Two different approaches have been exploited for preparation of filled capsules.

The preparation of filled capsules of the first type consisted of several steps (Figure 1). The first step (Figure 1a) was surface-controlled precipitation of labeled PSS (by complex formation with Y^{3+} ions) on the surface of $MnCO_3$.[8,28,29] By varying the number of precipitated layers, we were able to tune the surface density of adsorbed polymer and, therefore, the number of PSS molecules precipitated on $MnCO_3$ particles. In

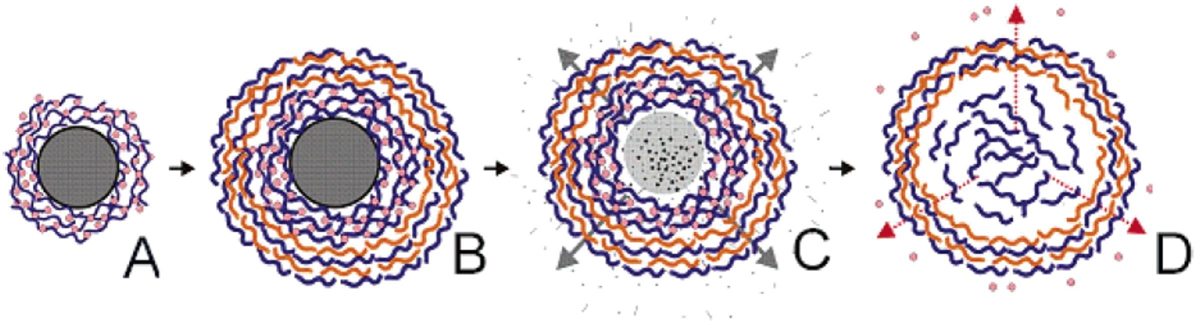

Figure 1. Scheme illustrating the preparation of "filled" microcapsules of the first type.

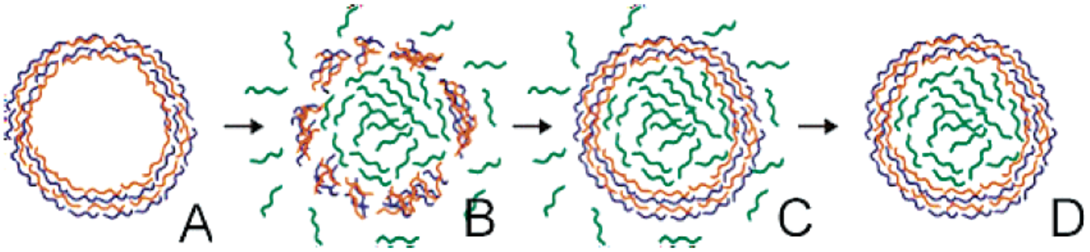

Figure 2. Scheme illustrating the preparation of "filled" microcapsules of the second type.

our experiments we prepared samples with 20−80 layers of adsorbed labeled PSS, which should lead to a surface density, ρ, in the range from 5×10^{-5} to 2×10^{-4} mol/m^2. These values were calculated by assuming that the surface density for a monolayer is constant and that the amount of adsorbed PSS grows linearly with the number of deposited layers.[18,29] As a result, each capsule contained up to a few picograms of PSS, depending on the template size and amount of assembled layers. With such a method, the concentration of encapsulated polyelectrolyte is approximately equal to $c = 3\rho/r_0$. The $MnCO_3$ particles were dissolved in ∼1 mol/L HCl after assembling of 7 layers in order to facilitate the process of core removal since shells with a thickness of more then 10 layers prevent ion penetration.[30] Core dissolution led to the formation of "double shell" structured capsules (Figure 1c). The inner shell formed by the PSS/Y^{3+} complex was not stable and was decomposed either by metal-ion complex agents (EDTA) or in salt solution. Yttrium ions were gradually expelled out of the outer stable shell formed by PSS/PAH while PSS molecules were released into the capsule interior (Figure 1d). Then the polyelectrolyte capsules were covered additionally with a number of layers varied in the interval from 1 to 13 to tune the final shell thickness, which, as a result, varied from 4 to 10 PSS/PAH bilayers.

