pH-Controlled Swelling of Polyelectrolyte Multilayer Microcapsules

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We explore quantitatively the effect of pH on the osmotically induced swelling of polyelectrolyte multilayer microcapsules filled with solutions of a strong polyanion. The shells of the microcapsules are composed of strong polyanions and weak polycations via a layer-by-layer electrostatic self-assembly. The equilibrium radius of the swollen capsules was found to be the same at low and neutral pH but increases at high pH, indicating the softening of the capsule shell. Such a softening probably reflects a decrease in the charge density of a polycation, which leads to a reduction in the number of ionic cross-links. The dramatic increase in size and softening of the capsules at high pH is accompanied by polyanion release from the capsule interior. No release was observed at low and neutral pH.

Introduction

Recently there has been much interest in studying polyelectrolyte multilayer microcapsules filled with neutral or charged polymer solutions. Such "filled" capsules represent a novel type of nanoengineered composite microstructures. They can be prepared by a variety of methods[1−7] and are potentially important in many areas of science and technology. For instance, they could serve as a new composite material with controlled stiffness[5] and allow one to mimic the advanced systems containing biopolymers.

The size, shape, and properties of filled capsules depend both on the multilayer shell[8,9] and on the polymer-containing interior.[4,5] Thus, the capsules filled with the polyelectrolyte could considerably swell due to excess osmotic pressure of the inner solution. The phenomenon of swelling was mentioned in earlier work.[3,5,6] However, the first attempt to quantify it was made only recently.[7] In this work, a theoretical model, which relates the size of the swollen capsules, concentration of the inner solution, thickness of the multilayer shell, and Young's modulus, was suggested. The model allowed us to design an appropriate swelling experiment, which, for an initial application of the approach, was done in pure water. One conclusion of this study was that Young's modulus of the multilayer shells falls in the range characteristic for *elastomers*.[10]

A typical mechanical behavior for elastomers reflects strong interactions between polyanions and polycations in the multilayer and indicates that we deal with a physically cross-linked network structure. Indeed, the high amount of ionic pairs present in the multilayers[11,12] might serve as the cross-linking units of such a network. If so, and if at least one polyelectrolyte in the multilayer is weak, the pH could be an important physicochemical parameter that will regulate ionic cross-link density and conformations and, therefore, affect the state of the multilayer shell and, as a result, the capsule swelling.

The effect of pH on the multilayers has been studied previously mostly as the factor controlling the growth,[13−15]

stability,[16] and permeability[17] of such systems, formation of microporous structures,[18] and in connection to the encapsulation of macromolecules.[2] The pH was recently found to play a role in controlling the stiffness of polyelectrolyte multilayer shells.[19] The stiffness of the multilayer shell was found to be largest at neutral pH and was getting much smaller in both acidic and alkaline solutions. It was suggested that the softening of the shells at high pH reflects a decrease in their Young's modulus. Low stiffness of the shells in the acidic solutions was explained in terms of enhanced permeability of the multilayer (larger pore formation). It was, however, difficult to draw a definite conclusion about Young's modulus of the multilayer films at low pH.

Here we study the effect of pH on the swelling of filled polyelectrolyte multilayer microcapsules. To our knowledge there have been so far no attempts to explore this phenomenon. As before,[4,5,7,19,20] we focus on the capsules with shells composed of layers of alternating polystyrene sulfonate (PSS) and polyallylamine hydrochloride (PAH). One reason for our choice is that this type of polyelectrolyte pair is composed of a strong polyanion (PSS), which should not respond to the pH changes, and a weak polycation (PAH) ($pK_a \sim 8.5$[21]), which state is expected to depend strongly on pH. Another is that this type of shell was used in the majority of previous studies, including those on mechanical properties.[7,9,19,20,22,23] We demonstrate that swelling of filled polyelectrolyte multilayer microcapsules is indeed pH-controlled. The capsules swollen in high-pH solution have much larger size than those immersed in low- and neutral-pH solutions. This indicates the softening of the multilayer shells, which is likely due to a decrease in charge density of polycations. The capsules swollen at low pH are of the same size as those immersed in neutral-pH solution, indicating the same number of ionic cross-links and the same value of Young's modulus.

