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Engineering the Interaction of Latex Spheres with Charged Surfaces: AFM Investigation of Spherical Polyelectrolyte Brushes on Mica

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Introduction. Colloidal particles are often stabilized by long polymeric chains grafted to their surface.[1] If two such particles are dispersed in a good solvent for the chains and these particles approach each other, a repulsive interaction results. The steric interaction thus effected has been studied for decades and is well understood by now.[2,3] It can be enhanced even more if the polymers attached to the surface carry charges. The resulting electrosteric interaction can be understood in terms of the increased osmotic pressure of the counterions if the polyelectrolyte chains attached to the surfaces of the particles are to share the same volume.[4,5] The great practical importance of electrosteric interaction is related to the fact that most industrial latexes are stabilized in this way.[6]

Application of latexes not only requires a fundamental understanding of mutual interaction, however. Controlling the interaction of the particles with solid shells is of comparable importance when considering latex particles as the base of paints and coatings.[6] A comprehensive investigation of these problems requires latex particles onto which the polyelectrolyte chains are firmly attached, i.e., by a chemical bond. Otherwise, the particles would disintegrate upon strongly interacting with a solid substrate. Moreover, the polyelectrolyte chains must be densely grafted to the particles. Colloidal objects carrying only a small number of chains can approach solid substrates so closely that their strong van der Waals interaction with the substrate becomes the leading effect.[1,7]

Recently, we demonstrated that colloidal particles with attached polyelectrolyte chains can conveniently be prepared by photoemulsion polymerization.[8] By this method the polyelectrolyte chains can be affixed rather densely to the surface of poly(styrene) latex particles so that the overall dimensions are much larger than their average distance on the surface of the particles. Hence, a spherical polyelectrolyte brush (SPB) results, having overall dimensions in the colloidal domain (Figure 1).

The chains are affixed to the particles by a chemical bond and exhibit an excellent stability against coagulation in solution.[9,10] Previous studies demonstrated that the dimensions of the shell can be tuned by the salt concentration in the solution.[9,10] Moreover, direct measurements of the osmotic pressure of aqueous solutions of the SPB[11] demonstrated that ca. 95% of the counterions are confined within the brush as predicted by theory.[12,13] Rheological measurements clearly pointed to the strong mutual repulsion of the particles when dispersed in water.[14]

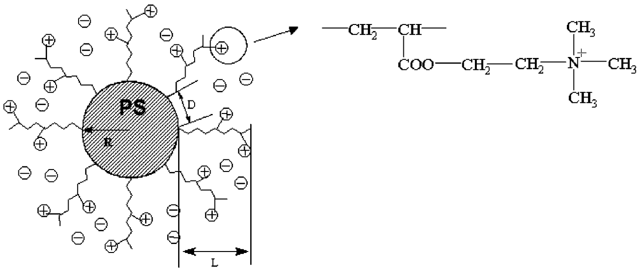

Figure 1. Scheme of the cationic spherical polyelectrolyte brush LA2 synthesized and used in this study. Long polyelectrolyte chains are densely attached to solid poly(styrene) particles so that a dense shell of charged chains results on the surface of the cores. The anionic latex LQ3 used herein has the same structure but with the cationic chains being replaced by the anionic poly(styrenesulfonic acid) chains.

Evidently, these SPB provide a good model system for a systematic study of the interaction of sterically stabilized particles with solid substrates. Here we present the first results of a study of SPB contacting a negatively charged mica substrate. Atomic force microscopy (AFM) in the intermittent contact mode[15] has been used as tool to investigate the topography and the phase contrast[16] of the samples. Phase contrast results from a combination of different tip−sample interactions such as local adhesion and capillary forces as well as viscoelastic damping. Recent investigations demonstrate that AFM is a powerful method to study the local organization of latex particles on solid substrates.[17−23]

