

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6894307>

Adhesion of Spherical Polyelectrolyte Brushes on Mica: An in Situ AFM Investigation

ARTICLE *in* LANGMUIR · SEPTEMBER 2006

Impact Factor: 4.46 · DOI: 10.1021/la060933u · Source: PubMed

CITATIONS

21

READS

28

4 AUTHORS, INCLUDING:



Matthias Ballauff

Helmholtz-Zentrum Berlin

434 PUBLICATIONS **13,688** CITATIONS

SEE PROFILE



Thomas Schimmel

Karlsruhe Institute of Technology

188 PUBLICATIONS **2,154** CITATIONS

SEE PROFILE

Adhesion of Spherical Polyelectrolyte Brushes on Mica: An in Situ AFM Investigation

Hartmut Gliemann,^{†,‡} Yu Mei,[§] Matthias Ballauff,[§] and Thomas Schimmel^{*,†,||,⊥}

Institute of Nanotechnology, Forschungszentrum Karlsruhe GmbH, D-76021 Karlsruhe, Germany, Institute of Physical Chemistry I, University of Bayreuth, D-95447 Bayreuth, Germany, Institute of Applied Physics, University of Karlsruhe, D-76128 Karlsruhe, Germany, DFG-Center for Functional Nanostructures (CFN), University of Karlsruhe, D-76128 Karlsruhe, Germany

Received April 6, 2006. In Final Form: June 14, 2006

We demonstrate that the adsorption of cationic spherical polyelectrolyte brushes (SPB) on negatively charged mica substrates can be controlled in situ by the ionic strength of the suspension. The SPB used in our experiments consist of colloidal core particles made of polystyrene. Long cationic polyelectrolyte chains are grafted onto these cores that have diameters in the range of 100 nm. These particles are suspended in aqueous solution with a fixed ionic strength. Atomic force microscopy (AFM) in suspension as well as in air was used for surface characterization. In pure water the polymer particles exhibit a strong adhesion to the mica surface. AFM investigations of the dry samples show that the particles occupy the identical positions as they did in liquid. They were not removed by the capillary forces within the receding water front during the drying process. The strong interaction between the particles and the mica surface is corroborated by testing the adhesion of individual particles on the dried surface by means of the AFM tip: After a stepwise increase of the force applied to the surface by the AFM tip, the polymer particles still were not removed from the surface, but they were cut through and remained on the substrate. Moreover, in situ AFM measurements showed that particles which adsorb under liquid in a stable manner are easily desorbed from the surface after electrolyte is added to the suspension. This finding is explained by a decreasing attractive particle–substrate interaction, and the removal of the particles from the surface is due to the significant reduction of the activation barrier of the particle desorption. All findings can be explained in terms of the counterion release force.

Introduction

Polymer nanoparticles are of increasing interest as a basis for technical products such as coatings, paints,¹ or paper products^{2,3} as well as for biotechnological purposes.^{4,5} All of these applications are based either on a specific adhesion of the particles on organic or inorganic surfaces or on a specific adsorption of molecules on the polymer particles. Therefore, optimizing the particle–surface interaction for a special application requires (i) the possibility to tailor the surface chemistry of the polymer particles and/or the substrate, (ii) ideal adsorption conditions such as temperature and ionic strength, and (iii) methods suitable for the investigation of particle adhesion on the surface.^{6,7}

Recently, we demonstrated that it is possible to engineer the interaction between spherical polyelectrolyte brushes (SPB) and mica by means of the charge of the particles.^{8,9} The focus was

on the question how the particle arrangement on the substrate is influenced by the charge of the polyelectrolyte chains, and AFM techniques in air were used to investigate the dry samples. Here we demonstrate for the first time the influence of the ionic strength on the adhesion of cationic SPB on mica using in situ AFM techniques under water.

Our SPB consist of a polystyrene core with a diameter of typically 90 nm onto which polyelectrolyte chains with contour lengths of the chains between 100 and 120 nm are grafted. As mentioned before, the charge of the polyelectrolyte brushes has significant influence on the patterns formed by the adsorption of SPB after drying drops of dispersions on a mica substrate.⁸ SPB consisting of negatively charged polyelectrolyte chains (anionic SPB) were shown to exhibit densely packed particle layers as capillary forces are controlling the arrangement of the particles on the surface.^{8,10} However, when the SPB carry positively charged polyelectrolyte chains (cationic SPB), network-like particle aggregates result after drying.⁸ As one possible explanation for this markedly different behavior, we suggested the counterion release force: The negatively charged surface becomes a multivalent counterion of the cationic brush particles thereby releasing the monovalent counterions within the brush layer. The counterion release force should lead to a strong attractive interaction between charged macromolecules and oppositely charged substrates and has been treated theoretically first by Manning et al. and by Fleck et al.^{11,12} First experimental

* Corresponding author. Phone: ++49-7247-82 3993. E-mail: thomas.schimmel@int.fzk.de.

