

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7902358>

# Effect of pH and Salt on the Stiffness of Polyelectrolyte Multilayer Microcapsules

ARTICLE *in* LANGMUIR · APRIL 2004

Impact Factor: 4.46 · DOI: 10.1021/la049934h · Source: PubMed

---

CITATIONS

66

---

READS

35

2 AUTHORS, INCLUDING:



[Olga I Vinogradova](#)

Russian Academy of Sciences

**111** PUBLICATIONS **3,382** CITATIONS

SEE PROFILE

# Effect of pH and Salt on the Stiffness of Polyelectrolyte Multilayer Microcapsules

Valentin V. Lulevich<sup>†,‡</sup> and Olga I. Vinogradova<sup>\*,†,‡</sup>

Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany, and  
Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry,  
Russian Academy of Sciences, 31 Leninsky Prospect, 119991 Moscow, Russia

Received January 8, 2004. In Final Form: January 23, 2004

By using a combination of atomic force and confocal microscopy, we explore the effect of pH and salt on the stiffness of polyelectrolyte microcapsules with shells composed of strong polyanions and weak polycations. The stiffness of the capsules was found to be largest in water. It decreases slightly with added salt and gets much smaller both in acidic and in alkaline solutions. The moderate softening of the capsules in electrolyte solutions indicates that even high salt concentration does not significantly dissociate polyelectrolytes in the multilayer. The dramatic softening of the capsules at high pH probably reflects a decrease in the charge density of a polycation, which leads to a reduction in the number of ionic cross-links. In contrast, low stiffness of the capsules in acidic solutions seems to be connected mostly with the enhanced permeability of the multilayer shell.

## 1. Introduction

Recently there has been much interest in studying polyelectrolyte multilayer microcapsules.<sup>1</sup> 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<sup>2–4</sup>), with the subsequent removal of the latter, and represent a convenient system for basic and applied studies. A novel and promising area of research is connected with the investigation of mechanical properties of such microstructures.<sup>5–7</sup> Mechanical properties of the capsules are potentially important for a variety of applications, such as drug delivery, catalysis, and biotechnology. At a more fundamental level, by studying them one might gain a better understanding of molecularly thin multilayers and of the ESA technique in general.

We have recently suggested two novel quantitative approaches to probe the elastic properties of polyelectrolyte multilayers forming the capsule shell. The first method is based on studying the swelling of the microcapsules filled with the solution of strong polyelectrolyte.<sup>8</sup> The second approach, motivated by earlier studies,<sup>7,9</sup> involves measuring the deformation of microcapsules under applied load using an atomic force microscope (AFM).<sup>10</sup> Both

methods have given the value of Young's modulus of the polyelectrolyte multilayer in water of the order of 1–100 MPa (depending on preliminary chemical treatment) which falls in the range characteristic for *elastomers*.<sup>11</sup> In other words, we found that multilayers represent a material comparable to cross-linked rubbers.

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<sup>12,13</sup> might serve as the cross-linking units of such a network. If so, the salt concentration could be an important physicochemical parameter which will regulate the strength of ionic bonding and, therefore, affect the state of the multilayer and its mechanical properties. Beside that, if at least one polyelectrolyte in the multilayer is weak, the pH can be used to control the ionic cross-link density and conformations and, therefore, should affect the stiffness of the capsules and Young's modulus of multilayer films.

The effect of salt and pH on the multilayers has been studied previously. These parameters were mostly explored as the factors controlling the growth,<sup>4,14,15</sup> stability,<sup>16</sup> and permeability<sup>17</sup> of such systems, formation of microporous structures,<sup>18</sup> and in connection to the encapsulation of macromolecules.<sup>19,20</sup> To our knowledge, there

\* To whom correspondence should be addressed. E-mail: vinograd@mpip-mainz.mpg.de.

<sup>†</sup> Max Planck Institute for Polymer Research.

<sup>‡</sup> Russian Academy of Sciences.

(1) Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, E.; Budde, A.; Möhwald, H. *Colloids Surf., A* **1998**, *137*, 253–266.

(2) Decher, G. *Science* **1997**, *277*, 1232–1237.

(3) Knoll, W. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 137–143.

(4) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319–348.

(5) Gao, C.; Donath, E.; Moya, S.; Dudnik, V.; Möhwald, H. *Eur. Phys. J. E* **2001**, *5*, 21–27.