The "filled" capsules of the second type were made from preformed "hollow" capsules.[31] The original "hollow" capsules were produced by a standard LbL assembly of 4 PSS/PAH bilayers on MF particles. MF particles coated with PSS/PAH multilayers were dissolved in ∼1 mol/L HCl, and MF oligomers were removed by washing, as described in ref 32. Then the encapsulation of polymer included several steps (Figure 2). The original "hollow" capsules (Figure 2a) were exposed to acetone/water mixture (1:1) to make the polyelectrolyte multilayer permeable for high molecular weight polymer,[9] and the PSS molecules were added to the mixture. The permeable state of the capsule shell allows the polymers to penetrate inside (Figure 2b). During the encapsulation process the PSS concentration was increased gradually to avoid an osmotic collapse of the microcapsules.[5] The initial concentration was 1 g/L and was doubled every hour. When the required concentration was reached, the mixture was diluted with water and the multilayer shells were assumed to return to an impermeable state (Figure 2c). After washing in pure water the capsules contain polymer solution (Figure 2d). With such a method, the concentration of encapsulated polyelectrolyte (before swelling) is approximately equal to the final concentration in the bulk.

Confocal Laser Scanning Microscopy. To scan the capsule shape and to measure the concentration of PSS inside the capsules, we used a commercial confocal microscope manufactured by Olympus (Japan) consisting of the confocal laser scanning-unit Olympus FV 300 in combination with an inverted microscope Olympus IX70 equipped with a high-resolution 100-oil immersion objective. The excitation wavelength was chosen according to the label Rhodamine (543 nm). The z-position scanning was done in steps of 0.2 μm. The diameters of the swollen capsules were determined optically with an accuracy of 0.4 μm. Concentration measurements were performed via the fluorescence 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.

Osmotic Pressure. The osmotic coefficient of the PSS solution was measured by means of vapor pressure reduction with a vapor pressure osmometer K-7000 (Knauer GmbH, Berlin). The osmometer was calibrated with commercial NaCl solutions before the amount of osmotically active ions for PSS solutions of various concentrations was measured.

Results and Discussion

3D confocal scanning showed that the capsules filled with PSS have spherical form. Immediately after the preparation the capsule sizes were close to the size of the templates used for their preparation. The capsules swell for at least several days before reaching their equilibrium size, so that all the measurements of the radius of the swollen capsules were performed 2 weeks after filling with PSS. Figure 3 (top) shows a typical confocal fluorescence image of the swollen capsules. The fluorescence intensity suggests a uniform concentration in the capsule's interior. The bright interior of the capsules did not change with time, and there was no fluorescence signal from water. This proves that the capsules are in the impermeable state. Typical fluorescence intensity profiles along the diameter of the capsules are presented in Figure 3 (bottom). One can see that the level of fluorescence from the wall is higher than from the interior, which could be connected with some adsorption of the inner polyelectrolyte.[18]

The size of the swollen capsules was determined as an average of 6−10 capsules. The variability in size of

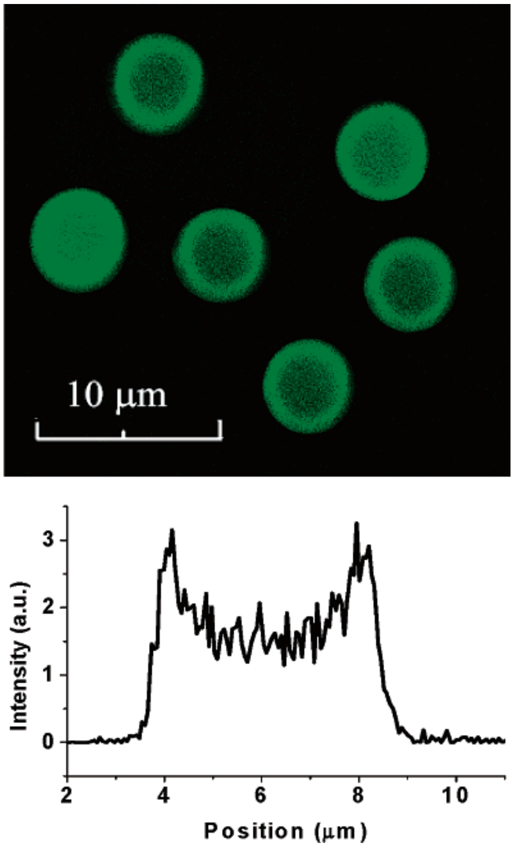

Figure 3. Confocal images of polyelectrolyte microcapsules filled with PSS (top) and typical fluorescence profile along the diameter of the capsule (bottom).