[†] Institute of Nanotechnology, Forschungszentrum Karlsruhe GmbH.

[‡] Present address: Institute of Technical Chemistry, Water Technology and Geotechnical Division, Forschungszentrum Karlsruhe GmbH, D-76021 Karlsruhe, Germany.

[§] Institute of Physical Chemistry I, University of Bayreuth.

^{||} Institute of Applied Physics, University of Karlsruhe.

[⊥] DFG-Center for Functional Nanostructures (CFN), University of Karlsruhe.

(1) Distler, D., Ed. *Wässrige Polymerdispersionen*; Wiley-VCH: New York, 1999.

(2) Kugge, C.; Craig, V. S. J.; Daicic, J. *Colloid Surf. A* **2004**, *238*, 1.

(3) Rigdahl, M.; Lason, L.; Hagen, R.; Karlsson, O.; Wesslen, B. *J. Appl. Polym. Sci.* **1997**, *63*, 661.

(4) Radomska-Galant, I.; Basinska, T. *Biomacromolecules* **2003**, *4*, 1848.

(5) Wittemann, A.; Haupt, B.; Ballauff, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1671.

(6) Evers, M.; Palberg, T.; Dingenouts, N.; Ballauff, M.; Richter, H.; Schimmel, Th. *Prog. Colloid Polym. Sci.* **2000**, *115*, 307.

(7) Gliemann, H.; Almeida, A. T.; Petri, D. F. S.; Schimmel, Th. *Surf. Interface Anal.* in press.

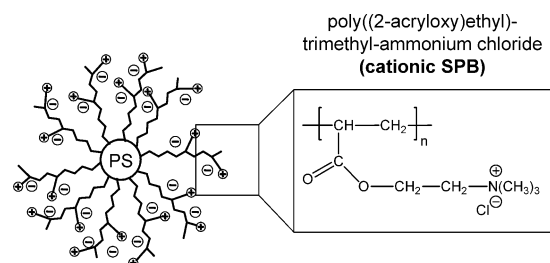
(8) Mei, Y.; Wittemann, A.; Sharma, G.; Ballauff, M.; Gliemann, H.; Koch, Th.; Horbach, J.; Schimmel, Th. *Macromolecules* **2003**, *36*, 3452.

(9) Gliemann, H.; Koch, Th.; Ballauff, M.; Schimmel, Th. *Photonik* **2005**, *37*, 81.

(10) Kralchevsky, P. A.; Nagayama, K. *Adv. Colloid Interface Sci.* **2000**, *85*, 145.

(11) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 954.

(12) Fleck, C.; von Grünberg, H. H. *Phys. Rev. E* **2001**, *63*, 061804.

Scheme 1. Scheme of the Cationic SPB Used Here^a

^a Chains of poly((2-acryloxy)ethyl)-trimethylammonium chloride are affixed to core particles of 90 nm in diameter. The particles are suspended in water.

evidence was given by Wagner et al. for DNA molecules.¹³ At high ionic strength, however, this force should vanish, and no adsorption is expected to take place anymore.

Here, we present for the first time an investigation of the adsorption of SPB on mica using in situ atomic force microscopy (AFM). As the counterion release force should depend on the ionic strength in solution, we study the influence of the amount of added electrolyte. We demonstrate that the counterion release force leads to a strong adhesion of the particles that can be tuned by the ionic strength of the solution.

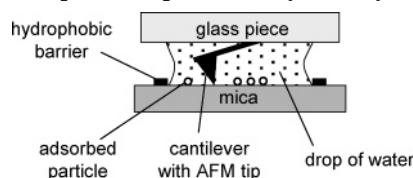
Experimental Section

Particle Preparation. The preparation of the cationic SPB is described in detail in refs 14 and 15. It includes three steps: (i) In the first step, a polystyrene core is prepared by a conventional emulsion polymerization. (ii) Then a thin shell of a photoinitiator is polymerized onto the polystyrene cores. (iii) Finally the monomers are added to the aqueous suspension of the PS particles, and the suspension is irradiated by UV-vis light to generate radicals on the particle surface. As a result, a radical polymerization process is started, and in this way a dense layer of polyelectrolyte chain brushes is generated on the particle surface by this grafting-from technique. The cationic SPB consist of poly((2-acryloxy)ethyl)-trimethylammonium chloride chains grafted onto the PS core (Scheme 1). The average diameter of the polystyrene core was determined to be 90 ± 3 nm, and the contour length thickness was 116 ± 4 nm.⁸ The aqueous suspension of the cationic SPB had a solid content of 2.8 wt % after preparation.