(6) Bäuml, H.; Artmann, G.; Voigh, A.; Mitlöhner, R.; Neu, B.; Kieseewetter, H. *J. Microencapsulation* **2000**, *17*, 651–655.

(7) Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. *J. Phys. Chem. B* **2003**, *107*, 2735–2740.

(8) Vinogradova, O. I.; Andrienko, D.; Lulevich, V. V.; Nordschild, S.; Sukhorukov, G. B. *Macromolecules* **2004**, *37*, 1113–1117.

(9) Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. *Macromolecules* **2003**, *36*, 2832–2837.

(10) Lulevich, V. V.; Andrienko, D.; Vinogradova, O. I. *J. Chem. Phys.* **2004**, *120*, 3822–3826.

(11) Shackelford, J. F.; William, A.; Juns, P. *Materials Science and Engineering Handbook*, 2nd ed.; CRC press, Boca Raton, FL, 1994.

(12) Lösche, M.; Schmitt, J.; Decher, G.; Bouwman, W. G.; Kjaer, K. *Macromolecules* **1998**, *31*, 8893–8906.

(13) Lowack, K.; Helm, C. A. *Macromolecules* **1998**, *31*, 823–833.

(14) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153–8160.

(15) Shiratori, S.; Rubner, M. *Macromolecules* **2000**, *33*, 4213–4219.

(16) Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J. *Langmuir* **1996**, *12*, 3675–3681.

(17) Antipov, A. A.; Sukhorukov, G. B.; Möhwald, H. *Langmuir* **2003**, *19*, 2444–2448.

(18) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017–5023.

(19) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Möhwald, H. *Macromol. Rapid Commun.* **2001**, *22*, 44–46.

(20) Ibarz, G.; Dähne, L.; Donath, E.; Möhwald, H. *Adv. Mater.* **2001**, *13*, 1324–1327.

have been no attempts to explore their role in controlling the stiffness of polyelectrolyte multilayer microcapsules.

Here we use the AFM approach in combination with confocal microscopy to study the effect of pH and salt on the mechanical properties of polyelectrolyte multilayer microcapsules. 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) and weak polycation (PAH). Another is that this type of shell was used in the majority of previous studies, including those on mechanical properties.<sup>1,5,8,10,21</sup> We show that both the electrolyte and deviations of the pH from neutral lead to a softening of the capsules. Depending on physicochemical conditions this softening is due to either an increase in the permeability of the capsules (low pH) or a decrease in Young's modulus of the multilayer (high pH, salt).

## 2. Experimental Section

**a. Materials.** The fluorescent dye Rhodamine B isothiocyanate (RBITC), hydron (alkaline) buffer solution, shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS;  $M_w \sim 70\,000$  g/mol) and poly(allylamine hydrochloride) (PAH;  $M_w \sim 70\,000$  g/mol) were purchased from Sigma-Aldrich Chemie GmbH, Germany. Citrate–sodium hydroxide buffer solution for acidic pH was purchased from Merck, Germany. Hydrochloric acid (HCl) and sodium chloride (NaCl) 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 dye PSS–RBITC for a permeability test, we used a method published in ref 8. Briefly, 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 dissolved in ethanol. The mixture was stirred for 4 h at room temperature. Afterward styrenesulfonate was added in an amount corresponding to a label grade of about 200 monomer equivalents. 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. The remaining PSS was chopped into small parts and washed with ethanol until no more color could be observed in the filtrate.

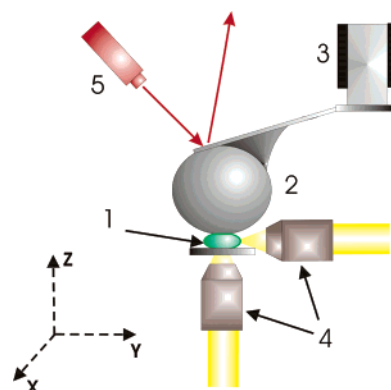
Suspensions of monodispersed weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of  $R_0 = 2.0 \pm 0.1\ \mu\text{m}$  were purchased from Microparticles GmbH (Berlin, Germany).

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 $\Omega$ /cm. The pH was measured by pH meter (InoLab, Germany) with the accuracy of  $\pm 0.5$ .