Experimental Section

Materials. The fluorescent dye Rhodamine B isothiocyanate (RBITC), hydrion (alkaline) buffer solution, shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; $M_w \sim$ 70 000 g/mol) and poly(allylamine hydrochloride) (PAH; M_w

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∼ 70 000 g/mol) were purchased from Sigma−Aldrich Chemie GmbH, Germany. Citrate−sodium hydroxide buffer solution for acidic pH and the initiator potassium peroxodisulfate ($K_2S_2O_8$) for the radical polymerization were obtained from Merck GmbH, Germany. Hydrochloric acid and sodium chloride were purchased from Riedel-de Haën; Germany. All chemicals were of analytical purity or higher quality and were used without further purification.

To produce fluorescent PSS−RBITC for encapsulation we used a modification of the method published in ref 7. Briefly, labeled allylamine was first produced, afterward mixed with sodium styrenesulfonate (SS), and then copolymerized radically. 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 1% $K_2S_2O_8$, related to the monomer concentration, was added to this solution for the 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.

Suspensions of monodispersed weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of $r_0 = 1.89 \pm 0.10$ μm 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 MΩ/cm. The pH of the solutions with no added salt was measured by pH meter (inoLab Level 3, Germany) with an accuracy of ±0.5. We always kept the concentration of buffer solutions below 0.025 mol/L to avoid their influence on the shell and/or inner polyelectrolyte solution.

Methods: a. Capsule Preparation. The original polyelectrolyte multilayer microcapsules were produced at 0.5 mol/L NaCl (pH 6) by a 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 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 24.

The filled capsules were made from preformed "hollow" capsules. The encapsulation of polyelectrolyte included several steps. Briefly, the original "hollow" capsules were exposed to acetone/water mixture (1:1) to make a multilayer shell permeable for a high molecular weight polymer,[7] 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.[23] The initial 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 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. Afterward, washing cycles with pure water were carried out twice carefully to remove the excess PSS molecules.

b. Confocal Microscopy. To scan the capsule shape and to measure the concentration distribution of PSS inside the

capsules, we use a commercial confocal microscope manufactured by Olympus (Japan) consisting of the confocal scanning unit Olympus FV 300 in combination with an inverted microscope Olympus IX70 equipped with a high-resolution 60× oil (N.A. 1.45) immersion objective. The excitation wavelength was chosen according to the label Rhodamine (543 nm). The z-position scanning was done in steps of 0.02−0.05 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.

c. Osmotic Pressure. The osmotic coefficient of the PSS solution was measured by means of vapor pressure reduction with a vapor pressure osmometer, Osmomat 070 (Gonotec GmbH, Berlin). The osmometer was calibrated with commerical NaCl or glycerol solutions before the amount of osmotically active ions for PSS solutions of various concentrations was measured.

Results and Discussion

Immediately after the preparation of filled capsules, the capsule sizes were close to the size of the original "hollow" capsules. The capsules swell for at least several days before reaching their equilibrium sizes. It was observed that during the swelling process the filled capsules show an unusual random motion, which more or less resembles the phenomenon of Brownian motion. Moreover, it was also found that the length of free pass of such a random motion increases with the polyelectrolyte concentration. This random motion of filled capsules was significant during several days. After about 1 week, most of the filled capsules were eventually immobilized and the measurements of the equilibrium radius were performed.