Two different SPB have been studied: (1) An anionic system consisting of chains of poly(styrenesulfonic acid). This system termed LQ3 has been synthesized and characterized in detail recently (see Table 1 in ref 10). (2) The SPB termed LA2 carrying positive charges. These particles have been synthesized and characterized for the present purpose. Figure 1 shows schematically the structure of the cationic SPB LA2. As cationic polyelectrolyte we used poly((2-acryloyl)ethyl)trimethylammonium chloride (poly(flocryl)), which carries quarternized ammonia groups. Poly(flocryl) chains hence represent a quenched polyelectrolyte in which the charges are independent of the pH in the system. The choice of this particular polyelectrolyte derives from its excellent solubility in water and use as technical flocculation agent.[6] The polyelectrolyte chains are attached to a poly(styrene) core of 136 nm (LQ3) and 90 nm (LA2) diameter with low polydispersity. Since the chains can be cleaved off after synthesis, their molecular weight and molecular weight distribution can be determined.[8] Moreover, the total charge of the SPB brush is determined by titration. Hence, all pertinent parameters of the particles are known.[8−10] The only parameter that was varied in our experiments was the charge of the SPB. Differences in the adsorption behavior can hence be explained by different interaction forces of the

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Table 1. Characterization of the SPB LA2 and LQ3[a]

sample	R [nm]	M_η [g/mol]	L_c [nm]	σ [nm^{-2}]	L_c/R	D [nm]
LA2	45	89 700	116	0.049	2.57	5.1
LQ3	68	88 000	108	0.039	1.59	5.7

[a] LQ3 = anionic core−shell latices with 20 mol % poly(NaSS); LA2 = cationic core−shell latices with 56 mol % poly(flocryl); R = core radius; M_η = molecular weight of grafted chains as determined by viscosimetry (see ref 8); L_c = contour length of grafted chains determined from M_η; σ = graft density on surface of core particles; D = the average distance between two neighboring graft points.

negatively charged mica surface with the positively charged LA2 particles or with the negatively charged LQ3 particles. Using these two types of particles, it will be shown that firmly attached polyelectrolyte chains are well-suited to control the interaction of latex particles with solid substrates.

Experimental Section. The synthesis of the cationic SPB proceeds along the lines given recently.[8] The photoemulsion polymerization described there proceeds in three steps: In a first step the poly(styrene) core particles are synthesized by a conventional emulsion polymerization. Then a thin shell of the photoinitiator 2-[*p*-(hydroxy-2-methylpropiphenone)]ethylene glycolmethacrylate (HMEM; see ref 8) is polymerized onto these core particles according to the method devised previously.[8] HMEM is a vinyl monomer, and the formation of the shell proceeds under starved conditions so that no new particles are formed in this second step.

In the third step UV/vis radiation is used to generate radicals on the surface of the particles[8,9] The monomer 2-(acryloyloxy)ethyltrimethylammonium chloride (flocryl, BASF-AG) forming the brush layer of the particles was added to the water phase, and a radical polymerization on the surface was started. In this way a dense layer of poly(((2-acryloyl)ethyl)trimethylammonium chloride) (poly(flocryl)) chains is generated on the surface of the particles by a grafting-from technique.

To avoid possible interaction of the negatively charged surfactant used in the previous synthesis, cetyltrimethylammonium bromide (CTAB; Fluka) has been used to stabilize the core latex particles. For similar reasons the cationic initiator 2,2′-azobis(2-aminopropane) dihydrochloride (V50; WAKO Chemicals) has been used to start the emulsion polymerization of the core particles. The particles are analyzed as described previously[8] by cleaving off the polycation chains by a strong base. The molecular weight of the chains cleaved from the surface of the particles has been determined by viscosimetry as shown recently.[8] Details of the respective steps in the synthesis of the particles and their characterization will be given elsewhere. Table 1 summarizes the characteristic data of both SPB.

All AFM images were taken with a commercial AFM operated in tapping mode. For phase contrast imaging, a home-built phase imaging electronics was used. The principle of phase imaging by AFM is explained elsewhere.[16] Imaging was performed at ambient conditions using bar-shaped silicon cantilevers with a force constant of 40 N/m and a resonance frequency of 170 kHz. The images show unfiltered original data, represented in a linear gray scale.

