

Binding of Oppositely Charged Surfactants to Spherical Polyelectrolyte Brushes: A Study by Cryogenic Transmission Electron Microscopy

Larysa Samokhina, Marc Schrunner, and Matthias Ballauff*

Physikalische Chemie I, University of Bayreuth, 95440 Bayreuth, Germany

Markus Drechsler

Makromolekulare Chemie II, University of Bayreuth, 95440 Bayreuth, Germany

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The formation of a complex between an anionic spherical polyelectrolyte brush (SPB) and the cationic surfactant cetyltrimethylammonium bromide (CTAB) is investigated. The SPB consists of long chains of the strong polyelectrolyte poly(styrene sulfonate) (PSS), which are bound chemically to a solid poly(styrene) core of 56 nm in radius. The SPB are dispersed in water, and the ionic strength is adjusted by addition of NaBr. The resulting complexes are investigated in dilute solution by dynamic light scattering, by electrophoretic light scattering, and by cryogenic transmission electron microscopy (cryo-TEM). The formation of the complex between the SPB and the surfactant can be monitored by a strong shrinking of the surface layer when adding CTAB to dilute suspensions (0.01 wt %) and by a decrease of the effective charge of the complexes. Complex formation starts at CTAB concentrations lower than the critical micelle concentration of this surfactant. If the ratio r of the charges on the SPB to the charge of the added surfactant is exceeding unity, the particles start to flocculate. Cryo-TEM images of the complexes at $r = 0.6$ measured in salt-free solution show that the surface layer composed of the PSS chains and the adsorbed CTAB molecules is partially collapsed: A part of the chains form a dense surface layer while another part of the chains or aggregates thereof are still sticking out. This can be deduced from the cryo-TEM micrographs as well as from the hydrodynamic radius, which is still of appreciable magnitude. The 1:1 complex ($r = 1.0$) exhibits a fully collapsed layer formed by the PSS chains and CTAB. If the complex is formed in the presence of 0.05 M NaBr, $r = 0.6$ leads to globular structures directly attached to the surface of the core particles. All structures seen in the cryo-TEM images can be explained by a collapse transition of the surface layer brought about by the hydrophobic attraction between the polyelectrolyte chains that became partially hydrophobic through adsorption of CTAB.

Introduction

Polyelectrolyte–surfactant complexes (PSC) have received a lot of attention recently, partly because of the fundamental interest in these systems and partly because of the potential application these systems may have.^{1–5} The micellar complexes of the polyelectrolyte chains and the surfactant are formed in salt-free solutions at the critical aggregation concentration, which is much lower than the critical micelle concentration (cmc) in the pure surfactant solution.⁶ In general, it is understood that the strong binding of the surfactant by the polyelectrolyte chains is driven by electrostatic as well as by hydrophobic interactions. Hence, the supramolecular structures resulting from this aggregation will depend directly on the details of the molecular structure.^{5–11} The interaction of free polyelectrolyte chains with surfactants

seems to be a well-studied problem by now and a rather clear understanding has emerged.

However, information on the interaction of surfactants with polyelectrolyte chains tethered to solid surfaces, that is, with polyelectrolyte brushes, seems to be scarce by now. While polyelectrolyte brushes have been the subject of intense research during the last 15 years,^{12–24} only a few studies have been devoted to the interaction of these systems with surfactants in aqueous solution.^{25–27} Thus, Pyshkina et al. studied the uptake of n -alkyltrimethylammonium bromides by dense planar brushes of poly(acrylic acid).²⁵ They found that the amount of bound

* To whom correspondence should be addressed. E-mail: matthias.ballauff@uni-bayreuth.de.

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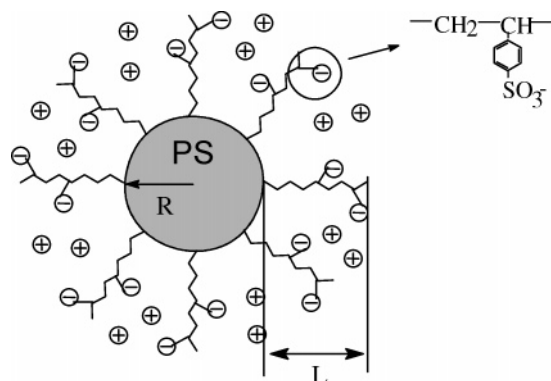


Figure 1. Schematic representation of a spherical polyelectrolyte brush. The colloidal particles consist of a poly(styrene) core onto which long chains of PSS have been grafted. The thickness L of the brush can be measured by dynamic light scattering.