Sample Preparation and AFM Investigation. The suspension was diluted with deionized water until a solid content of 0.14 wt % was reached. After dilution, the suspension was treated in the ultrasonic bath for 10 min to re-suspend possible aggregates of polymer particles. For the adsorption experiments a $3 \text{ mm} \times 5 \text{ mm}$ piece of mica (Pelco, USA) was cleaved three times to get four fresh mica surfaces with identical surface areas. Each mica sample was placed in a small polymer container (polystyrene, Eppendorf, Germany) filled with 1 mL of the diluted suspension. The samples were removed from the suspension after different dwelling times, rinsed with deionized water and subsequently dried in ambient air. The particle density on the substrate surface was investigated with an atomic force microscope (DI, USA) operated in the intermittent contact mode. Bar shaped Silicon cantilevers (NT-MDT, Russia) with average force constants between 0.15 N/m and 0.6 N/m were used.

For the AFM investigation of the adsorption behavior of the particles in liquid, a piece of mica was freshly cleaved, and a circle line was drawn on the mica surface with a water resistant marker (see Scheme 2). This line acts as a hydrophobic barrier which avoids the spreading of the suspension over the entire surface area. A drop of diluted suspension of the SPB (300 μL) was deposited on the

Scheme 2. Experimental Setup for the in Situ AFM Study of the Adsorption of Spherical Polyelectrolyte Brushes



inner part of the circle. To avoid the adsorption of the particles on the back of the cantilever during the AFM investigation which would result in a loss of laser light intensity reaching the photodiode of the AFM, the suspension was subsequently substituted by a drop of deionized water after exposure to the suspensions. This washing procedure was repeated five times and removes most of the suspended polymer particles. Then the substrate was fixed on the sample holder of the AFM, and the AFM tip on the cantilever, which is mounted underneath a glass piece, is approached to the surface of the mica substrate. A stable meniscus is formed between the substrate and the glass piece, and the hydrophobic barrier avoids the spreading of the suspension (Scheme 2). For the investigations in liquid, the AFM was operated in the intermittent contact mode with bar-shaped silicon cantilevers having an average force constant of 1.75 N/m. The operation frequency of the cantilevers was approximately 30 kHz for all experiments done in situ. For the intermittent contact mode investigations, the tip amplitude is damped to 80% of the free off-surface value before the feedback loop is triggered and the tip is withdrawn.

Results and Discussion

Kinetics of Adsorption. We first investigate the kinetics of the adsorption of the particles on surfaces in order to assess the time needed to reach equilibrium. Investigations done with an AFM typically needed 5–10 min for each image. We studied (i) the effect of the adsorption time on the density of adsorbed particles on the mica surface and (ii) the time scale when the saturation of adsorbed particles is reached so that a change in particle density during an AFM scan is negligible. For this experiment, four mica samples were prepared as described in the Experimental Section. The mica samples were immersed in a diluted suspension of cationic latex spheres for different times, that is, for 1, 5, and 20 min, respectively. An additional sample was kept for 22 h in the suspension. In the case of the first two experiments, the adsorption times are shorter or comparable to the times necessary for an AFM scan. Therefore, it was necessary to “freeze” the state of adsorption and to investigate the surface afterward with the AFM technique. In this work, the “freezing” was carried out by washing the samples with deionized water to remove the loosely bound particles from the surface and by subsequently drying the sample. Then the mica substrates were investigated with the AFM operated in the intermittent contact mode.

Figure 1 shows representative $10 \mu\text{m} \times 10 \mu\text{m}$ AFM topography images of the three samples, representing the substrates after 1 min (Figure 1a), 5 min (Figure 1b), and 20 min (Figure 1c) adsorption time, respectively. Individual particles and small particle aggregates can be detected on the surfaces. The AFM study of different areas of the samples showed that for every sample the average particle density is between 150 and 200 particles per $100 \mu\text{m}^2$ independent of the adsorption time. The same result was obtained for the sample which was 22 h in contact with the particle suspension. The statistical fluctuation of the particle density on the surfaces was about 20% in all cases. Therefore, it can be concluded that the adsorption equilibrium is reached during the first minute. Preliminary studies do not indicate a significant dependence of the equilibrium particle

(13) Wagner K.; Harries, D.; May, S.; Kahl, V.; Radler, J. O.; Ben-Shaul, A. *Langmuir* **2000**, *16*, 303.