Figure 1 shows a typical confocal fluorescence image of the filled capsules swollen at different pH. Three-dimensional (3D) confocal scanning showed that the filled capsules swollen at acidic and neutral pH always have a spherical form. Typical fluorescence intensity profiles along the diameter of filled capsules are presented in Figure 2. At low and neutral pH, fluorescence intensity suggests a strong adsorption of PSS at the (inner) wall and slightly nonuniform distribution of the PSS concentration in the central part of the capsules. Also included in Figure 2 are the results obtained for hollow capsules treated by fluorescently labeled PSS solution but without adding acetone (here we used only solutions of low concentration to avoid osmotic buckling of the hollow capsules). In this case, PSS molecules cannot be encapsulated but adsorb to the (outer part of the) shell, by making it fluorescent. This scenario is reflected in the corresponding spectrum, which shows that no fluorescence intensity is coming from the central part of fluorescently labeled hollow capsules. Essentially, the hollow capsules treated by fluorescently labeled PSS are the size of the original template.As is seen from Figure 3, the capsules swollen at alkaline solutions show two types of shape. One is spherical and the other is collapsed/broken (flowerlike) shape. The fraction of broken capsules increases with the concentration of encapsulated PSS (from 20−30% in ∼0.05 mol/L solution to roughly 40% in ∼0.14 mol/L solution). The level of fluorescence from the wall is again higher than from the interior, but adsorption peaks are smaller and often wider than in case of low and neutral pH
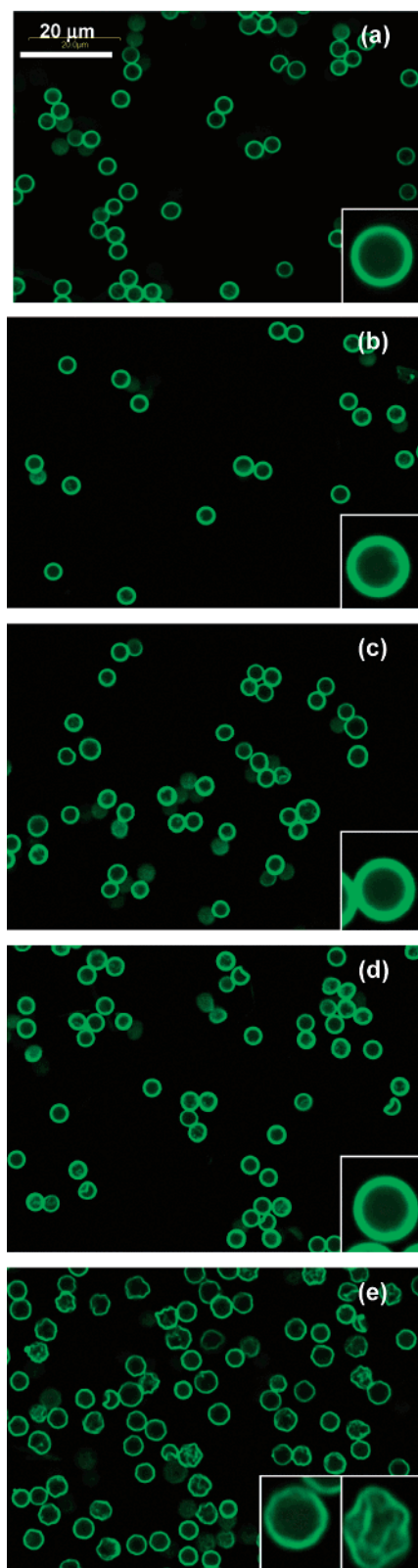
Swelling of Polyelectrolyte Microcapsules

J. Phys. Chem. B, Vol. 108, No. 24, 2004 **8163**

Figure 1. Confocal fluorescence images of the filled capsules swollen at different pH: (a) pH 3, (b) pH 5, (c) pH 7, (d) pH 8, and (e) pH 10. The polyelectrolyte concentration inside the capsule (C_{PSS}, moles per liter) of the filled capsules used was ~0.14 mol/L. The insets show higher magnification of the corresponding images.

Figure 2. Typical fluorescence intensity profiles along the diameter of the filled capsules swollen at acidic (green curve, pH 3) and alkaline (blue curve, pH 10) solutions. Red curve is a fluorescence profile measured for hollow capsules. C_{PSS} of filled capsules was ~0.14 mol/L.
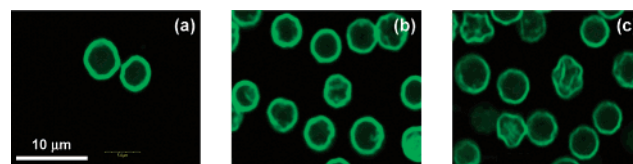
Figure 3. Confocal fluorescence images of several filled capsules swollen at pH 10. C_{PSS} values of filled capsules used were (a) ~0.05 mol/L, (b) ~0.09 mol/L, and (c) ~0.14 mol/L.