the similarly prepared capsules was always within the error of optical measurements. We found that the "filled" capsules are always larger than the original colloidal template and that their radius depends on the size of the original template, number of the bilayers in the shell, and the amount of encapsulated polyelectrolyte.

The measurements of the osmotic pressure of the bulk PSS solutions of different concentrations (up to 0.5 mol/L) have demonstrated that the amount of osmotically active ions is proportional to the concentration $c$of the polymer, which confirms the validity of eq 2. The value of the osmotic coefficient φ, given by the slope of this linear dependence, was $\varphi \sim 0.8$.

Figure 4 shows the typical dependence of the equilibrium radius on the shell thickness. Here, the results for the first type of "filled" capsules ($MnCO_3$ template) filled with PSS solutions of different concentrations and made on the particles of the same size $r_0 = 1.85 \pm 0.2$ μm are given. It was previously found[3,33] that the thickness of a PSS/PAH bilayer varies in the range 3−5 nm. To calculate the thickness of the shell with a known number of PSS/PAH bilayers, we used the average value of 4 nm, as before.[5,7] The radius of the swollen capsules decreases with the shell thickness and is larger for the capsules with higher concentration of the inner polyelectrolyte solution. We fitted these experimental results to eq 6 taking Young's modulus E as a fitting parameter and obtained the value of $E = 130 \pm 40$ MPa for the bottom and $E = 170 \pm 40$ MPa for the top curve presented in Figure 4. One can see that the agreement between the theoretical model and the experimental data is good, which hints that the continuum mechanics approach is applicable for a molecularly thin multilayer film.

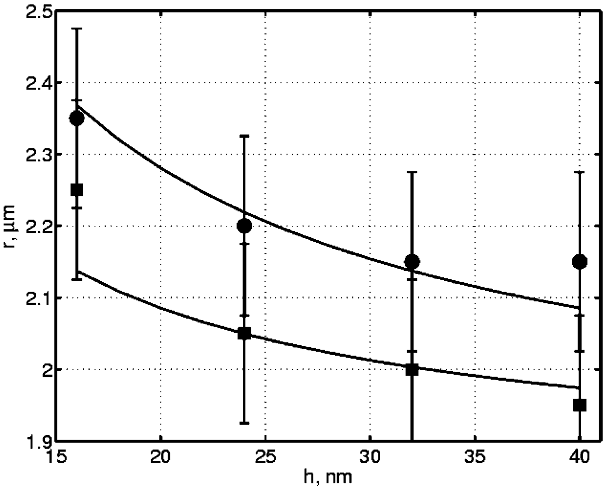

Figure 4. Radius of the swollen capsule made on the $MnCO_3$ template of radius 1.85 μm as a function of the shell thickness. Two concentrations are shown: 0.16 mol/L (squares) and 0.32 mol/L (circles). Solid curves corresponds to $E = 160$ MPa.

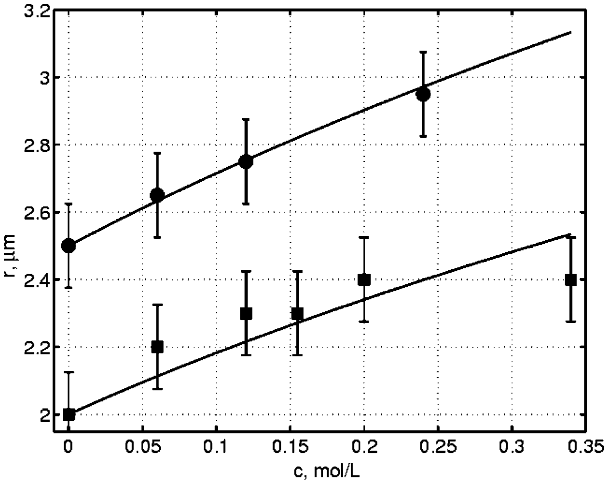

Figure 5. Radius of the swollen capsule as a function of monomer concentration in the inner solution. Fitting (solid curves) $E = 240$ MPa ($MnCO_3$ template, circles) and $E = 200$ MPa (MF template, squares).