**b. Methods. Capsule Preparation.** The capsules were produced at 1 mol/L NaCl (pH 6) by LbL assembly of four pairs of poly(styrenesulfonate) (PSS) and poly(allylamine) (PAH) on MF particles. After each adsorption step, the system was rinsed with pure water to remove excess polymer and salt. MF particles coated with multilayers were dissolved in HCl at pH 1.2–1.6, and MF oligomers were removed by washing, as described in ref 22.

Before measurements at low and high pH, the capsules were exposed to acidic and alkaline solutions for 1 h. Treatment by salt solution before measurements was for at least 24 h.

**Atomic Force and Confocal Microscopy.** The schematic of the experimental setup is shown in Figure 1. Briefly, load (force) vs deformation curves were measured with the Molecular Force Probe device (MFP) 2D (Asylum Co., Santa Barbara, CA), which has a nanopositioning sensor. This sensor can correct piezo ceramic hysteresis and creep of the AFM piezotranslator. For



**Figure 1.** Schematic of the experimental setup: (1) capsule, (2) glass sphere, (3) piezotranslator, (4) confocal microscope objectives, and (5) laser.

force measurement we used V-shaped cantilevers (Micromash, Estonia, spring constants  $k = 2.5$  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.<sup>10</sup> Here we performed the measurements at intervals of piezotranslator speed from 2 to 20  $\mu\text{m/s}$ . The result of measurement represents the deflection  $\Delta$  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.<sup>7</sup> 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  $\mu\text{m}$  and from the AFM load vs deformation curves (as in ref 7). The relative deformation  $\epsilon$  of the capsule was then calculated as  $\epsilon = 1 - H/(2R_0)$ , where  $H$  is the minimum sphere/substrate separation.<sup>7,10</sup>

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 deformed capsules the high-resolution (60 $\times$ ) bright (NA = 1.45) immersion oil objective was used. The  $z$ -position in confocal scanning was done in steps of 0.02–0.05  $\mu\text{m}$ . High resolution and contrast of the confocal images was achieved due to use of the fluorescent dye PSS–RBITC taken at the concentration of  $\sim 10^{-6}$  mol/L.

As was reported before<sup>7</sup> the capsules reveal some variability in behavior. Therefore, to get reliable results we have performed several (at least 5–10) experiments for each solution. Typically 5–10% of the capsules were too stiff (due to the MF fragments of the initial templates remaining in the shells) or too soft (being broken during the template dissolution process) compared with the average value in the series. In these cases we have not observed the typical (quantitatively) force curves. These data were ignored in our analysis.

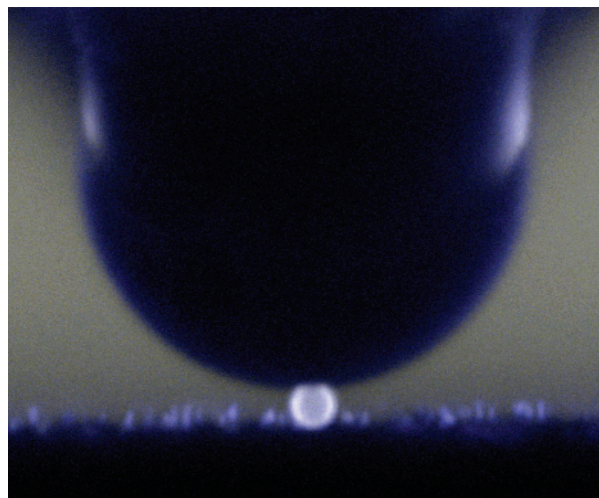
## 3. Results

**a. Deformation Profiles and Images of Confocal Scanning.** The typical 3D confocal scanning image of a capsule confined between a sphere and a substrate ( $\epsilon = 0.2$ ) is shown in Figure 2. To make this image, the AFM head and the substrate were rotated around the objective of the confocal microscope through 90°. The scanning suggests that the free area of slightly compressed capsules has spherical shape, confirming the assumptions made in ref 10.

