

Shape Investigations of Charged Block Copolymer Micelles on Chemically Different Surfaces by Atomic Force Microscopy

M. Regenbrecht, S. Akari,* S. Förster, and H. Möhwald

Max-Planck-Institute of Colloid and Interface Science, 14424 Potsdam, Germany

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In the present paper, shape transitions of charged diblock copolymer micelles of Poly(ethylethylene-*b*-styrene sulfonic acid) (PEE-PSSH) were studied by dynamic scanning force microscopy (SFM) above the glass transition temperature of the polymer. Changing the ionic strength in the applied solution induced shape transitions from spherical micelles to network-like structures and/or spherical vesicles have been observed. The adsorption behavior of the structures was studied on different chemical surfaces. Neutral (Graphite) as well as positively charged (Polyethylenimine- and MgCl_2 -modified) mica surfaces were applied for this purpose. The adsorption structures of the micellar aggregates on a substrate is strongly influenced by the chemical modification of the surface. The formation of vesicles on positively charged surfaces from vesicle free solutions could also be observed.

Introduction

Among the block copolymers, amphiphilic diblock copolymers are attracting increasing attention due to their ability to build well defined geometrical structures via self-assembly in corresponding solutions. Spherical micelles with a size in the nanometer-range, vesicles in the microsecond down to the nanometer range, and wormlike structures with variable persistence lengths can be formed, and shape transitions can be induced in a controlled manner by varying the conditions in the solutions, e.g., the ionic strength and the pH.^{1–4} A large number of these aggregates are spherical with a core of an insoluble, and a shell of a soluble, block.^{5–7} Their similarity to biological systems in the nanometer-range and their shape transitions give an interesting aspect in the development of models for biological cells.^{8,9} An increasing number of practical applications of amphiphilic block copolymers are attracting industrial attention, e.g., in microemulsions, block copolymers can function as stabilizers or as reactors to create nanoparticles and nanostructured materials, for the enhancement of drug solubility, or for extracting contaminated solids.^{10–14} In view of these important applications, fundamental structural studies of the block copolymer aggregates down to the nanometer scale are essential for understanding the growth processes. Thus intensive efforts by several groups are in progress to investigate their morphology: light-scattering methods,^{14–17} time-resolved fluorescence spectroscopy,¹⁸ and X-ray and neutron scattering^{19–22} were performed on various systems. Shape transitions on the so-called crew-cut aggregates could be observed by using transmission electron microscopy (TEM),^{1,2,4} but this technique is almost not applicable to liquid samples.

Scanning force microscopy (SFM) is becoming an efficient tool to image single polymers and biomolecules^{23,24} to obtain information about the elasticity of single polymer chains²⁶ or even to image individual polyelectrolyte molecules with chemical sensitivity.^{28,29} SFM-studies of diblock copolymers

in the solid state with equally long blocks and with high glass transition temperatures $> 80^\circ\text{C}$ were performed by Spatz et al.^{30–32}

In our study, the conformation of single diblock copolymer micelles of poly-(ethylethylene-*b*-styrene sulfonic acid) (PEE-PSSH) and their adsorption behavior on chemically different surfaces were a subject of investigations using scanning force microscopy. Various hydrophobic, as well as hydrophilic, substrates with atomically flat surfaces were used as received or have been chemically modified to get a positively charged surface. An adsorption of the diblock-copolymers on the latter surfaces is preferred since the sulfonic acid block is negatively charged. The soft hydrophobic PEE block has a glass transition temperature of -25°C . Thus, PEE-PSSH block copolymers can be directly dissolved in water even at large degrees of polymerization of the PEE block (> 1000). This fact enables for the first time the study of micellar shape transitions under thermodynamic equilibrium conditions. Shape transitions are expected for these micelles due to varying the ionic strength in the solution. Current investigations of PEE-PSSH solutions made by Förster et al.²² using light and small-angle neutron scattering showed the presence of different micellar topologies such as spherical micelles or vesicles. Scattering curves of solutions at higher salt concentrations indicated the formation of more complex particle shapes, whose structure could not be elucidated unambiguously. Therefore, an aim of this study is to investigate the aggregation behavior of the formed PEE-PSSH micelles at different ionic strengths. It will also be shown that analogous to the surfactants,^{33,34} amphiphilic block copolymers merge to vesicles and not only to wormlike micelles, if the ambient conditions such as ionic strength and concentration have been changed.