Figure 4. Equilibrium radius of the filled capsules swollen at different pH as a function of polyelectrolyte concentration inside the capsule (C_{PSS}, moles per liter). Fitting (solid curves) corresponds to $E = 120$ MPa (pH 3−8) and $E = 40$ MPa (pH 10). In the case of broken capsules swollen at high pH, the diameter was taken as an average size corresponding to several cross-sections of more than 10 capsules.

(Figure 2). We also remark that the central part of the capsules swollen at high pH show much more uniform distribution of concentration of encapsulated PSS. Another important point to note is that fill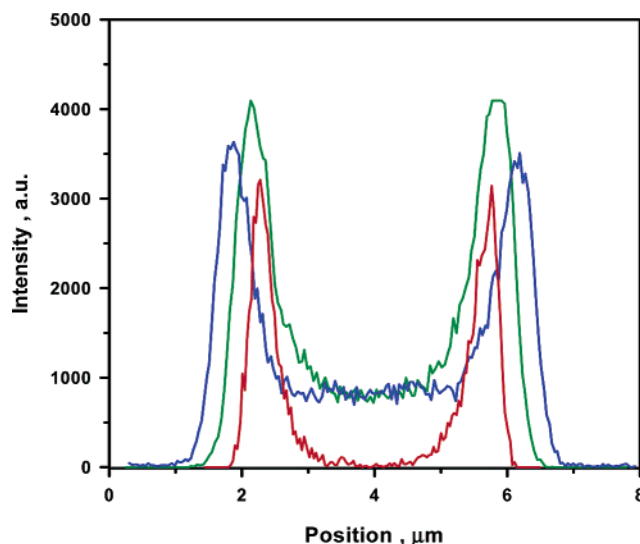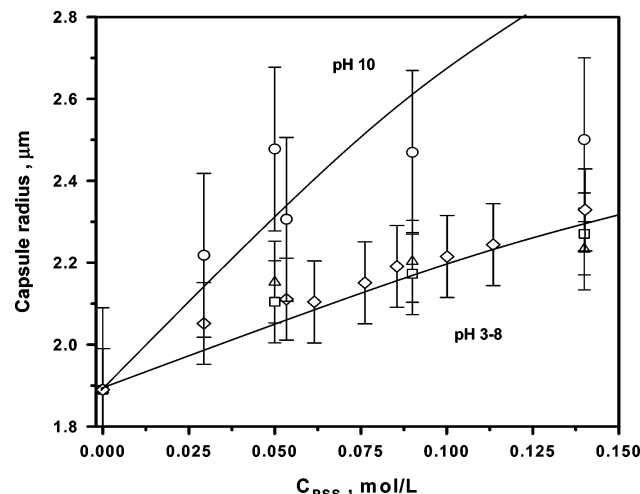ed capsules are somewhat nonadhesive at low and neutral pH. However, filled capsules swollen at pH 10 were quickly adhered to the surface of glass and did not move even after gentle shaking of the filled capsule suspensions. In all cases filled capsules were larger than the original colloidal template, and their radius was found to depend on the amount of encapsulated polyelectrolyte and pH.

Figure 4 shows the typical dependence of the equilibrium radius on the concentration of the inner polyelectrolyte. The
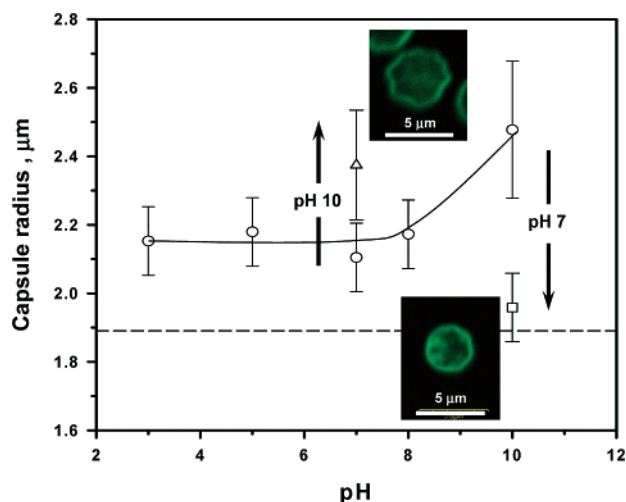
Figure 5. Equilibrium radius of the swollen filled capsules as a function of pH (○). C_{PSS} of filled capsules used was ~0.05 mol/L. The dotted line indicates the radius of the original template. (△) Swelling of filled capsules when the capsules swollen first in pure water were deposited in a high-pH solution. (□) Deswelling when the capsules swollen at high-pH solution were again immersed in pure water.