The dependence of the equilibrium radius on the concentration of the inner polyelectrolyte, both the fitting curves and the experimental data, is shown in Figure 5. Here we present data both for the capsules of the first ($MnCO_3$ template) and the second (MF template) types. The capsules are made on the templates of different size, $r_0 = 2.5 \pm 0.2$ μm and $r_0 = 2.0 \pm 0.1$ μm, correspondingly. The shell was always composed of four PSS/PAH bilayers. From the fit of experimental data we obtained $E = 240 \pm 60$ MPa for the first type and $E = 200 \pm 30$ MPa for the second type of capsules.

One can conclude that our swelling experiment gives Young's modulus E of a PSS/PAH multilayer of the order of 100 MPa. This result supports our previous AFM studies[7] implying that we are dealing with an *elastomer*.[6] In other words, the value of Young's modulus of the PSS/PAH multilayer falls in the range typical for cross-linked rubbers. Such a mechanical behavior is probably due to strong interaction between polyanions and polycations in the PSS/PAH multilayer. Our model also shows that the final permeability of the shell to water is very important for the stabilization of the microcapsules, increasing the threshold of the buckling transition.[5]

To our knowledge, this work is the first attempt to study quantitatively swelling of polyelectrolyte microcapsules. The results obtained here might be applicable only for PSS/PAH multilayers. The mechanical properties and permeability of capsules made of different polyelectrolytes can have significantly different properties, depending on the amount of hydrophobic fragments, degree of cross-linking, etc.

We also note that the current method has fewer assumptions, when compared to the buckling transition and AFM measurements. The theory of buckling assumes that the capsule is highly permeable to water even on a short time scale of relaxation of the buckling deformation. The AFM experiment-based model postulates a priori spherical shape of the capsule (except in the contact regions), and conservation of the capsule volume. There is no need in these assumtions to describe capsule swelling: the capsule shape is always spherical and swelling is a slow process; i.e., the diffusion of water through the capsule shell takes place and does not affect the swelling.

The only remaining and absolutely crucial assumption is that the capsule deformations are elastic. This assumption is present in the theory of buckling[5] as well as in the model used to describe the AFM experiment[7] and is correct only if deformation is *completely reversible*. It is difficult to address the reversibility issue here, but to our previous knowledge,[7] stretching of a multilayer film is reversible and may be considered as elastic for relatively small deformations. Direct experimental verification of the complete reversibility for larger deformations is technically envolved and is currently in progress. We shall, however, mention that the theoretical model we use can be easily accommodated for the case of plastic deformations; in particular, it points out that the presence of nonelastic deformations would lead to underestimation of Young's modulus.

Finally, we would like to mention several other factors that are not included in our model but might affect the value of the Young's modulus. Partial condensation of the counterions on the polyelectrolyte shell or their escape outside the capsule would effectively reduce the osmotic pressure estimated from the concentration of polyelectrolyte chains. This would effectively lead to overestimation of Young's modulus.

Conclusion

We have provided a theoretical model, which relates Young's modulus, shell thickness, capsule radius, and concentration of the inner polyelectrolyte solution. The validity of the model was experimentally verified and confirms the applicability of the macroscopic continuum mechanics approach to polyelectrolyte multilayer microcapsules. Young's modulus for the molecularly thin PSS/PAH multilayer was found to be of the order of 100 MPa, which is close to the elasticity of an *elastomer*. Such a value reflects a high degree of local interactions between polyanions and polycations. Hence, for small deformations, the polyelectrolyte (PSS/PAH) multilayer resembles mechanically a cross-linked rubber material.

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