Experimental Section

The PEE-PSSH was prepared from a polystyrene-*b*-polybutadiene precursor by subsequent hydrogenation and sulfonation. It has a degree of polymerization of $N_{\text{PEE}} = 144$ and $N_{\text{PSSH}} = 136$, a degree of sulfonation of 85%, and a molecular weight of 29330 g/mol. PEE-PSSH aggregates were adsorbed onto

* Author to whom correspondence should be addressed.

TABLE 1: Observed Heights of Aggregates Adsorbed from a PEE-PSSH Solution Containing no NaCl

surfaces/ aggregates	HOPG height [nm]	PEI surface height [nm]	MgCl ₂ surface height [nm]
vesicles	12	20	2.5–6
micelles	3	2–3	0.7

TABLE 2: Observed Heights of Aggregates Adsorbed from a PEE-PSSH Solution Containing a NaCl Concentration of 0.05 Mol/L

surfaces/ aggregates	HOPG height [nm]	PEI-surface height [nm]	MgCl ₂ -surface height [nm]
vesicles	12	4	2.5–6
micelles	3	1.7	1

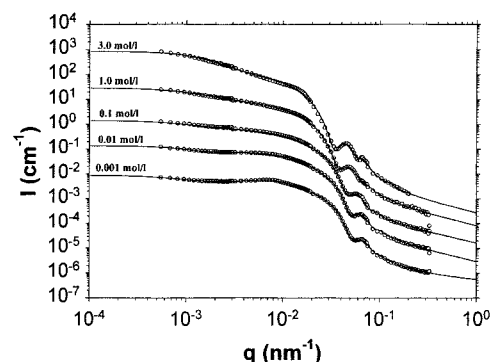
TABLE 3: Observed Heights of Aggregates Adsorbed from a PEE-PSSH Solution Containing a NaCl Concentration of 1 mol/L

surfaces/ aggregates	HOPG height [nm]	PEI surface height [nm]	MgCl ₂ surface height [nm]
vesicles	12	16	
micelles	2.5		1.2

different substrates. As a neutral and hydrophobic substrate, samples of highly oriented pyrolytic Graphite (HOPG) were cleaved simply by the use of an adhesive tape. Positively charged surfaces were obtained by modifying freshly cleaved mica surfaces by covering the surface with a layer of the positively charged polyethylenimine (PEI) or by ion exchange of the K⁺ ions located between the crystal layers of the mica with bivalent ions of Mg²⁺. The mica sheets were dipped into an aqueous 10^{−7} mol/L MgCl₂ solution for 1 min and dried with a stream of argon or immersed into an aqueous 10^{−4} mol/L PEI solution, rinsed with water for 1 min, and dried under an argon stream.

Freshly cleaved graphite and chemically modified mica surfaces were immersed in aqueous PEE-PSSH solutions containing different NaCl concentrations. Varying the immersion time regulated the adsorption density. For the creation of monolayers of PEE-PSSH, the substrates were dipped in the prepared solutions for few seconds and dried under an argon stream immediately. The final concentrations are given in Tables 1–3. To exclude a possible influence on the morphology due to the preparation method, we prepared the PEE-PSSH solution following two different ways: The PEE-PSSH was dissolved in water purified by a Millipore Q apparatus in an ultrasonic bath. After the solubilization and addition of different NaCl concentrations, we arrived the solutions mentioned in Tables 1–3. In the second way of preparation, the PEE-PSSH was dissolved in the final NaCl solutions at 70 °C for 13 h. The PEE-PSSH concentration was kept at 1.7 × 10^{−6} mol/L. These solutions were used for the AFM measurements. No differences between these two ways of preparation could be observed.

