Communication

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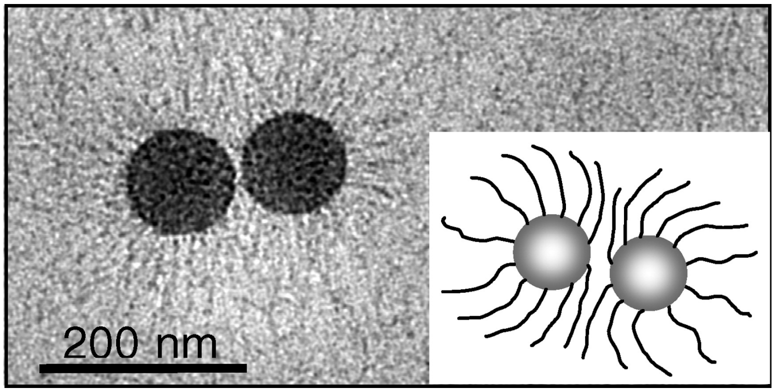

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# High Elongation of Polyelectrolyte Chains in the Osmotic Limit of Spherical Polyelectrolyte Brushes: A Study by Cryogenic Transmission Electron Microscopy

Alexander Wittemann,*,[†] Markus Drechsler,[‡] Yeshayahu Talmon,[§] and Matthias Ballauff*,[†]

*Physikalische Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany*

Received March 2, 2005; E-mail: Alexander.Wittemann@uni-bayreuth.de; matthias.Ballauff@uni-bayreuth.de

If long chains of polyelectrolytes are affixed to planar or curved surfaces, a polyelectrolyte brush results.[1] The term "brush" denotes a polymeric layer where the radius of gyration of the individual chains is much greater than the average distance of the grafting points. Spherical polyelectrolyte brushes (SPB) present colloidal particles onto which polyelectrolyte chains have been grafted. Pincus[2] as well as Borisov et al.[3] were the first to predict that the counterions are mostly localized within the brush layer. Hence, the thickness of the brush is determined by a balance of the osmotic pressure of the entrapped counterions within the layer and the configurational elasticity of the chains. In the *osmotic regime* at low ionic strength the polyelectrolyte chains are nearly stretched to full length (osmotic brush). In contrast, at high ionic strength electrostatic interactions within the brush layer are screened, and the *salted brush* resembles a neutral polymer brush.[4]

The marked osmotic pressure within the brush layer is therefore the decisive feature of planar[4] as well as of spherical polyelectrolyte brushes.[5] It can be used to generate metallic nanoparticles within the brush layer using the confinement of gold or silver ions.[6] Moreover, partial counterion release is the driving force for the adsorption of proteins to SPB.[7]

Here we present for the first time model-independent, direct cryo-transmission electron microscopy (cryo-TEM)[8] images of polyelectrolyte chains in the osmotic limit, preserved in their native state. We use the spherical polyelectrolyte brushes shown schematically in Figure 1. Long chains of poly(styrene sulfonate) have been grafted to core particles made from poly(styrene) latex of 100-nm diameter. The polyelectrolyte shell is made up of the strong electrolyte poly(styrene sulfonate). The grafting density of the brush is in the region of 0.1 nm$^{-2}$. These well-defined core−shell latexes were prepared by photoemulsion polymerization.[9]

To enhance the contrast of the particles in the micrographs, cesium ions were induced by ultrafiltration. In a second step bovine serum albumin (BSA) was adsorbed within the brush layer. A previous SAXS study has shown that BSA fully penetrates into the polyelectrolyte brush.[10] Cryo-TEM specimens were prepared by vitrification of thin liquid films supported on a TEM copper grid (600 mesh, Science Services, Munich, Germany) in liquid ethane at its freezing point. The specimen was inserted into a cryo-transfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss EM922 EFTEM (Zeiss NTS GmbH, Oberkochen, Germany). Examinations were carried out at temperatures around 90 K. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images were taken under reduced dose conditions (500−2000 e/nm$^2$). All images were recorded digitally by a bottom-mounted CCD camera system (UltraScan 1000, Gatan, Munich, Germany) and processed with a digital imaging processing system (Digital Micrograph 3.9 for GMS 1.4, Gatan, Muenchen, Germany).