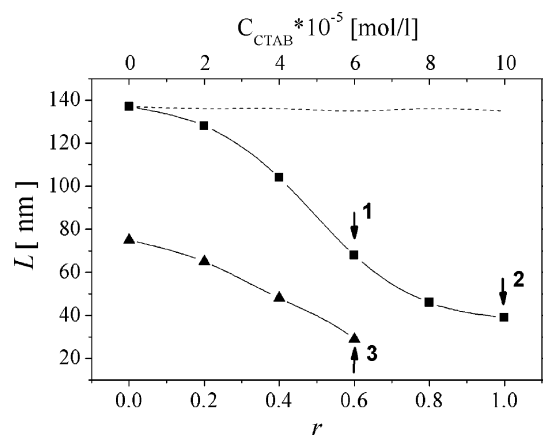


Figure 2. Influence of complex composition on the brush thickness of polyelectrolyte spheres in the salt-free solution (squares) and in 0.05 M NaBr (triangles). The dashed line marks the respective change of L brought about by adding the same equivalent of NaBr to the solution. The arrows mark the compositions where the respective cryo-TEM images have been taken: arrow 1, Figure 4; arrow 2, Figure 5; arrow 3, Figure 6.

surfactant depends strongly on the grafting density. At lower grafting density, there was a second step in the binding isotherm, which was interpreted as the onset of a lamellar mesophase within the brush layer. Konradi and R  he studied the interaction of cationic surfactants on brushes obtained by chemical grafting of poly(methacrylic acid).²⁶ They determined the uptake of the surfactant, the degree of dissociation of the brush, and the height of the brush in a very detailed manner. A key result of this investigation is the uptake of surfactants and a concomitant decrease of the brush height takes place at very low surfactant concentrations. The authors explained this by the binding of the surfactant to the polyelectrolyte chains which thus become hydrophobic. In this way, a collapse transition is induced even if the uptake of surfactant is very small. At a critical concentration, which is found to be slightly lower than the cmc, the brush takes up a large amount of surfactant and shrinks further. In this regime, the degree of binding is approaching unity. From these results, Konradi and R  he suggested a model of the local structure that surmises the formation of spherical micellar structures by the surfactant within the brush layer. Finally, Tirrell and co-workers investigated the interactions of poly(styrenesulfonate) brushes in the presence of cationic surfactants.²⁷ Using the surface force apparatus, they also found contraction of the brush at very low surfactant concentrations. At sufficiently high surfactant concentration, they found the onset of attractive interaction between the brush layers, which was explained by hydrophobic forces.

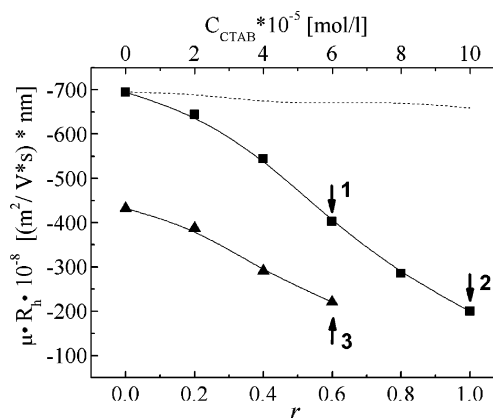


Figure 3. Analysis of the electrophoretic mobility of the particles in presence of the surfactant CTAB. The mobility multiplied by the hydrodynamic radius R_H (see Figure 2) is plotted as the function of the charge ratio in the salt-free solution (squares) and in 0.05 M NaBr (triangles). The arrows mark the compositions where the respective cryo-TEM images have been taken: arrow 1, Figure 4; arrow 2, Figure 5; arrow 3, Figure 6.