The SFM measurements have been performed using a standard atomic force microscope (Nanoscope Multimode IIIa, Digital Instruments, Santa Barbara). The microscope was operated in the TappingMode using silicon tips at resonance frequencies of 290–310 kHz under ambient conditions. The cantilever was forced to oscillate near its resonance frequency. The laser beam was centered on the tip of the cantilever and reflected on a photodiode. Because of the vertical oscillation of the tip, a sinusoidal signal results. When the tip approaches the surface, a damping of the free amplitude is taking place due to the interaction between the tip and the surface. The feedback system compares the low pass filtered amplitude (damped) with a set point in order to keep the tapping force at

**Figure 1.** SLS/SANS curve obtained for PEE-PSSH solution containing 5 g/L.

a constant value by piezoelectrically controlling the cantilever movement. The deflected laser beam contains information about the vertical height and surface properties. To minimize the surface deformation of the sample by the tip, the so-called “light tapping” was applied.³⁵ This means that the r_{SP} ratio, which is defined as $r_{SP} = A_{SP}/A_0$, was about 0.8, where A_{SP} is the set-point amplitude and A_0 is the free amplitude in air. The free amplitude of the oscillation was about 40 nm. The spring constants of the used cantilevers are in the range of 40 N/m with tips of a curvature radius >10 nm (Nanosensors, Jena, Germany).

Additionally, a comparison between structures present in the bulk solution with adsorbed morphologies was possible by static light scattering (SLS) and small angle neutron scattering (SANS) measurements. The concentration of the used polymer solution was 1.7 × 10^{−4} mol/L. Details of the instrumentation, data reduction and analysis of the scattering curves can be found in the accompanying publication.

Results and Discussions

The aggregate structures in solution could be characterized by SLS and SANS. Figure 1 shows the measured SLS/SANS curves for polymer solutions at various salt concentrations increasing from 0.001 to 3 mol/L. The solid lines are fits to analytical expressions for form factors of fractal networks and spherical micelles. One can observe a characteristic Porod q^{-4} scattering at large scattering vectors ($q > 0.02 \text{ nm}^{-1}$) arising from micellar cores. From the position of the damped oscillations one obtains the micellar core radii which increase from 9.2 nm at the lowest salt concentration to 13.7 nm for the highest salt concentration. Above a salt concentration of 0.1 mol/L one observes a characteristic linear increase (in the double logarithmic presentation) of the scattering intensity at low q ($q < 0.01 \text{ nm}^{-1}$) due to the formation of large self-similar associate structures. The low- q -scattering is most pronounced for the highest salt concentration indicating the presence of very large networks. The scattering curves can be analyzed quantitatively as outlined in ref 22 to obtain the size and fractal dimension as well as the topological structure of the networks. Accordingly, toroid micronetworks of fractal dimension 1–2 are formed upon addition of salt to the dilute polymer solution.

Because of the SLS/SANS measurements mentioned above, expected aggregates of PEE-PSSH polymers in an aqueous solution in the absence of salt are spherical micelles with a diameter of about 20 nm, vesicles with a diameter of 70–150 nm, and network structures (see Figure 2a). Figure 2b schematically illustrates for clarity the confirmation of the PEE-PSSH aggregates on the used substrates at small NaCl concentrations as they were observed by scanning force microscopy. Adsorption