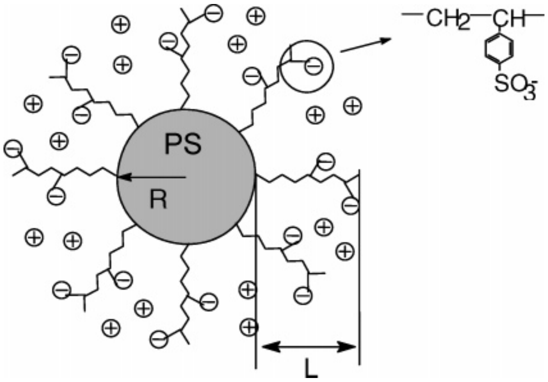

***Figure 1.*** Schematic representation of the spherical polyelectrolyte brush. The colloidal particles consist of a poly(styrene) core onto which long chains of poly(styrene sulfonate acid) (PSS) have been grafted. The thickness of the brush, given by *L*, depends on the osmotic pressure of the counterions that are confined in the brush layer. If no salt is added (osmotic limit), the strong osmotic pressure is stretching the chains to nearly full length. Hence, *L* is of the order of $L_c$, the contour length of the polyelectrolyte chains.[5]

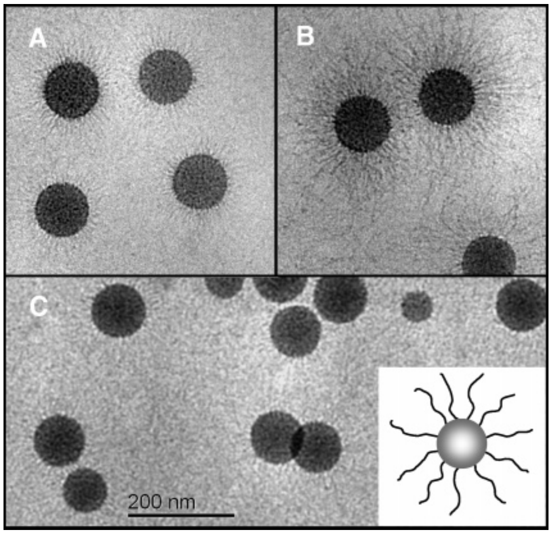

***Figure 2.*** Cryo-TEM images of vitrified 1 wt % SPB suspensions. The contrast is enhanced compared to the original particles (C) by replacing the sodium counterions of the polyelectrolyte chains by cesium ions (A) and, additionally, by BSA molecules (537 mg per g SPB) which are adsorbed in close correlation to the polyelectrolyte chains (B).[10]

The cryo-TEM image in Figure 2 clearly indicates the core−shell-morphology of the brush particles. The images show a core diameter in the range of 100 nm which is in full accordance with DLS data.[5] The shell of polyelectrolyte chains is visible, and Figure

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[†] Physikalische Chemie I, University of Bayreuth, 95440 Bayreuth, Germany.
[‡] Makromolekulare Chemie II, University of Bayreuth, 95440 Bayreuth, Germany.
[§] Permanent address: Department of Chemical Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel.