All investigations done so far on complexes between polyelectrolyte brushes and surfactants have solely been done on planar systems. In this paper, we present the first investigation of the interaction of a spherical polyelectrolyte brush (SPB)^{18–23} with a cationic surfactant cetyltrimethylammonium bromide (CTAB). We use SPB with long chains grafted to a poly(styrene) core of 56 nm in radius. The structure of these particles is shown schematically in Figure 1. The polyelectrolyte shell is made up by the strong electrolyte poly(styrenesulfonate) (PSS), which is charged regardless of the pH or salt concentration within the system.²⁰ In this quenched polyelectrolyte brush,^{18,20} the pH is therefore not a decisive variable. The grafting density of the brush is of the order of 0.1 nm^{-2} . These well-defined core–shell latexes were prepared by photoemulsion polymerization.¹⁹ Previous work done on these systems has demonstrated that spherical polyelectrolyte brushes present well-defined model systems that can be compared directly to the respective planar brushes.^{18–23}

Two aspects of the previous work on SPB are central for the present study: (i) Nearly all counterions are confined within the brush layer and thus create an enormous osmotic pressure within this layer.^{12,13} For the quenched SPB under consideration here, this has been shown directly by osmotic measurements.²¹ Most of the confined counterions are directly bound to the polyelectrolyte chains.²⁸ (ii) Spherical polyelectrolyte brushes present an ideal model system for studies by cryogenic transmission electron microscopy (cryo-TEM).²³ The suspension of the particles is vitrified by rapid freezing and the spatial structure of the particles can be studied directly; no staining or other preparatory steps are necessary. Hence, the formation and the spatial structure of the complex of the SPB with the surfactant CTAB can be seen and analyzed directly.

Materials and Methods

Reagents. Sodium bromide (Merck, analytical grade) and hexadecyltrimethylammonium bromide were used as received. Water was purified by reverse osmosis and subsequent ion exchange (Millipore Milli-Q). The SPB nanoparticles synthesized and characterized as described previously^{19,20} have low polydispersity as determined by transmission electron microscopy. The grafting

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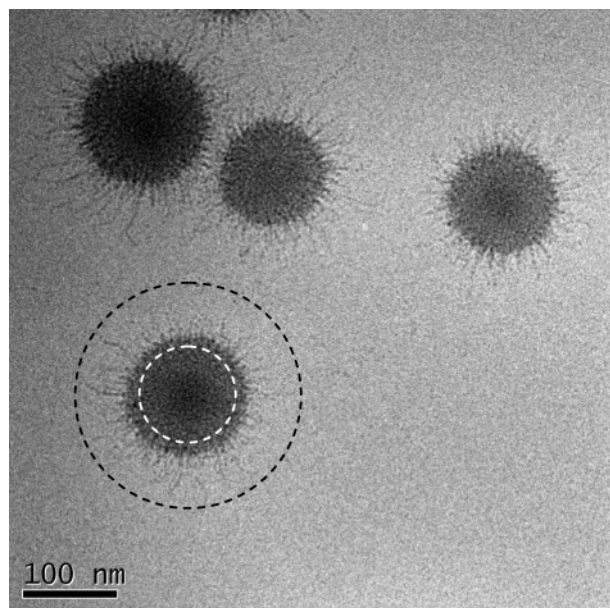


Figure 4. Cryo-TEM image of the PSC at a charge ratio of 0.6 in salt-free solutions (see arrow 1 in Figures 2 and 3). The radius of core indicated by a short-dashed line is 56 nm. The radius of polyelectrolyte–surfactant shell obtained from the DLS experiment is indicated as a long-dashed line.