(14) Guo, X.; Ballauff, M. *Macromolecules* **1999**, *32*, 6043.

(15) Guo, X.; Ballauff, M. *Langmuir* **2000**, *16*, 8719.

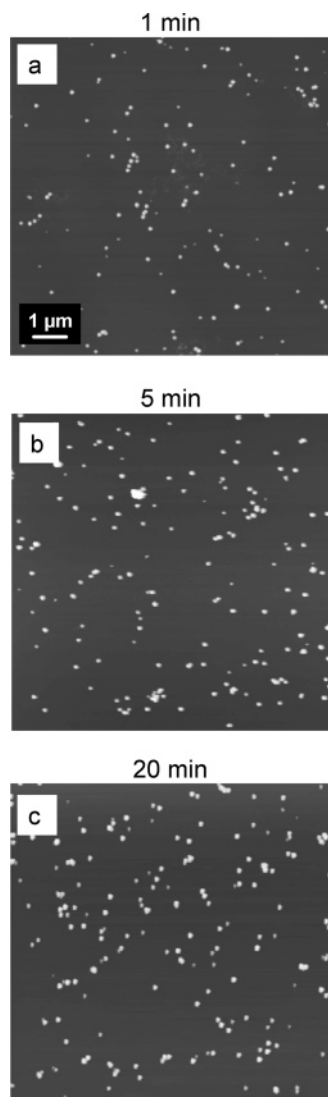


Figure 1. AFM topography images of three different mica substrates after they were immersed in a suspension of cationic SPB for 1 min (a), 5 min (b), and 20 min (c), subsequently rinsed with deionized water, and dried in air. The AFM was operated in the intermittent contact mode. A saturation of particle density on the surface is reached during the first minute; z scale for all images: 200 nm.

density on the surface under liquid on the particle concentration in the suspension.

Adsorption of Particles Investigated by in Situ AFM. Figure 2 shows the liquid-AFM amplitude images (intermittent contact mode) of cationic SPB adsorbed on a mica substrate 5 min (Figure 2a) and 1 h (Figure 2b) after the suspension was dropped onto the mica substrate. For the analysis of the AFM results obtained in the liquid, the amplitude images are used, because they show a much better contrast between the particles and the substrate than the corresponding topography images. Figure 2b shows a zoom-out image of Figure 2a. It was obtained after 12 AFM image scans of the surface area displayed in Figure 2a. The number of particles on the $10 \mu\text{m} \times 10 \mu\text{m}$ surface area in Figure 2b is about 220, a number comparable to that described above in Figure 1 and also comparable to the results described recently.⁸

All particles which can be observed in Figure 2a can also be found in Figure 2b. This indicates that no particles were removed during the 12 AFM image scans which took place before the zoom-out displayed in Figure 2b was carried out. The zoom-out in Figure 2b also shows that there are no particles deposited along the border of the scan area shown in Figure 2a (represented

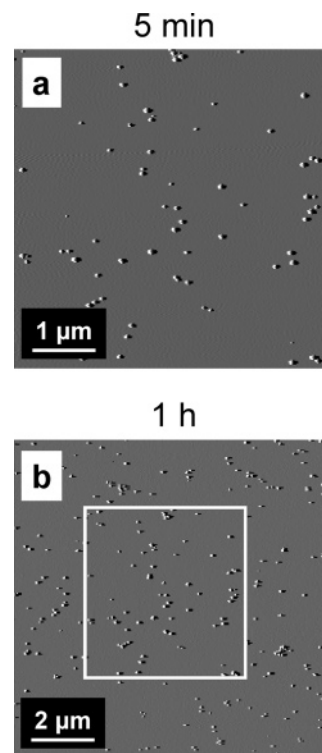


Figure 2. Liquid-AFM amplitude images (intermittent contact mode) of cationic SPB on mica (a) 5 min and (b) 1 h after the suspension was dropped onto the mica surface and after 12 subsequent AFM scans. Images a and b show different magnifications of the identical location on the sample surface. The white frame in image b marks the scan area of image a. The particle density for image b is about 220 particles/ $100 \mu\text{m}^2$. All particles observable in image a can also be found in image b, and no scan window can be detected in image b, indicating that the particles are not (re)moved by the scanning AFM tip. Scan area in image a: $5 \mu\text{m} \times 5 \mu\text{m}$; scan area in image b: $10 \mu\text{m} \times 10 \mu\text{m}$.

by the white frame in Figure 2b). This is an important indicator that no particles were removed from their positions during the scan 5 min after the suspension was dropped onto the mica surface.