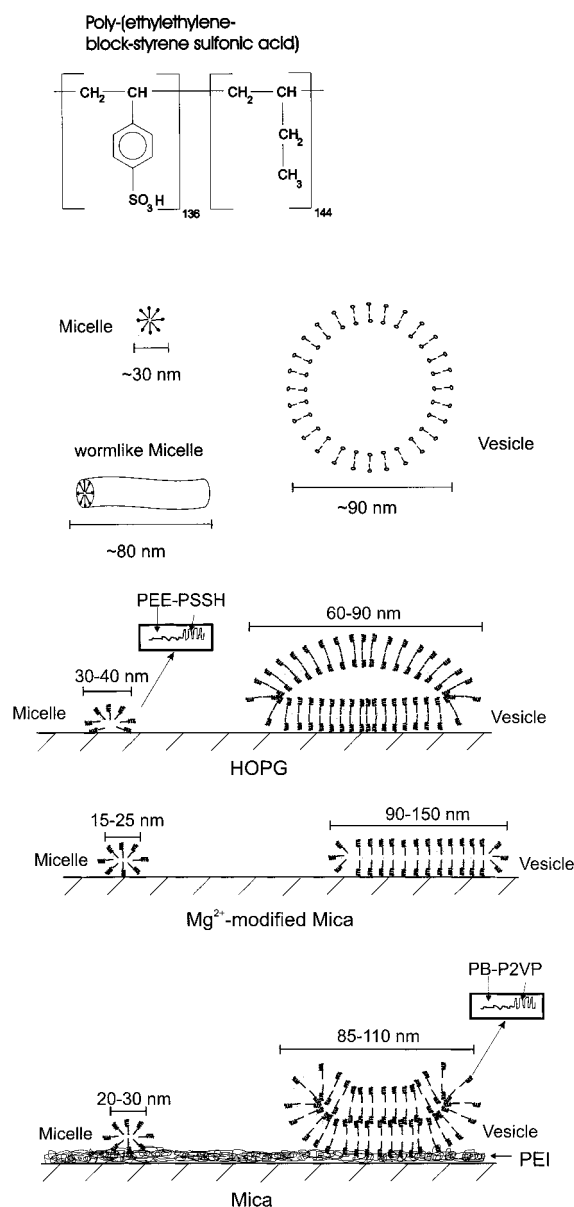


Figure 2. (a) Schematic diagram of the conformation of the PEE-PSSH aggregates in solution. (b) Schematic diagram of the aggregate shapes of PEE-PSSH diblock copolymers on the used substrates as they were observed by the SFM in this study at small concentrations of NaCl salt.

from an aqueous PEE-PSSH solution onto an HOPG surface resulted in single monodisperse spherical micelles with a diameter of 30–40 nm (Figure 3a). After the addition of NaCl salt (0.05 mol/L), we observed additional wormlike micelles with a diameter of 23 nm and a length of 70 nm and vesicles with a diameter of 70–90 nm (Figure 3b). Upon increasing the NaCl concentration to 0.5 mol/L, a further growth of the cylindrical micelles into micronetworks and a trend to build up loops was observed (Figure 3c). Adsorbing aggregates from a polyelectrolyte solution containing a NaCl concentration of 1 mol/L strong interlinking of the wormlike micelles could be determined (Figure 3d). These morphologies were very stable and could be even adsorbed from a 5-month-old solution standing at room temperature. From a solution containing 2 mol/L NaCl, a further growth of the vesicles up to a length of 190 nm was observed. A screening of the SO₃[−] ions probably caused a decrease of the electrostatic and steric repulsion between the hydrophilic chains by the Na⁺ ions added to the

solution. The smaller graft density on the ends of the spherical micelles leads to a one-dimensional growth and additional vesicle formation. The change of the morphology is directly correlated with the salt concentration. At small NaCl concentrations, vesicles with diameters of 70–90 nm and, at higher concentrations, vesicles with diameters of up to 190 nm were observed. From these results, we suppose that vesicles originate from spherical micelles. The fact that coiled wormlike micelles were observed is a result of the end-cap energy, which is large enough to favor bridging between wormlike micelles.³⁶ The growth of the cylindrical micelles and vesicles are equally preferred for polymer chains with approximately the same length.

The adsorption behavior of the aggregates was studied for positively charged surfaces of polyethylenimine- (PEI) and Mg²⁺-modified mica.^{37,38} On the PEI surface, adsorption of more than a monolayer of micelles and a relatively high density of vesicles for an equal immersion time is taking place. This is due to the expected electrostatic attraction between PEI molecules and the negatively charged PSSH segments without adding salt. The diameter of the vesicles was about 85–110 nm (Figure 4a). This diameter, however, could not be exactly determined, because of the high density of adsorbed aggregates. This fact will be discussed later on in this paper. Since at equal preparation conditions, vesicles could not be observed on Graphite surfaces, we conclude that the vesicles are not originating from the prepared solution and their growth has been induced on the PEI surface. This result is consistent with observations on the positively charged Mg²⁺ surface. An adsorption of the polyelectrolyte aggregates produced from solutions with a NaCl concentration of 0.05 mol/L resulted in fewer aggregates adsorbed on the PEI surface and a shape deformation of the vesicles (Figure 4b). Since on HOPG no shape deformations of the vesicles were observed for equal force conditions, a tip-induced deformation is unlikely. The Cl[−] ions compensate a part of the surface charge, which could be the reason for the less pronounced vesicle and micelle adsorption. Increasing the sodium chloride concentration to 1 mol/L leads to a total screening of the positive charge of the PEI molecules, and only very few aggregates could be adsorbed on the surface (Figure 4c). After dipping a Mg²⁺-modified mica surface into an aqueous PEE-PSSH solution, micellar structures (with typical diameter of vesicles) in a collapsed state as well as spherical micelles have been determined. The diameter of the vesicles and micelles were in the range of 90–150 and 15–25 nm, respectively (Figure 5a). Similar observations have been published by Feder et al. and Rädler et al.^{37,38} From these results we conclude that the bigger spreaded aggregates were vesicles. A convolution between tip and the aggregates can be neglected since the tip radius is smaller than 10 nm. Similar sizes and shapes were observed by adsorbing from a solution containing NaCl-concentrations of 0.05 mol/L (Figure 5b). At a NaCl concentration of 1 mol/L bigger aggregates and wormlike micelles could be observed (Figure 5c). The diameter of the wormlike micelles was in the range of 30 nm.