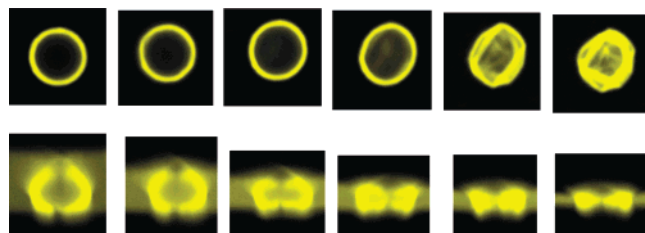
Figure 3 shows the images of confocal scanning at different stages of deformation (directions  $XY$  and  $Z$  in Figure 1) obtained in normal mode (AFM head is above the confocal microscope objective). The top images were created in  $XY$  confocal mode, and the microscope was

(21) Sukhorukov, G. B. In *Novel methods to study interfacial layers*; Mobius, D., Miller, R., Eds.; Elsevier: Amsterdam, 2001; pp 384–414.

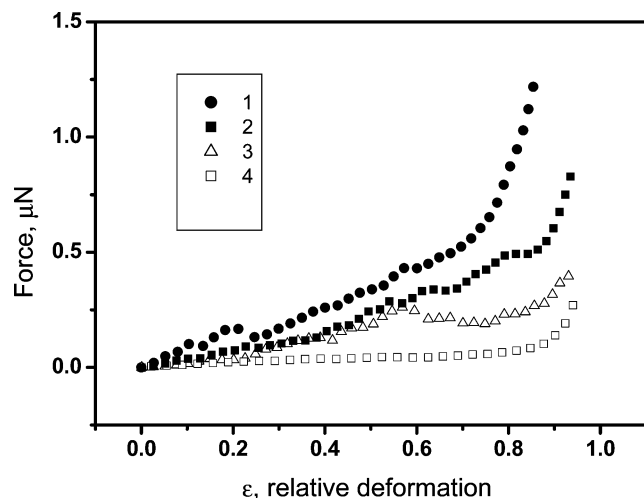
(22) Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Möhwald, H. *Polym. Adv. Technol.* **1998**, 9, 759–767.



**Figure 2.** The confocal image of the polyelectrolyte microcapsule compressed between a glass sphere and a glass substrate (relative deformation  $\epsilon = 0.2$ ) in the AFM force experiment.



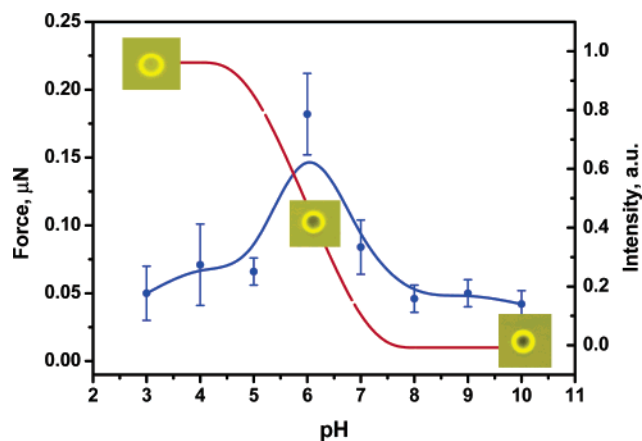
**Figure 3.** Typical confocal images of capsules obtained on different stages of deformation. From left to right  $\epsilon = 0, 0.1, 0.25, 0.5, 0.75$ , and  $0.9$ .



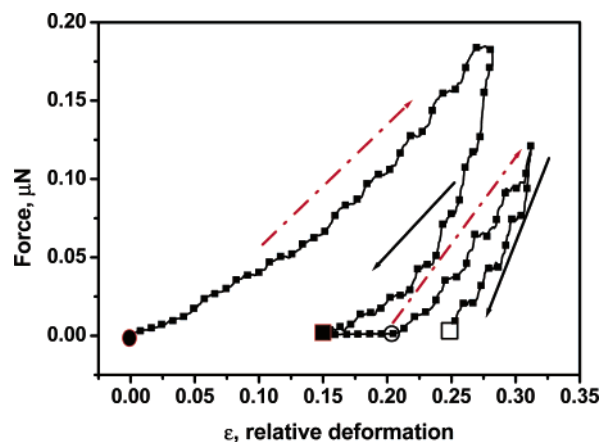
**Figure 4.** Typical load-deformation curve for capsules in water (1), salt (2), acidic, pH 3, solution (3), and alkaline, pH 10, solution (4).

focused onto the equator of the deformed capsule. To make side images (bottom), the 3D scanning mode was used. Figure 4 shows typical load vs deformation profiles for PSS/PAH capsules measured in different physicochemical conditions. By analyzing these profiles and images in water, we have confirmed the conclusions made before.<sup>7,9,10</sup> Similar behavior was found in salt solutions, although the capsules become slightly softer. The capsules seem to get very soft both at low and high pH.