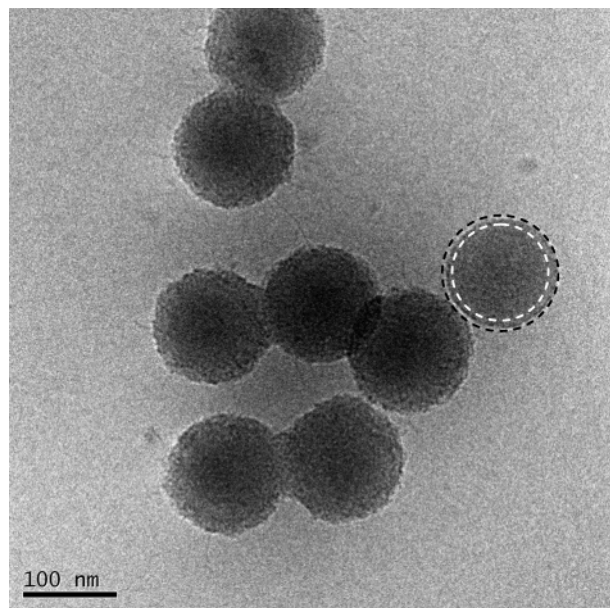


Figure 5. Cryo-TEM image of the PSC at a charge ratio $r = 1$ in salt-free solutions (see arrow 2 in Figures 2 and 3). The radius of core indicated by a short-dashed line is 56 nm. The radius of polyelectrolyte–surfactant shell obtained from the DLS experiment is indicated as a long-dashed line.

density is of the order of 0.1 nm^{-2} . The hydrodynamic radius is 188 nm as measured by dynamic light scattering (DLS) in 1 mM NaBr solution.

The aqueous solutions of polyelectrolyte–surfactant nanoparticle complexes were prepared by mixing concentrated solutions of the respective surfactant and the latex suspension (0.1 wt %) in order to get the required charge ratio r . This parameter characterizes a degree of binding of surfactant monomers by the brush surface and is calculated as the ratio of the number of positive charged ions to the total number of sulfonate groups in the polyelectrolyte layer. The latter number can be determined precisely from titration experiments. In order to ensure equilibrium, all samples were prepared a day before doing the analysis.

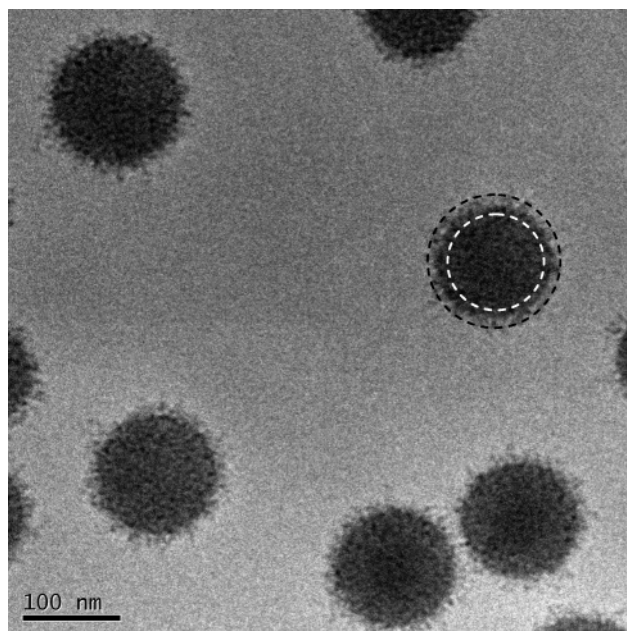


Figure 6. Cryo-TEM image of the PSC at a charge ratio of 0.6 in 0.05 M NaBr (see arrow 3 in Figures 2 and 3). The radius of polyelectrolyte–surfactant shell is ~ 30 nm and corresponds to the one obtained from the DLS experiment (long-dashed circle).

Methods. Cryo-TEM specimens were prepared by vitrification of thin liquid films supported on a TEM copper grid (600 mesh) in liquid ethane at its freezing point. Details of the procedure may be found in ref 23. The size (hydrodynamic radius) and electrophoretic mobility of the spherical nanoparticles were studied by dynamic and electrophoretic light scattering methods. The measurements were carried out with the Zetasizer Nano ZS, Malvern Instruments (4-mW He–Ne laser of 633 nm) at 25 °C under an angle of 173°. For all our samples, the folded capillary cells (Malvern Instruments) were used in the electrophoretic mobility study and glass cuvettes to measure the size. Scattering data were analyzed by the CONTIN algorithm to estimate the diameter of the nanoparticles.