A disadvantage of the tapping mode force is that on soft molecules the measured heights do not correspond to the true heights.^{24,25} Since a deformation of the soft molecules by the tip is rather possible, the oscillation conditions of the tip are actually very critical parameters. In our measurements the r_{sp} value was varied to estimate the height dependency of the amplitude damping. From low to high damping ($r_{sp} = 0.8–0.4$) the height of aggregates was reduced from 3 to 2 nm for single micelles. Therefore, it cannot be excluded that even at

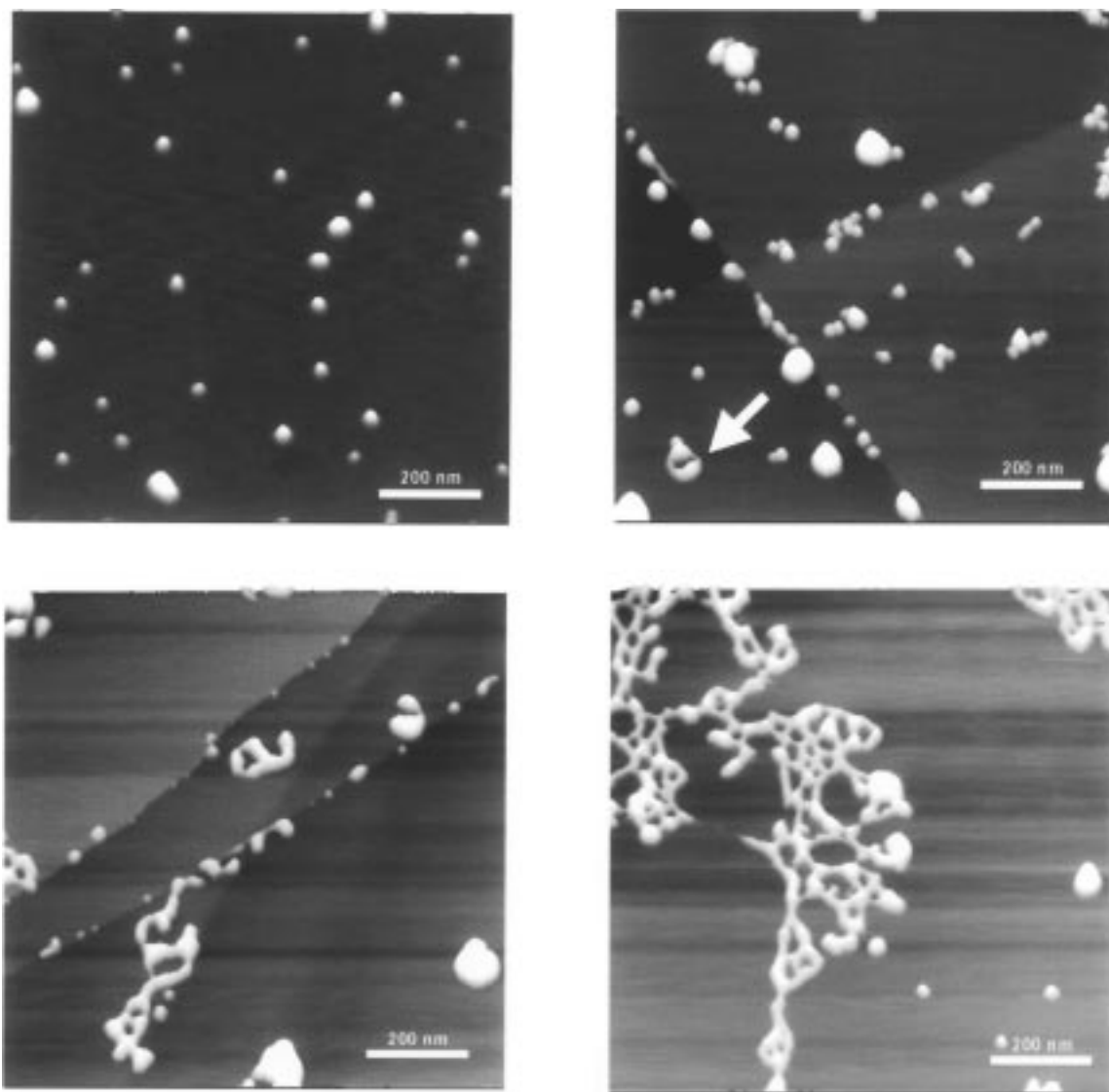


Figure 3. (a) SFM image (tapping mode, height) of polydisperse micelles on HOPG surface adsorbed from a PEE-PSSH solution without added NaCl. (b) SFM image (tapping mode, height) of spherical and wormlike micelles and vesicles on HOPG surface adsorbed from a PEE-PSSH solution containing a NaCl concentration of 0.05 mol/L. The white arrow indicates a single toroidal structure. (c) SFM image (tapping mode, height) of micelles, wormlike micelles and vesicles on HOPG surface from a PEE-PSSH solution containing NaCl concentration of 0.5 mol/L. (d) SFM image (tapping mode, height) of adsorbed aggregates on HOPG surface from a PEE-PSSH solution containing a NaCl concentration of 1 mol/L.

high r_{sp} -values a deformation is underlying. Nevertheless, since the apparent heights in our measurements are varying significantly by varying the substrates, a discussion although speculative seems to be necessary. From the investigations a correlation between the measured heights and the applied substrates was observed. On HOPG and Mg^{2+} surfaces the height of the aggregates was independent from the NaCl concentration for all structures (compare columns 1 and 2 of Table 1–3). On PEI surface the height is decreasing when adding NaCl salt (compare columns 2 of Table 1–3). Since from DLS measurements round structures of 30 nm have been observed, we conclude that the aggregates investigated are adsorbed in a compressed manner. On the hydrophobic and neutral HOPG surface the hydrophobic block of the aggregates is directly binding to the surface. On the positively charged PEI substrates the images show that the surface is completely covered with aggregates of PEE-PSSH (see granulate structures in Figure 4a). A part of the vesicles are embedded both in a layer of small size aggregates and collapsed vesicles, which have a large contact area to the PEI-surface (Figure 4a). Another part seems

to lay on the top of the aggregate layer (possibly with clearly less contact area to the PEI surface). The height of the latter part of vesicles is the highest observed (about 20 nm) and can be explained by the electrostatic repulsion between the negatively charged segments of the vesicles and the negatively charged layer of the PEE-PSSH aggregates. On the PEI-modified surface the measured average height of the micelles was in the range of 3 nm. At a salt concentration of 0.05–1 mol/L a deformation of the vesicles to ring like structures was observed and the height was reduced to 4 nm (Figure 4b). These ringlike structures could be a result of removing of the ambient solution from the hollow vesicles due to the absorption on positively charged surfaces. At the same time a reduction of the height of the micelles to 1.5 nm was observed. Because of the addition of small concentrations of NaCl salt (0.05 mol/L), a partial charge compensation of the negatively charged PEE-PSSH segments and the positively charged PEI surface occurs. This leads to a reduction of the electrostatic interactions between the vesicles/micelles and the surface. At large salt concentrations