For anionic SPB, a high mobility of the particles on the mica surface during the evaporation process of the water was found.⁸ As a result, a densely packed, well ordered particle array was formed after drying the sample.⁸ This behavior was explained by strong capillary forces between the particles caused by the receding water droplet so that the adhesion force between the anionic particles and the surface is overcompensated. Therefore, the effect of the drying process on the particle position on the surface can be used as a first qualitative indicator for the force with which a particle is adsorbed on the surface.

As the next step, we investigated the effect of the drying process on the adsorption of the cationic SPB. AFM studies of identical sample areas before and after drying the surface were carried out. Figure 3A shows the liquid AFM amplitude image ($10 \mu\text{m} \times 10 \mu\text{m}$) of cationic SPB on mica, and Figure 3B shows the image of the identical sample area after drying the suspension. It is obvious that the particle density has increased during the drying process. This can be explained by the fact that during the washing process described in the experimental part not all dispersed particles are removed from the liquid above the surface. During the drying process these particles reach the surface and adsorb. The images a and b in Figure 3 show AFM zoom-ins of the surface areas displayed in panels A and B (white frames), respectively. They give more detailed information about the influence of the drying process on the adsorbed particles. To

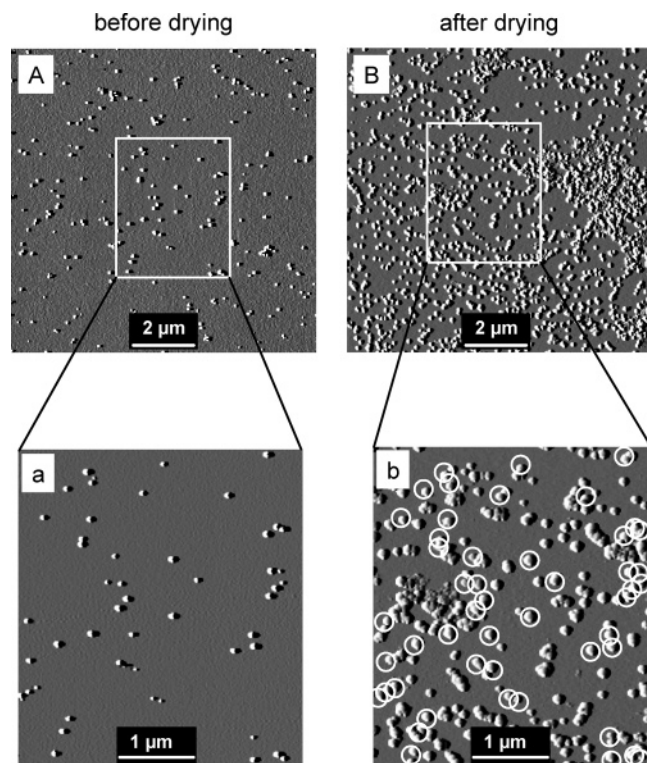


Figure 3. AFM amplitude images (intermittent contact mode) of cationic SPB adsorbed on mica. (A) An image obtained in liquid and (B) an image of the identical surface area after drying the substrate. Images a and b were obtained by zooming into panels A and B (white frames), respectively. The white rings in image b mark those particle positions which are occupied by a particle in image a. As a result all particle positions from image a remain occupied in image b without exception, which means that no particles were removed from their original positions despite the strong capillary forces acting during the drying process.

compare images a and b, all particles of image a (before drying) were marked with a circle. In a second step, this arrangement of the circles and the AFM image of the corresponding surface area after drying were superposed and image 3b was obtained. As the center of each circle is occupied by a particle in Figure 3b, it can be concluded that no particle which can be detected in Figure 3a was removed during the drying process.

This indicates a strong interaction between the particles and the surface. In the case of a weak particle–surface interaction the capillary forces, operative during the drying process, would remove the particles from their original positions. This was shown recently for anionic SPB on mica.⁸ However, it is not observed in the case of the cationic SPB studied here in situ.

To exclude possible changes of the mica surface due to cleavage in air and the surface exposure to the particle suspension, additional experiments were carried out where mica was cleaved *within the suspension*. There were no significant differences in particle density between mica substrates which were cleaved in liquid or in air.