For sample preparation, a droplet of 20 μL of a solution containing the respective polymer particles dispersed in pure water was put onto a freshly cleaved mica surface (muscovite white mica) and dried in air. The concentration of the particles was chosen small enough to avoid multilayer formation. The adsorption experiments and AFM experiments were reproduced several times and with different particle series independently yielding comparable results. After drying, studies of the long-time behavior were performed to check whether the particle structures change with time. No such changes as a function of time were observed in our experiments. All AFM data shown in this article show typical structures which are representative for the corresponding sample.

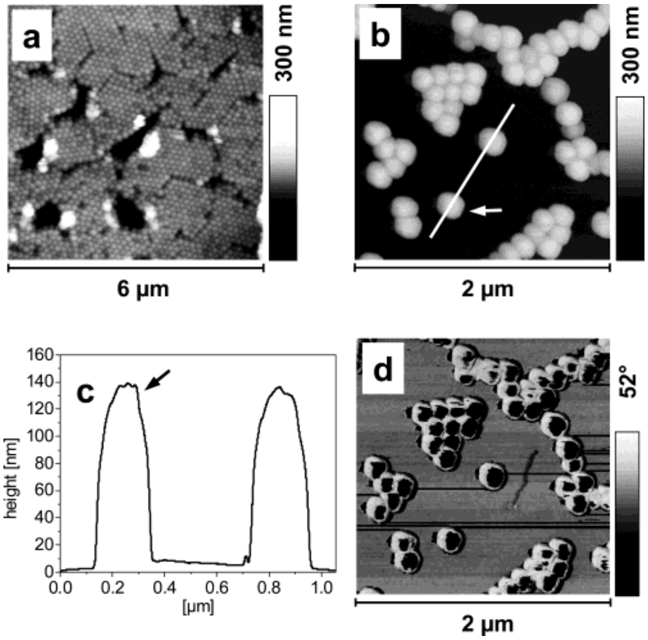

Figure 2. Intermittent contact mode AFM images of topography (a, b) and phase contrast (d) of SPB LQ3 on mica. (c) shows the cross section of two single particles along the white line in (b); the arrow in (b, c) assigns the particle in (b) to the corresponding cross section. It is seen that the particles exhibit sharp regular boundaries and smooth surfaces. They show well-defined phase contrast between the particle and the substrate (d) and form a layer that exhibits two- and three-dimensional long-range order on the surface (a).

Results and Discussion. a. Anionic Particles LQ3. We first discuss the results obtained by AFM for the anionic system LQ3. Figure 2a displays the topography of a larger area, and Figure 2b,d shows images of the spatial structures and the phase imaging data obtained by AFM in intermittent contact mode for LQ3 at larger magnification.

Figure 2b shows the topography of single polymer particles and small particle aggregates. In Figure 2c the cross section of two single particles marked as a white line in Figure 2b shows the regular border of the particles with an average diameter of 200 nm. Taking a closer look at the structure of the particles in Figure 2b, one can see that each particle exhibits a bright center region, which also is obvious as a dark, well-defined area with an average diameter of about 150 nm in the corresponding phase image in Figure 2d. When operating an AFM in intermittent contact mode to image phase contrast, the phase shift is recorded that results between the cantilever excitation piezo driven by a frequency generator and the vibration detected optically by the four-segment photodiode of the AFM. The phase shift depends on the dissipative tip−sample forces such as local adhesion, capillary forces, and viscoelastic damping. The difference in phase shift detected at the edges of the latex spheres seen as a bright rim in Figure 2d compared to the phase shift at the center part of the latexes seen as black areas can be explained as a result of the different tip−sample contact areas (and thus different dissipative tip−sample forces) when the AFM tip scans across the particle. The tip contacts the rim of the polymer particle with the tip flank whereas the tip apex gets in contact with the center part of the SPB.

The spherical shape of the particles that is expected from synthesis is visible even within the aggregates. The comparison of the particle dimensions reveals that the diameters of the particle images in Figure 2b are comparable with the corresponding diameters in Figure 2d but are significantly smaller (50−60%) than the diameter of the LQ3 cores plus twice the contour lengths of the attached polymer chains (cf. Table 1). Obviously, the poly(styrenesulfonic acid) chains have contracted during the drying process on the substrate. As intermittent contact mode images from pure PS core latexes show a very similar phase contrast as LQ3 particles (not shown here), we can assume that the LQ3 particles exhibit a dense solid shell as expected.