size of the swollen capsules was determined as an average of 6–10 capsules that were randomly selected. Around 10% of the capsules were too big or too small compared to an average value and thus were ignored in the analysis. In cases when the observed variability in size of the swollen capsules was within the error of optical measurements (low and neutral pH), we plotted the error bar, which reflects the optical error. At high-pH solutions we have measured the sizes of both types of filled capsules and took the average value. Specifically, the diameter of broken capsules was taken as an average of size corresponding to several cross-sections (see Figure 3). With such a method the actual error of measurements was larger than optical error. This is reflected in twice larger error bars we use in Figures 4 and 5. Nevertheless, we can see clearly the size of capsules swollen at high pH is much larger than that of capsules swollen at low and neutral pH (see Figure 1). We have also studied the diameter of hollow capsules exposed to the same buffer solutions. No dependence of the size of hollow capsules on pH was found within the accuracy of confocal measurements. The radius r of the swollen capsules increases with the amount of encapsulated PSS. It seems to remain the same at the buffer solutions of low and neutral pH, and in pure water, and is getting larger at high pH. To examine the significance of high pH more closely, the same set of data is reproduced in Figure 5 in the form of dependence of the equilibrium radius on pH. One can find that the radius of the swollen capsules is almost the same (but larger than that of the original template) at low and neutral pH and increases dramatically at high pH.

Figure 4 includes theoretical curves calculated from[7]

$$r = \frac{1}{2}r_0 \left(1 + \sqrt{1 + \frac{2\pi r_0}{h} \frac{(1-\nu)}{E} \varphi cRT} \right) \quad (1)$$

Here h is the shell thickness, E is Young's modulus, ν is Poisson's ratio ($\nu \approx 0.5$), c is the concentration of the PSS solution in the capsule before it swells, φ is the osmotic coefficient, R is the universal gas constant, and T is temperature. Here the measurement of the osmotic pressure of the bulk PSS solutions of different concentrations has demonstrated that in all solutions the amount of osmotically active ions is proportional to the concentration c of the polymer. The value of the

osmotic coefficient φ, given by the slope of this linear dependence, was ~0.8. It was previously found[9,25] that the thickness of a PSS/PAH bilayer varies in the range of 3–5 nm. Although the adsorption[15] and pore formation[18] studies allow one to suggest that the polyelectrolyte multilayers might swell in both acidic and alkaline solutions, there have been no direct measurements of the change in the thickness of the multilayers prepared at neutral pH and then immersed in the low- and high-pH solutions. Therefore, to calculate the thickness of the shell with a known number of PSS/PAH bilayers we used the average value of 4 nm obtained at neutral pH, as before.[20,23] If there were swelling of the shell, we would then have overestimated the value of Young's modulus. We fitted our experimental results to eq 1, taking Young's modulus E as an adjustable parameter, and obtained the value of $E = 120 \pm 20$ MPa for acidic and neutral pH and $E = 40 \pm 10$ MPa for high pH solutions. One can see that the fit is quite good. The values of Young's modulus are slightly larger than those obtained in the recent AFM experiment. This reflects the fact that the model used to describe the AFM force experiment gives the *lower* limit of Young's modulus,[20] while the theory of swelling allows us to extract the *upper* limit of Young's modulus.[7] It has to be stressed, however, that due to the possible counterion ion leakout from the capsule, the effective value of φ can be smaller than in the bulk experiment.

The experimental data and values obtained from fitting can be explained as follows. At acidic and neutral pH we obtain minimum swelling and largest Young's modulus, which suggests that the multilayer shells are at the maximum of their stiffness. The values of Young's modulus are consistent with the previous results obtained in pure water.[7,20] This result seems to be very reasonable, taking into account that both shell-forming polyelectrolytes, PSS and PAH, are fully ionized at low and neutral pH. The significant swelling of the capsules at high pH is because under these conditions Young's modulus of the multilayer film considerably decreases. This pH trend can be rationalized in the following manner. The PAH is a weak polycation, so that its linear charge density is tunable by simple pH adjustment. At high pH the charge density of PAH decreases (ammonium groups become deprotonated), which could both cause a change of PAH conformation and reduce the density of ionic cross-links. As a result Young's modulus gets much smaller.