All findings are easily explained in terms of the counterion release force: As soon as the particles come into contact with the substrate, the negative counterions of the positively charged SPB chains are substituted by the negative charges of the freshly cleaved mica substrate. Concomitantly, the positive counterions of the mica are substituted by the positive charges of the SPB chains. As a result of the process of adsorption, a corresponding number of counterions are released and the entropy of the entire

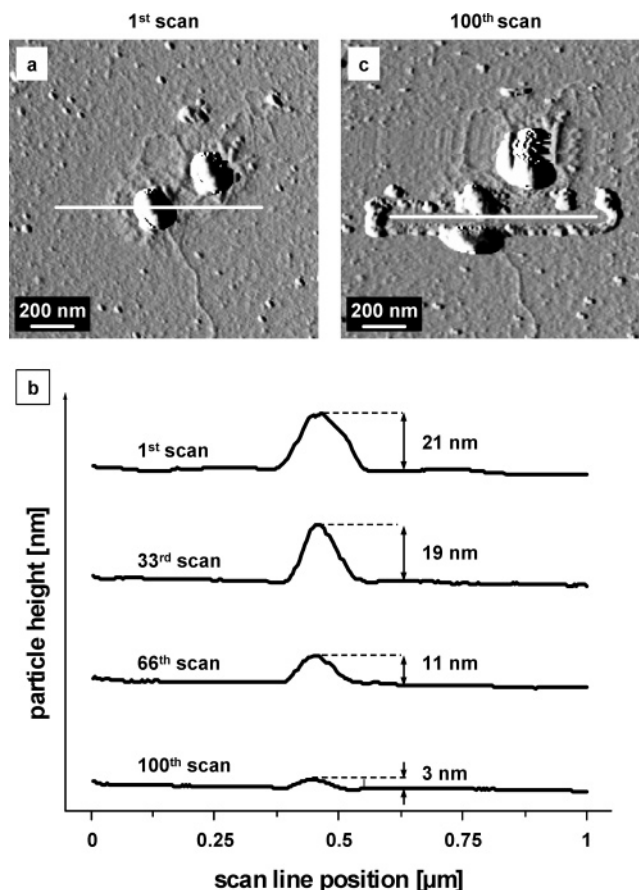


Figure 4. AFM amplitude images of two cationic SPB particles adsorbed on mica. The images were taken in the intermittent contact mode. (a) The image before the line scans of the AFM tip in contact mode with incrementally increased force load were carried out and (b) the cross-sections of the center part of a cationic SPB (along the white line in image a) on freshly cleaved mica. With increasing scan number the force load applied to the AFM tip was increased. The decrease of height of the polymer particle with increasing force from the 1st to the 100th line scan is the result of the removal of polymer material by the scanning AFM tip. (c) The AFM amplitude image of the particles after the line scan experiment. The investigated cationic SPB was cut in two pieces by the AFM tip.

solution is increased. This creates a strong adhesion of the particles, the strength of which will be addressed in the subsequent section.

Strength of the Adhesive Force. To assess the strength of the adhesion between the cationic SPB and the dried mica surface, an individual particle was selected on the surface and an intermittent contact mode AFM scan was carried out to obtain an image of this particle which is in the center of a $2\ \mu\text{m} \times 2\ \mu\text{m}$ scan area. Then, the scan in the slow scanning direction of the AFM (“y-scan”) was disabled as soon as the AFM tip reached the center of the polymer particle and the AFM tip was lifted up. After the AFM operation mode was switched to the contact mode, the fast scan frequency was reduced to its minimum (0.1 Hz). Finally, the tip was approached to the surface again, and line scans with $1\ \mu\text{m}$ length across the particle were carried out. After each line scan, the normal and lateral force exerted on the particle by the AFM tip was increased by increasing the deflection of the cantilever stepwise. For each setpoint of the force load, the corresponding cross-section was recorded as a line-scan: Figure 4a shows the amplitude image of two SPB adsorbed on mica after the drying process. In Figure 4b, four cross sections of the center part of the selected SPB (see white line in Figure 4a) are shown. They represent the height profile of the particle