Results and Discussion

As demonstrated in previous investigations, DLS is ideally suited to determine the overall size of the spherical polyelectrolyte brushes in solution.^{19,20} DLS leads to the hydrodynamic radius R_H of the particles with great precision. Since the radius R of the practically monodisperse core particles¹⁹ is known precisely, the thickness L of the polyelectrolyte layer on the surface of these core particles (see Figure 1) can be obtained through $L = R_H - R$. Previous work done by DLS on quenched SPB has demonstrated that L decreases with increasing salt concentration.²⁰ This is due to the increasing ionic strength, which causes the transition from the osmotic brush to the salted brush at high salt concentration.^{12,13,15,18–20} However, while electrostatic interaction will determine the brush height L at low salt concentrations, ion-specific interactions may play a role at higher salt concentrations and may even lead to a total collapse of the brush layer.^{16,29} For the SPB, this is followed by a flocculation of the particles.²⁹ The phase transition within the brush layer can be reversed at higher concentrations of added salt leading to a salting-in again.²⁹ These investigations have also demonstrated that equilibrium may always be attained in the brush layers due to their relatively small height L of the brush layer (30–200 nm).

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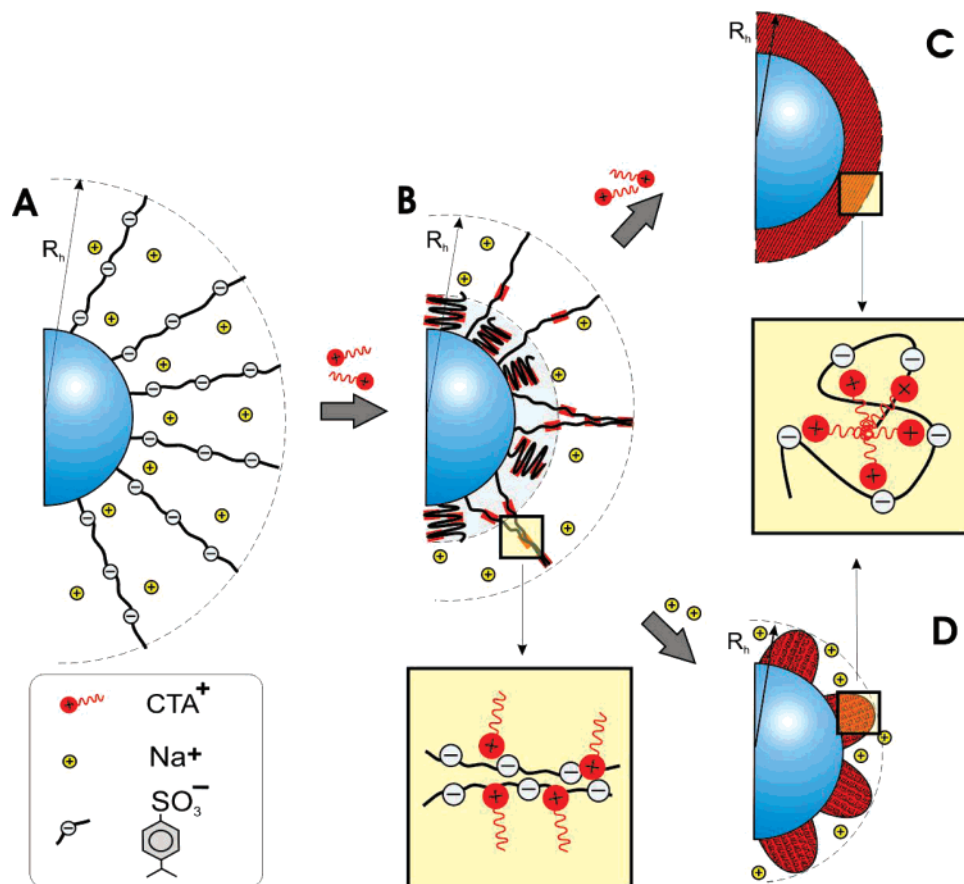


Figure 7. Schematic model of the spatial structure of the complexes from spherical polyelectrolyte brushes and the cationic surfactant CTAB. Model A corresponds to the spherical polyelectrolyte brush in salt-free solution, that is, with sodium counterions. Models B and C refer to the complex of the brush particles with CTAB at $r = 0.6$ (B) and 1.0 (C) at a low ionic strength. This corresponds to the cryo-TEM images in Figures 4 and 5, respectively. Model D refers to the structure formed by the brush particles and the surfactant at a higher ionic strength (50 mM NaBr). The corresponding cryo-TEM image is shown in Figure 6.