One of the crucial assumptions of the theoretical model used is that the shell deformation is elastic. This assumption is also present in the theory of osmotic buckling[23] of the capsules as well as in the model describing deformations of capsules in the AFM experiment.[20] To our previous knowledge, stretching of the multilayer shell is elastic and reversible for relatively small deformations.[20] This is correct only if deformation is completely reversible. Another assumption is that the capsule shell is permeable to the solvent (on a time scale larger than the characteristic diffusion time) but impermeable for encapsulated polymer. A similar assumption was used in the early work.[23] Direct experimental verification of the complete reversibility for larger deformations is technically involved and is currently in progress. Here, however, we have performed a simple deswelling and consequent swelling test. The capsules swollen at high pH were immersed into water and kept for 5 days. It was observed the filled capsules swollen at high pH were shrunk almost to the radius of original hollow capsules. Accordingly, the fluorescence intensity from the interior slightly decreased. These indicate both the reversibility of deformation and polymer release. In opposite, the filled capsules swollen first in pure water

Swelling of Polyelectrolyte Microcapsules

J. Phys. Chem. B, Vol. 108, No. 24, 2004 **8165**

were deposited to a high-pH solution and also kept for 5 days. These capsules start to swell further and reach the size typical for the capsules swollen at high pH from the beginning. These results (see Figure 5) are consistent with the assumption that the deformations are elastic and reversible. One can also suggest that we are always in the elastic regime of stretching of the multilayer, because its rupture likely occurs before plastic deformations come into play.

We have reported before that the PSS/PAH shell is highly permeable for the PSS at low pH but not at neutral and high pH.[19] Our previous conclusion was based on the observation of encapsulation of the PSS into the preformed multilayer shell. The same conclusion, but concerning the permeability of PSS/PAH multilayers for a neutral polymer, was made before.[2] Our results suggest that, for a charged polymer, encapsulation in and release from are essentially two different processes. Indeed, here we do not detect any release of PSS from the capsules at low pH but observe it at high pH. The release at high pH can partly be explained by the increase in the size of nanopores due to significant stretching of the multilayer shells and their ruptures. This hypothesis cannot, however, explain the absence of release at low pH. One can speculate that the absence of release might be connected with the fact that the inner polyelectrolyte has a charge opposite to that of the shell (four-bilayer shell is positively charged at low and neutral pH), providing a stable electrostatic configuration. In contrast, at high pH, the multilayer shell is charged negatively, because the charge density of PAH decreases. Therefore, the shell and the inner polymer likely have charges of the same sign, which might make such a configuration unstable. Another reason for the absence of PSS release from the capsules might be connected with the inner thick adsorption layer, which might block the nanopores of the multilayer shell. This subject, however, is beyond the scope of the present paper and will be discussed elsewhere.

Conclusion

Thus, the results presented extend our early work.[7,19] They show that swelling of polyelectrolyte multilayer microcapsules is a pH-controlled process. This confirms that the elastomerlike mechanical response of the multilayer shells is, at least partially, due to ionic cross-links. Therefore, the stiffness of the shells (Young's modulus) can be adjusted by variation of pH. For PSS/PAH multilayers in particular, this can be done by increasing the pH. This conclusion strongly supports the results of our recent AFM experiment.[19]

There is also an important new conclusion that the pH changes do not influence the stiffness (Young's modulus) of the multilayer films in the case when both polyelectrolytes are fully ionized. In particular, Young's modulus of PSS/PAH multilayer used here remains the same in acidic and neutral solutions.

Finally, by studying microcapsule swelling we have obtained some results that may add a new dimension to the problems of encapsulation/release and permeability of multilayer shells for polyelectrolytes. We found that the encapsulation of strong polyelectrolyte is not a reversible process. The release of inner polyelectrolyte seems to be pH-dependent and indicates that the charge of the shell and of the inner polyelectrolyte (as well as its distribution inside the capsule) may be important in controlling the release of encapsulated material.

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