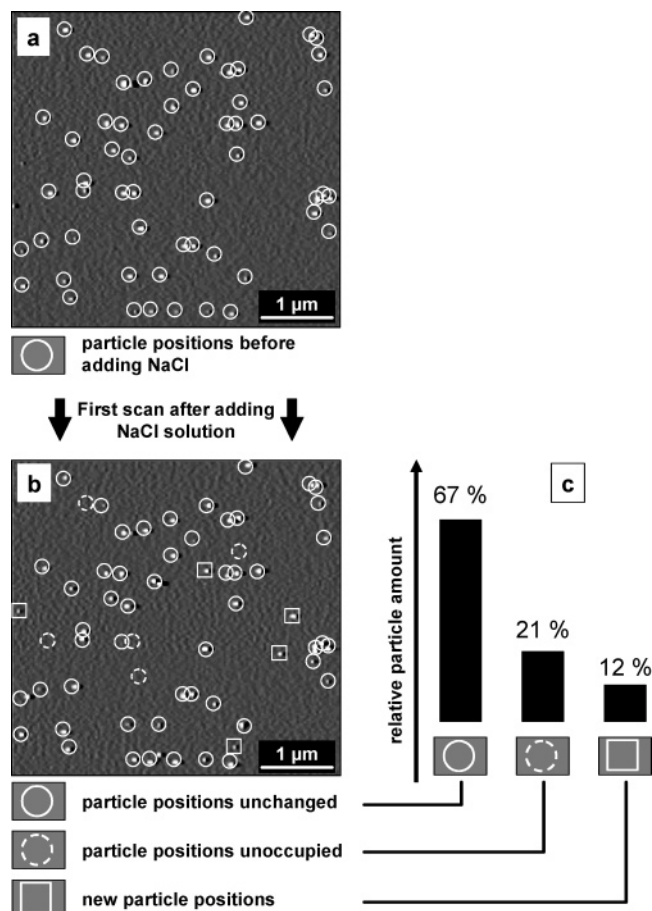


Figure 5. Liquid-AFM amplitude images (scan area $5.3 \mu\text{m} \times 4.7 \mu\text{m}$) of cationic SPB adsorbed on freshly cleaved mica. In image a, the ionic strength is ca. 10^{-4} mol/L. Image b shows the first AFM scan after increasing the ionic strength to 10^{-2} mol/L by adding aqueous solution of NaCl. The statistics in panel c summarize the influence of the increase in ionic strength on the particle density and on the particle distribution on the surface.

after the first line scan, the 33rd, the 66th, and the 100th line scan, respectively. The increasing line scan number hence corresponds to a higher cantilever deflection and therefore to a higher force which is applied to the surface by the AFM tip. The force applied to the surface by the AFM tip was about 20 nN for the lowest setpoint and about 60 nN for the highest setpoint. These forces were determined on the basis of standard force–distance measurements, whereas the deflection of the cantilever was measured when approaching and disapproaching the AFM tip to and from the mica surface.

It is shown that the height of the particle is reduced with increasing force because of the removal of polymer material of the SPB by the AFM tip. The effect of the line scans on the particle can be observed when comparing the amplitude images of the cationic particle before (Figure 4a) and after (Figure 4c) 100 scans: Figure 4c proves that the particle was not removed from the surface at a certain force threshold as might be expected but it is cut through. The removed polymer material is deposited as debris along the scan line, mostly at its ends. This demonstrates the strong adsorption of the polymer particle on the mica surface. The drag which is visible in the upper half of image 4c could be due to the restarting of the slow scan which was deactivated for the line scans and due to material which is deposited on the AFM tip during the polymer displacement.

Influence of Ionic Strength. We now discuss the influence of the ionic strength onto the counterion release force in solution.

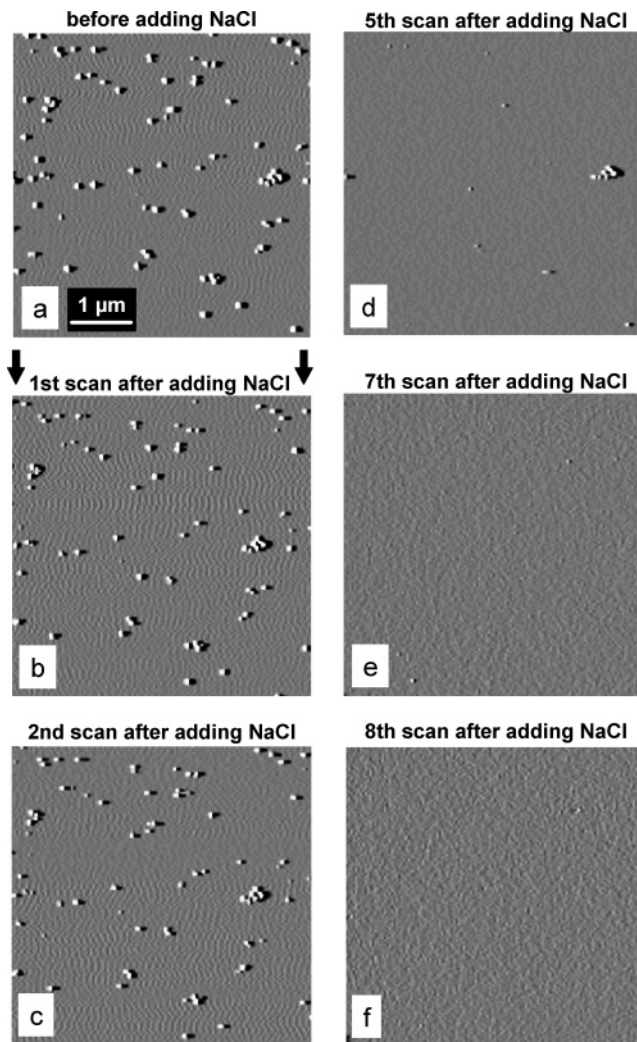


Figure 6. Liquid-AFM amplitude images ($5 \mu\text{m} \times 5 \mu\text{m}$) of cationic SPB adsorbed on freshly cleaved mica without adding aqueous solution of NaCl to the suspension (a), immediately after the increase of the ionic strength to 10^{-2} mol/L (b), and after different numbers of scans after NaCl addition (c–f). All images represent the identical surface area. Eight image scans after addition of NaCl, no particles were detected on the surface any more.