**b. Role of pH.** The load at a fixed relative deformation  $\epsilon = 0.2$  for PSS/PAH capsules measured in normal, acidic, and alkaline solutions is shown in Figure 5. Both decrease



**Figure 5.** Force at a fixed relative deformation,  $\epsilon = 0.2$ , (blue line) and the intensity of fluorescence for PSS-RBITC (red line) as a function of pH.



**Figure 6.** Typical load-deformation curves for the capsules in acidic solutions (pH 4). Two loading/unloading cycles, 1st (the beginning and the end of cycles are represented by filled symbols) and 51st (the beginning and the end of cycles are represented by open symbols), for the same piezo displacement (of 1.6 microns) are shown. The position of the curve between the end of the 1st cycle and beginning of the 51st cycle corresponds to the consequent loading/unloading, which was not recorded. Measurements were performed at the driving speed of 5  $\mu\text{m/s}$ .

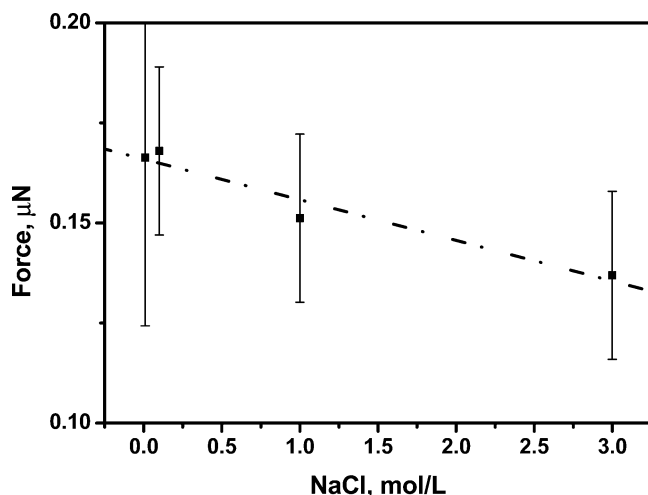
and increase in the pH value lead to a dramatic softening of the capsules.

By analyzing the original load vs deformation profiles at small deformations at neutral and high pH, we found that the deformation is always completely reversible. The profiles do not depend on the driving speed, and the loading/unloading hysteresis is small. We have also always observed zero pull-off force. In other words, at high pH qualitatively the capsules behave like in water systems,<sup>7,10</sup> although they are getting much softer.

By performing the same analysis of the small deformation force profiles obtained at low pH, we found that the deformation is often only partially reversible. This is seen in Figure 6, which shows the typical first and later cycle of loading/unloading. We have also detected a sensitivity to the driving speed in the interval used. The capsules are getting stiffer with an increase in the driving speed. Another difference from the behavior at low and neutral pH is that the loading/unloading hysteresis is relatively high.

Since these differences might be caused by pore formation<sup>9,18,19</sup> and fast drainage of the inner solution during the AFM force experiment, we have explored the perme-





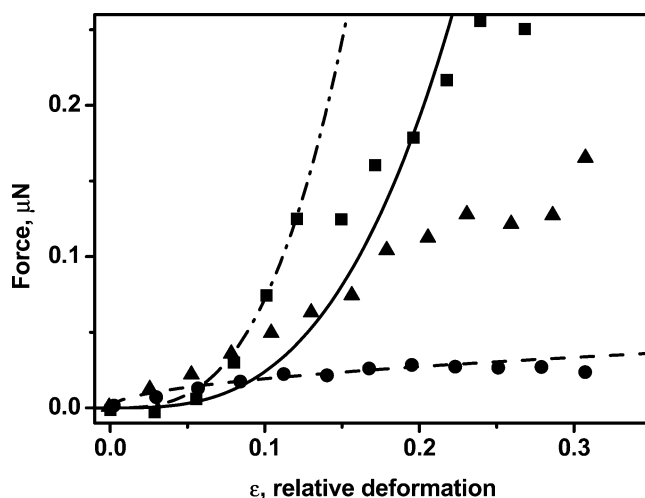
**Figure 7.** Dependence of the force at a fixed relative deformation,  $\epsilon = 0.2$ , on the concentration of NaCl.