Figure 2 displays the brush thickness L of the SPB measured in dilute solution (0.01 wt %) in the presence of an increasing concentration of CTAB. The parameter of the curves is the ionic strength in solution. At lowest ionic strength (squares in Figure 2), there is a marked decrease of L even at the smallest surfactant concentration. It needs to be noted that the concentration of CTAB is far below its cmc (10^{-3} M) but of the same order of magnitude as the critical association concentration of free PSS chains (see ref 6). The dashed line shows the experimental data obtained by DLS upon addition of the same amount of NaBr.

Virtually no shrinking takes place due to screening of charges at these low concentrations. This indicates that the interaction of CTAB with the brush layer is mainly determined by hydrophobic interaction of the alkyl chains of the surfactant with the hydrophobic parts of PSS chains.

Adding salt leads to a marked shrinking of the brush layer as already observed in previous investigations.^{15–17,19,20,26} If added salt is present, adding CTAB leads to a marked shrinking as well that, however, is less pronounced than in the case of salt-free solutions. Moreover, a new feature enters above $r = 0.6$: Here the suspension flocculates, and it is evident that the colloidal stabilization of the SPB by the polyelectrolyte chains is not operative anymore.

Figure 2 indicates that there must be a strong binding of CTAB even at lowest surfactant concentrations. This is well supported by a qualitative analysis of the electrophoretic mobility μ of the SPB as the function of CTAB concentration. Neglecting the contribution of the counterions to the measured mobility, μ is

proportional to the effective charge of the particles and inversely proportional to its hydrodynamic radius R_H .³⁰ Figure 3 therefore displays the product of μ and the hydrodynamic radius R_H . From the strong decrease of the effective charge that is evident from Figure 3 we conclude that virtually all of the CTAB molecules in the system are taken up by the brush layer. This is in accordance with previous studies.²⁶

As already mentioned in the Introduction, cryo-TEM allows us to observe directly the structure of the complex between the SPB and CTAB. It should be noted that the surface layer of the PSS chains in the absence of CTAB is practically invisible in the cryo-TEM images. The contrast provided by the sodium counterions is too small and heavy ions such as, for example, cesium or iodine counterions would be needed.²³

We first discuss the experiments done in salt-free solutions. The cryo-TEM images of PSS/CTAB complexes shown in Figure 4 and Figure 5 refer to the charge ratio $r = 0.6$ (arrow 1 in Figures 2 and 3) and $r = 1.0$ (arrow 2 in Figures 2 and 3, respectively), both taken in salt-free solutions. Both clearly indicate the core-shell morphology of the SPB and their complexes with CTAB. The larger long-dashed lines around one particle indicate the overall dimensions as determined by DLS while the smaller dashed circle indicates the size of the core. Figure 4 and Figure 5 now give a clear idea of the structural transition effected by adding CTAB: The contraction of the surface layer as measured through the decrease of L (see Figure

(30) Evans, D. F.; Wennerström, H. *The Colloidal Domain Where Physics, Chemistry, and Technology Meet*; Wiley-VCH: New York, 1994.

2) is brought about by a strong adsorption of surfactant to the polyelectrolyte chains. At $r = 0.6$ displayed in Figure 4, chainlike objects extending from the surface become visible. Since single chains are practically invisible under the present conditions, we conclude that a part of the chains have aggregated to form bundles. However, the hydrodynamic radius of the particles is still considerably higher than the extension of the chains or aggregates seen in Figure 4. Obviously, there must be a part of the chains that do not aggregate but remain strongly stretched as in the surfactant-free state.