Figure 2a shows a two-dimensional long-range order within the layer of the LQ3 particles. The layer shows small highly ordered arrays of particles divided by cracks or voids. These features have been seen in other studies of negatively charged latexes as well.[17,18] The formation of the arrays takes place in a multistep process: After the deposition of a drop of latex dispersion on the mica surface, the water begins to evaporate and the concentration of the particles increases. Gravitational forces on the small LQ3 particles can be neglected,[25] and the electrosteric stabilization of the particles must lead to a strong mutual repulsion as long as water is present.[9,10,14] This can be argued from the finding that even high concentrations of monovalent added salt (up to 3 M) have no influence on the colloidal stability of these systems.[10] However, when the thickness of the liquid layer of the drying droplet becomes smaller and smaller, the strong lateral capillary force leads to an attractive interaction between the particles. Thus, the film formation and deposition of the particles are expected to take place at the withdrawing rim of the drying drop.

The growth of the two-dimensional array is facilitated by a convective liquid flow at the rim of the drop which is responsible for the transport of the particles to the boundary of the drop. As LQ3 latices consist of a PS core and a negatively charged polymer brush, only a repulsive interaction between the particles and the mica surface is expected. Therefore, particles should move to the boundary of the drop by convective flow without sticking to the surface. Hence, if the evaporation of the water is slow enough, the particles have the possibility to rearrange within the wet latex film. Therefore, this rearrangement leads to the densely packed arrangement of the particles as seen in Figure 2a. This also corresponds to the case of bare poly(styrene) particles studied by many groups so far.[17−22]

b. Cationic Particles LA2. A totally different ordering behavior is seen when using suspensions of the cationic SPB LA2 on mica. Figure 3a shows the large-scale arrangement of the particles resulting from drying a dilute suspension at the mica surface. The particles are arranged in long chains that form a two-dimensional network on the substrate. Moreover, Figure 3a shows that the drying process of the droplet has generated a gradient in particle concentration that increases from the upper right to the lower left of the picture. In-situ AFM investigations of freshly cleaved mica immersed in a LA2 latex suspension showed that the polymer particles seem to stick to the surface as soon as they get into contact with it.

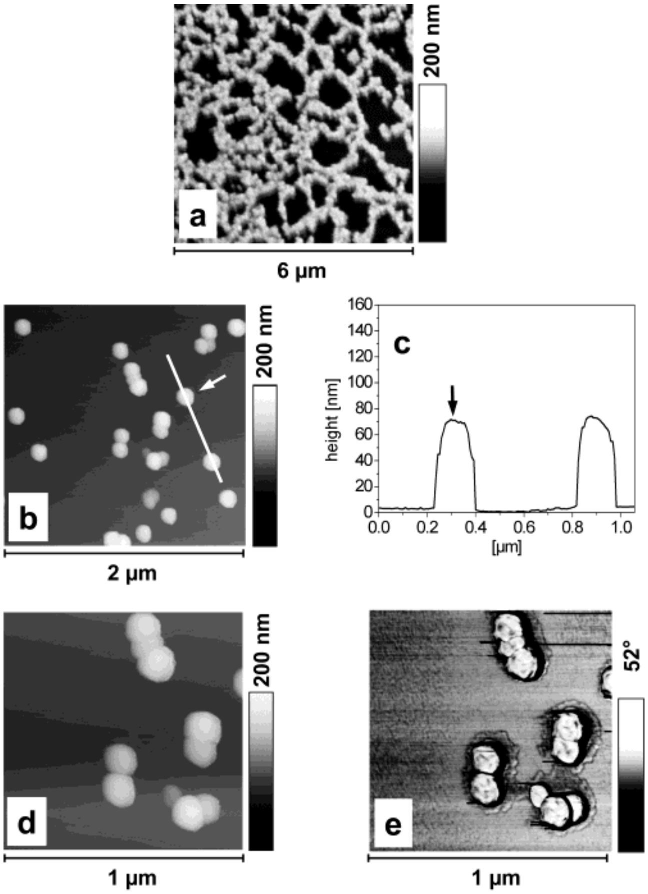

Figure 3. Intermittent contact AFM images of the topography (a, b, d) and phase contrast (e) of the cationic SPB LA2 having poly(flocryl) chains attached to their cores. The solid substrate is mica. (c) shows the cross section of two single particles along the white line in (b), and the arrow in (b, c) assigns the particle in (b) of which the cross section has been taken. In (e) the particles show an irregular phase distribution on their surfaces. They are surrounded by a corona of the polyelectrolyte chains that are attached to the solid surface. As shown in (a), the particles tend to form network-like aggregates on the surface without long-range 2D order.