ability of the capsules for a test PSS–RBITC dye solution as a function of pH. The capsules were exposed to the dye solution for several hours, and then the intensity of fluorescence from the capsule interior was measured. These data are included in Figure 5 (right-hand scale) together with the typical confocal images of the capsules made in water and at pH 3 and 10. It can be seen that the capsules are permeable to large PSS–RBITC molecules at low pH and that there is no diffusion into the capsules at high pH. It has been reported before<sup>19</sup> that at low pH the PSS/PAH multilayer is permeable for dextran (neutral polymer) molecules. Our permeability results suggest that the PSS/PAH capsules at low pH are “open” also for charged molecules of PSS.

**c. Role of Salt.** Figure 7 shows the force at a fixed relative deformation  $\epsilon = 0.2$  measured at different salt concentrations. The data suggest that some softening of the capsules takes place. However, the measured values are of the same order of magnitude, even at 3 mol/L NaCl. This indicates that even high salt concentration does not completely dissociate polyelectrolytes in the multilayers. By analyzing the load vs deformation profiles at small deformations, we have made exactly the same observations as for neutral and high pH. We have also found that there is no difference between the permeability of the capsules for PSS–RBITC molecules in water and NaCl solutions in the range of the concentrations used. Therefore, we do not confirm the conclusions of ref 20 about the enhanced permeability of PSS/PAH capsules for polymers in NaCl solutions. However, it has to be mentioned that all the measurements of ref 20 were done with PAH, which might behave differently from PSS we use here.

#### 4. Discussion

The essential observation is this: The polyelectrolyte multilayer microcapsules in water (i.e., without added salt and at neutral pH) seem to be at the maximum of their stiffness. Why and what does this mean? The softening of microcapsules can be caused by two extreme situations. One can be connected with the softening of the multilayer itself.<sup>20</sup> Such a softening can be due to weakening of the ionic cross-links, reorganization of polyelectrolytes in the multilayers, their conformation changes, swelling, etc. Despite these changes, the nanopore structure of the original multilayer can remain the same and not affect the drainage of water through the shell in the AFM experiment. Another might be connected with the enhanced permeability (connected, for instance, with



**Figure 8.** Three types of the load-deformation curves at small relative deformations: squares illustrate the behavior of the impermeable capsules, circles correspond to the situation of permeable capsules, and triangles correspond to the intermediate situation. Dash-dotted and solid curves represent a fit to eq 1 (both correspond to an impermeable capsule). Dashed curve is a fit to eq 2 (a permeable capsule). The data corresponding to the intermediate situation were not fitted.

the formation of larger pores), allowing the inner solution to easily drain out even in the short time of the AFM force experiment.<sup>18,19</sup> These two extreme situations can be described by two theoretical models providing relative deformations are small.

If we can neglect water drainage through the shell, the dependence between force and relative deformation is given by<sup>10</sup>

$$F \sim 4\pi EhR_0\epsilon^3 + \frac{\pi Eh^2\epsilon^{1/2}}{2(2^{1/2})} \quad (1)$$

where  $E$  is Young's modulus of the multilayer and  $h$  is its thickness.

If the shell is permeable to water, then the deformation of stretching can be ignored, and the force would be entirely due to bending of the shell near the contact line. In this case as a very rough estimate of the bending force, one can simply use the bending contribution to eq 1

$$F \sim \frac{\pi Eh^2\epsilon^{1/2}}{2(2^{1/2})} \quad (2)$$

These two models predict different functional dependence of force on relative deformation, so that it is intuitively clear which one should be applied in the limiting experimental situations. It is also clear that in the general case the data could be confined between the predictions of the models described by eqs 1 and 2. To examine this more closely, the small-deformation regions for the typical experimental situations are given in Figure 8. We have fitted these load-deformation profiles to eq 1 and eq 2 taking Young's modulus,  $E$ , as a fitting parameter. The value of  $h$  was calculated from the number of PSS/PAH bilayers in the shell and the thickness of one bilayer. The values reported for a bilayer thickness prepared according to the procedure we used here, and kept in water, vary in the range  $\sim 3$ – $5$  nm.<sup>1,22</sup> It was suggested that a high concentration of salt can cause some (up to  $\sim 10\%$ ) swelling of the multilayer.<sup>23</sup> Although the adsorption<sup>15</sup> and pore formation<sup>18</sup> studies allow one to suggest that the polyelectrolyte multilayers might swell both in acidic and in