Figure 5 shows that the surface layer is entirely collapsed if the charge ratio r is adjusted to unity. The surfactant has been fully adsorbed by the polyelectrolyte brush layer, and the now hydrophobic chains of the polyelectrolyte/surfactant complex form a dense layer. Since $r = 1$, all electrostatic repulsion is gone and the bundlelike aggregates seen for $r = 0.6$ must collapse. This is also evident from the hydrodynamic radius indicated by the larger dashed circle in Figure 5. Here R_H agrees with the dimensions of the particles visible by cryo-TEM. The full collapse of the chains attached to the surface must obviously lead to a total loss of colloidal stability. Hence, the complex of the SPB and CTAB must flocculate, which is indeed observed. This is also evident from Figure 5 showing clusters of aggregated SPB spheres.

Figure 6 displays the cryo-TEM micrographs referring to a charge ratio $r = 0.6$ but at higher ionic strength (0.05 M NaBr). Evidently, the long bundlelike aggregates are gone and much smaller globular structures become visible that are attached directly to the surface. Moreover, the hydrodynamic radius (see larger dashed line in Figure 6) virtually coincides with the overall dimensions of the particles. Thus, the rather high ionic strength leads to a screening of the mutual repulsion of the still negatively charged surface structures at $r = 0.6$. The colloidal stability is very weak, and adding more surfactant at this ionic strength is followed by flocculation. However, the residual interaction between the complexes attached to the surface prevents the formation of a dense surface layer as observed at $r = 1.0$ (see Figure 5).

All findings discussed in conjunction with Figures 2–6 suggest that the adsorption of the hydrophobic CTA⁺ ions leads to marked structural changes at the surface of the spherical polyelectrolyte brushes. A possible explanation of these observations, in particular of Figure 4, may be sought in a collapse of the brush layer due to the partial hydrophobization of the polyelectrolyte chains by the adsorbed CTAB. Recent theoretical models suggest that under certain conditions the collapse of a polymer or polyelectrolyte brush can be accompanied by an intrabrush microphase segregation and bimodal distribution of the chains with respect to their extension above the surface. Hence, a dense layer is formed near the grafting surface by a population of collapsed chains, while other chains remain extended in the solution and form a dilute peripheral part of the brush. This part determines the hydrodynamic radius. In particular, in ref 31 this mechanism was proposed in the case of brush collapse due to formation of

clusters comprising multiple monomers of grafted chains. Pryamitsyn et al.³² have demonstrated that a weakly dissociated polyelectrolyte brush may undergo a collapse transition in a poor solvent resulting in a bimodal distribution of the surface chains. A bimodal chain end distribution has also been predicted in ref 33 where complexation of nonionic polymer brushes with surfactants has been considered. This theoretical model is in qualitative agreement with the interpretation of Figure 4. A part of the chains not included in this surface layer is seen from the hydrodynamic radius, which is still of appreciable magnitude. Hence, there must be a bimodal chain end distribution.

Conclusion

Figure 7 summarizes the above findings in a schematic manner: At low ionic strength, that is, without added salt, the surfactant ions form a complex with the polyelectrolyte chains on the surface of the SPB already at lowest concentrations of the surfactant. This strong tendency for assembly is driven by ionic attraction and by the hydrophobic interaction of the alkyl moieties. This was already obvious from previous investigations using planar brushes.^{25–27} The entirely new feature shown here by cryo-TEM is the formation of bundlelike aggregates at finite charge ratio r leading to a laterally inhomogeneous surface layer (see Figure 4). The peculiar structure is thus indicative for a collapse transition³¹ of the surface layer due to the partial hydrophobization of the polyelectrolyte chains. This is shown schematically in Figure 7B. This transition within the brush layer leads to a bimodal distribution of the chains where a part is localized in a dense surface layer and another part still is stretching out as is seen from the hydrodynamic radius of the particles. If the ionic strength is increased by adding NaBr, the collapse of the brush induced by added surfactant is not accompanied by intrabrush segregation and only collapsed (relatively dense) layer proximal to the surface is found. Moreover, in this regime, the collapsed layer may lose its lateral continuity and split into pinched collapsed domains (see Figure 7D). Only if $r = 1$, at total collapse is seen regardless of the salt concentration (Figure 7C) and the PSS chains together with the CTAB form a dense homogeneous layer on the surface of the core. The balance of hydrophobic attraction and electrostatic repulsion can therefore lead to a collapse transition of the surface layer, which is laterally inhomogeneous.

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