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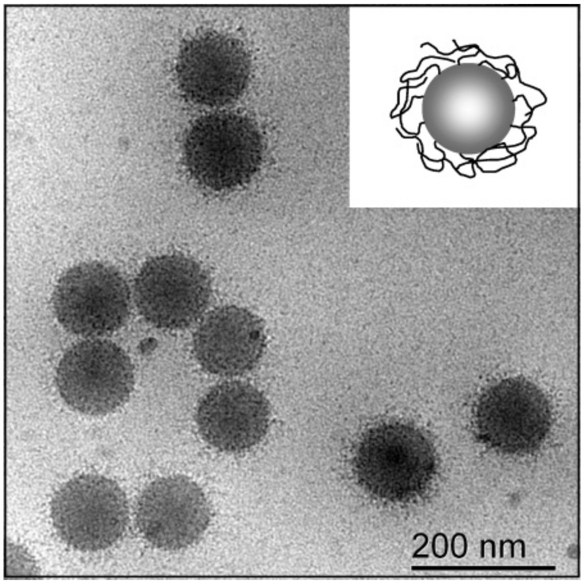

***Figure 3.*** Vitrified 1 wt % suspensions of SPB in MES buffer (pH 6.1) loaded with 125 mg BSA per gram SPB. The image clearly demonstrates that the brush layer is nearly collapsed at high ionic strength (507 mM added salt).

2 suggests that the chains are strongly stretched, as expected. However, the contrast induced by the cesium ions is too low to render the polyelectrolyte chains clearly visible.

Proteins such as BSA can be absorbed within the polyelectrolyte layer, if the ionic strength is low.[7] A recent SAXS study has demonstrated that the BSA molecules are closely correlated to the polyelectrolyte chains.[10] Since BSA has good contrast in TEM, the adsorbed protein molecules should make the polyelectrolyte chains clearly visible. Figure 2 demonstrates that this is the case indeed: The brush layer can now be resolved up to a thickness of 130 nm which is already quite close to the DLS results of 169 nm. Hence, the marked elongation of the polyelectrolyte chains in the osmotic limit can be made visible by cryo-TEM. Moreover, Figure 2 corroborates the analysis by SAXS inasmuch the strong correlation of the BSA molecules to the polyelectrolyte chains is immediately evident.

Cryo-TEM may also be used to monitor the transition from the osmotic brush to the salted brush at high ionic strength. Studies by dynamic light scattering have demonstrated that the chains are coiled again in this limit.[5] The contrast was enhanced by adsorbing a small amount of BSA (125 mg/g SPB) and adjusting the pH to 6.1. Figure 3 displays the cryo-TEM image of the salted SPB. It demonstrates that the polyelectrolyte layer on the surface has indeed become much thinner than the one observed in the osmotic limit.

Figures 2 and 3 also show that there are many configurations in which two or more particles lie close to each other. The reasons for this unexpected finding is not yet clear, because all investigations done in dilute solutions have not indicated any attractive force between these particles. Nevertheless, configuration in which two particles are located near to each other may now be used to study the conformation of the polyelectrolyte chains for two interacting SPB.

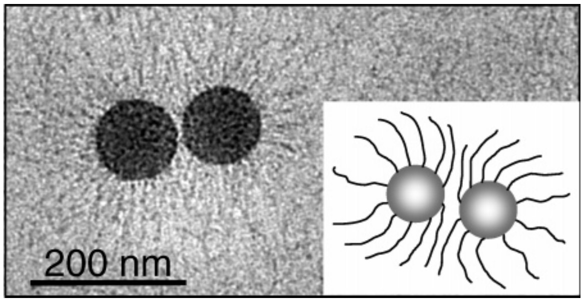

***Figure 4.*** Interaction of SPB in suspension: when two particles approach each other, the electrostatic repulsion leads to distortion of the spherical geometry of the brushes which seems to lead to bending of the chains.

Figure 4 shows a typical example of interacting SPB at low ionic strength. Most cryo-TEM images indicate that the chains of the two brush layers are bending away when two particles approach each other. Recently, a retraction of overlapping particles was also predicted for polyelectrolyte stars.[11]

In conclusion, cryo-TEM is shown for the first time to directly image the osmotic limit of polyelectrolyte brushes: The chains are strongly stretched in the osmotic limit but assume a coiled conformation in the limit of the salted brush. Moreover, the present data strongly suggest that spherical polyelectrolyte do not interdigitate. Work is under progress to improve the resolution and obtain finer details of the system.

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