alkaline solutions, there have been no direct measurements of the change in the thickness of the multilayers prepared at the neutral pH and then immersed at the low and high pH solutions. Therefore, for a bilayer thickness in all the solutions we use the average value of 4 nm obtained at neutral pH, and take  $h = 16$  nm. If there were swelling, we would then have overestimated the value of Young's modulus. The fitting curves are shown in Figure 8.

The data obtained from fitting can be summarized and explained as follows. At neutral pH the Young's modulus was always confined to values between 70 and 100 MPa (solid and dash-dotted curves in Figure 8, correspondingly). These values are consistent with the previous results.<sup>8,10</sup> The effect of salt on the multilayer is that of softening. Young's modulus slightly decreases, but remains of the same order as in pure water, and in a 3 mol/L NaCl solution reaches the values of 40–80 MPa. This indicates that the PSS/PAH multilayers cannot be deconstructed at high ionic strength. In other words, salt does not reverse the polyelectrolyte association. Of course, this conclusion is drawn only for 1:1 electrolyte. The effect of multivalent ions could be different. This work is currently in progress and will be published elsewhere.

Young's modulus of the multilayer film considerably decreases at high pH. Its value at pH 10 is of the order of 10–20 MPa. This pH trend can be rationalized in the following manner. At neutral pH the polycation chains are fully ionized, leading to a high amount of ionic cross-links in the multilayer. However, 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.

We cannot draw a definite conclusion about Young's modulus at low pH, mostly because a considerable set of the deformation profiles have revealed a qualitative behavior confined between that predicted by eq 1 and eq 2 (triangles in Figure 3). This indicates that some stretching of the free area of the capsules can take place despite the presence of the large pores. Our preliminary analysis suggests that Young's modulus might remain

the same as in pure water or even increase (despite the fact that the capsule itself is getting softer). However, if we assume that the pore formation is accompanied by an increase in the multilayer thickness,<sup>18</sup> one can speculate that Young's modulus could slightly decrease. Therefore, at low pH we observe a softening of the capsules, which is due to the pore formation<sup>18,19</sup> and fast drainage of the inner solution but is likely not connected with the decrease in Young's modulus. This result seems to be very reasonable, taking into account that the PSS is a strong polyanion, so that it remains fully ionized at low pH.

In summary, our experiment has shown that the stiffness of polyelectrolyte microcapsules is determined both by elastic properties of the shells and by their permeability. We have also demonstrated that the mechanical behavior of the multilayer films is that of an *elastomer* in all the intervals of parameters used. The observed dependence of Young's modulus on pH and salt is consistent with the idea of ionic cross-links. One can surmise that the decrease in Young's modulus at high pH and with salt reflects a reduction in the number of ionic cross-links caused by physicochemical conditions.

One can also suggest that our results may be useful for understanding the stability of the multilayers. Indeed, although the ESA technique is based on electrostatic attraction between positively and negatively charged species, the factors responsible for the multilayer stability are not entirely clear. Polyelectrolyte adsorption under the normally chosen conditions is nearly irreversible,<sup>14,16</sup> so it is considered that the multilayer films do not represent equilibrium structures.<sup>4</sup> Despite that, the ESA films usually show good aging properties and long-term stability in various solutions. The reasons for such a stability are not entirely clear. One can speculate that it can be attributed to the same type of ionic cross-linking as that responsible for an elastomer-like mechanical behavior, which reduces the mobility of the polyelectrolyte chains, thus freezing the structure of the adsorption layers. This question is however beyond the scope of the present paper and will be discussed elsewhere.

**Acknowledgment.** We thank D. Andrienko and G. B. Sukhorukov for helpful discussions and S. Nordschild for capsule preparation.

LA049934H

(23) Sukhorukov, G. B.; Schmitt, J.; Decher, G. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 948–953.