It is therefore obvious that the attractive interaction between the cationic LA2 particles and the mica surface is much stronger than between LQ3 spheres and mica. As a consequence of this, capillary forces that lead to a dense packing of the anionic spheres is now partially balanced by the adsorption of the cationic LA2 spheres onto the mica surface. Moreover, the adsorbed particles obviously act as nucleation centers for other polymer spheres. This becomes more evident when zooming into Figure 3a. Figure 3b shows that only small disordered aggregates of particles are formed. Therefore, the aggregates seen in Figure 3a consist of few particles only that form a networklike structure.

Zooming into Figure 3b, Figure 3d,e corroborates this explanation for the totally different behavior of the cationic particles LA2 as compared to the anionic particles LQ3: First of all, Figure 3d,e demonstrates that the adsorbed SPB LA2 shows different shapes in the topography image as compared to the corresponding phase image. This is in contrast to the behavior observed for the anionic system LQ3 (see Figure 2b,d). The topography cross section of Figure 3c shows a regular shape of the particles as in the case of LQ3. The phase contrast image of the particles in Figure 3e, however, is not as smooth and well-defined as in the case of LQ3 (Figure 2d). Most importantly, in Figure 3e a corona is observed which is surrounding the particles. This corona is clearly visible in the phase image of Figure 3e but can hardly be detected in the topography image in Figure 3d. It exhibits an average diameter of 220 nm. The size of the particle itself is roughly the same in topography and phase images. The particle diameter thus determined is considerably lower than the diameter of the particles corresponding to fully extended chains (ca. 320 nm; diameter of core plus twice the contour lengths of the attached chains, cf. Table 1). From these finding it must be concluded that the LA2 particles strongly interact with mica.

The corona visible in Figure 3e is due to the positively charged polymer chains on the surface of the LA2 particles that are strongly attached to the negatively charged mica surface. The phase-sensitive detection in the AFM analysis is able to visualize these attached chains directly. Moreover, Figure 3e demonstrates that the chains have not retracted during the drying process. This indicates that the interaction between the polyelectrolyte chains and the surface already exists when water is still present. For geometrical reasons the diameter determined from Figure 3e must still be smaller than the maximal diameter of the particles (cf. Table 1). This is found indeed when comparing the overall diameter including the corona as detected by AFM (ca. 220 nm) to the maximum size derived from the core diameter and the contour length of the chains (ca. 320 nm; see above).

A schematic rendition of the process of drying is given on the right-hand side of Figure 4: The substrate becomes the counterion for the positively charged polyelectrolyte chains and balances a part of the charge of the shell of LA2. The sodium counterions as well as the cations balancing the charge of the mica surface are released in this way. Thus, the entropy of the entire system is increased. This “counterion release force” has recently been the subject of a thorough theoretical study.[23] It is seen experimentally in investigations of the interaction of DNA with appropriate solid substrates.[26,27] The strong interaction of the positive polyelectrolyte chains and the negative surface thus effected must lead to a partial spreading of the chains which is obvious from Figure 3e. Moreover, this attachment counterbalances partially the strong capillary forces that tend to aggregate the particles during the drying process. As a consequence of the sticking of the particles to the surface, a loose network of particles is formed upon drying (see Figure 3a), but no close packing is observed as in the case of the LQ3 particles (see Figure 2a).