Evidently, a sufficiently high concentration of added salt is expected to diminish this force significantly and no adsorption should take place any more. Figure 5a shows a liquid AFM amplitude image ($5.3 \mu\text{m} \times 4.7 \mu\text{m}$) of polymer particles adsorbed on the mica surface. As about 5% of the counterions of the SPB polyelectrolyte chains leave the shell material, the ionic strength within the suspension is about 10^{-4} mol/L. No additional electrolyte was added to the solution. The particle density in Figure 5a is about 210 per $100 \mu\text{m}^2$. This is in accordance with the value of approximately 150–200 particles per $100 \mu\text{m}^2$ determined for the time-dependent adsorption experiments of dried samples mentioned above (Figure 1). The ionic strength was then increased within the meniscus between the mica substrate and the glass piece (Scheme 1) by lifting up the AFM tip and adding one drop ($30 \mu\text{L}$) of an aqueous 0.1 M NaCl solution to the suspension. In this way, the ionic strength of the volume was increased to ca. 10^{-2} mol/L. The first amplitude image of the surface 9 min after the electrolyte was added is shown in Figure 5b, which represents the identical surface area as Figure 5a.

From the first scan after increasing the ionic strength, we see that about one-quarter of the particles were removed from the surface. Figure 5c shows that after the first scan about 70% of

the particle positions occupied in Figure 5a remain occupied, whereas about 20% of the particles were removed from their original positions. The relatively high amount of particles (about 10%) appearing on new positions in Figure 5b may be the result of the particle displacement by the AFM tip and/or an additional adsorption due to the increased ionic strength.

The results of the AFM investigation presented in Figure 5 show that the adhesion force of the particles is significantly reduced due to the reduced activation barrier for the particle desorption which is the result of the increased ionic strength.

This has also been proved directly by repeated AFM scans after increasing the ionic strength of the solution. Figure 6a–e shows a sequence of liquid-AFM amplitude images of the identical mica surface area before (Figure 6a) the addition of the aqueous solution of NaCl and after the increase of the ionic strength of the suspension. The parameter of the different graphs in Figure 6 is the number of scans. Each scan removes more and more particles from the surface. Figure 6e shows that after 90 min (corresponding to eight intermittent contact mode image scans) no more particles can be detected on the substrate surface any more. This result must be compared to the corresponding results of the in situ AFM studies in pure water mentioned earlier, where at low ionic strength no particle was removed even after 12 scans (Figure 2). This demonstrates clearly a significantly reduced adhesion force between the particles and the surface if the ionic strength is sufficiently high.

Conclusion

The adsorption behavior of cationic Spherical Polyelectrolyte Brushes on mica substrates was investigated in situ, i.e., in

suspension, by AFM. The results show that the adsorption of the particles on negatively charged mica substrates is influenced by the particle–surface interaction. Strong adhesive interaction between the cationic SPB and the mica surface is present within suspensions in pure water. Increasing the ionic strength in the system leads to a weakening of the particle–substrate interaction. The results demonstrate that the counterion release force is responsible for the strong interaction between the particles and the surface in the case of cationic SPB suspensions. From a practical point of view, this means that it is possible (i) to control the adhesion force of the cationic SPB on the substrate by varying the ionic strength within the suspension and (ii) to remove particles from the substrate which are already adsorbed by increasing the ionic strength. The findings presented here open up new perspectives for technological application. Future goals will be (i) the quantitative investigation of the adhesion force of cationic SPB on a mica surface and (ii) the determination of the threshold of the ionic strength necessary to remove single SPB from the surface by varying the ionic strength stepwise.

Acknowledgment. This work was supported within the DFG-Center for Functional Nanostructures (CFN) and by the Research Prize for Applied Science (“Landesforschungspreis”) Baden-Württemberg. Y.M. and M.B. acknowledge financial support by the Deutsche Forschungsgemeinschaft, SFB 481, Bayreuth, by the European Community, Project “POLYAMPHI”, and by the Fonds der Chemischen Industrie.

LA060933U