It is now obvious that the anionic particles LQ3 (see Figure 2) must interact in a totally different fashion as shown schematically on the left-hand side of Figure 4: The particles are at first repelled from the negatively charged surface. The counterions are kept within the shell upon drying, and a smooth surface results. After evaporation of water the particles are attracted to the surface only by conventional van der Waals attraction if their distance to the surface is small enough.[7] The chains on the surface keep the cores sufficiently above the surface, however, unless all water has evaporated. Hence, the van der Waals interaction of the particles with the surface remains small, and their surface diffusion remains unhampered up to the point where virtually all water has been evaporated. This results in a long-range two-dimensional order of the particles on the surface as seen in Figure 2a.

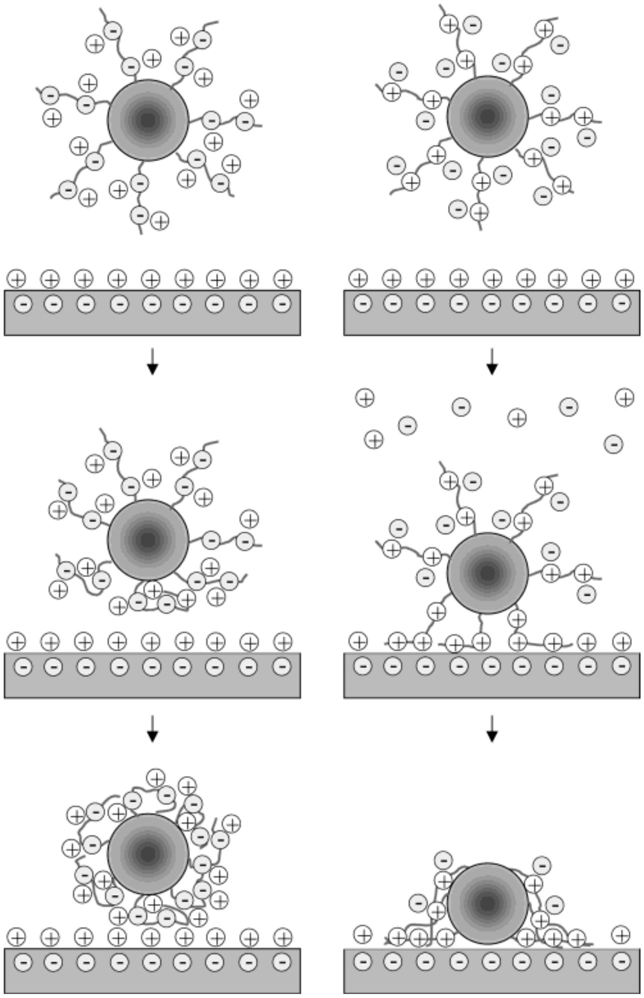

Figure 4. Scheme of the interaction of the anionic and the cationic SPB with negatively charged surfaces. The left-hand side displays schematically the interaction of the negatively charged particles LQ3 (see Table 1) with the solid mica substrate whereas the right-hand side displays the interaction of the positively charged spherical polyelectrolyte brushes LA2. The solid substrate which bears a negative charge becomes the counterion of the positive chains attached to the particles. The respective number of counterions both of the particles and of the substrate is therefore released. This leads to a strong attractive force between the particles and the substrate (“counterion release force”; see refs 23, 26, and 27 for further details). The negatively charged particles LQ3 (left-hand side), on the other hand, do not exhibit this interaction with the mica surface. Their spatial structure obtained upon drying resembles the result found for uncoated poly(styrene) particles in previous investigations.[17,18]

Conclusions. An investigation of the interaction of spherical polyelectrolyte brushes with negatively charged surfaces by AFM operated in intermittent contact mode was presented. It was demonstrated that the negative SPB LQ3 forms two-dimensional aggregates of densely packed polymer particles. This can be explained by a particle−particle interaction dominating the repulsive interaction of the particles with the substrate. The positively charged SPB LA2 exhibits a completely different particle–surface interaction behavior as expected. Here networklike structure films of dried particles without long-range 2D order are formed. This is due to the strong attractive particle–surface interaction of positively charged polyelectrolyte chains in the shell of the LA2 particles. These chains spread over the negative surface and anchor the particles. Hence, a shell of polyelectrolyte chains is a highly efficient means of adjusting the interaction of colloidal particles with solid substrates.

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