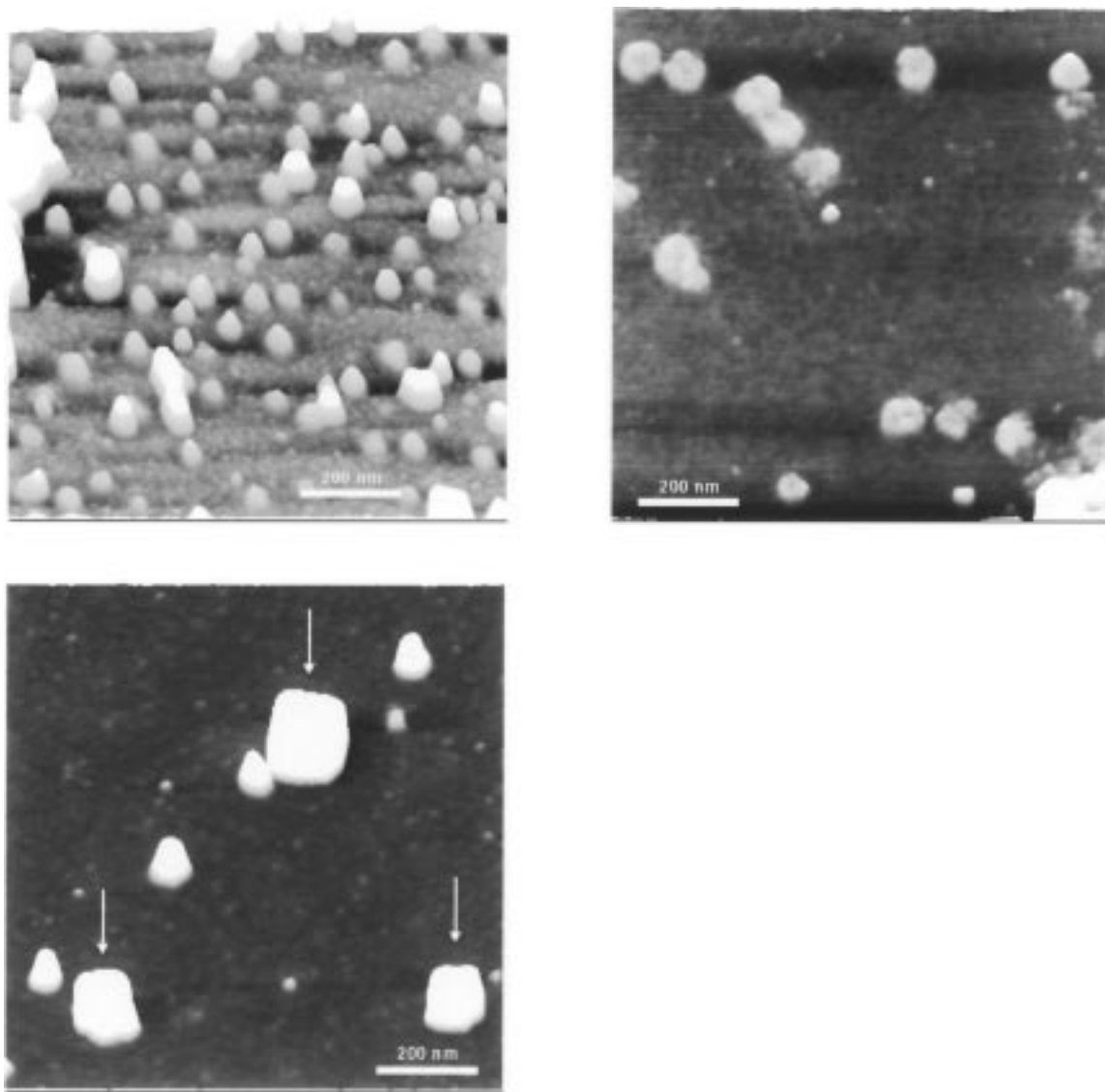


Figure 4. (a) SFM image (tapping mode, height) of PEE-PSSH micelles and vesicles adsorbed on a PEI modified surface from a solution without added NaCl. (b) SFM image (tapping mode, height) adsorption of micelles and compressed vesicles on a PEI-modified surface from PEE-PSSH solution containing a NaCl concentration of 0.05 mol/L. (c) SFM image (tapping mode, height) of vesicles, spherical micelles, and NaCl crystals on a PEI-modified surface from a PEE-PSSH solution containing a NaCl concentration of 1 mol/L. The arrows point at cubic NaCl crystals with some surrounding PEE-PSSH aggregates.

a complete neutralization is obtained and only van der Waals forces are acting resulting in an increase of the vesicle height to 16 nm.

Adsorbing the aggregates on Mg^{2+} modified Mica surfaces from a PEE-PSSH solution resulted in collapsed vesicles with clearly smaller heights in the range of 2–6 nm. Feder et al. and Rädler et al.^{37,38} observed similar structures. With NaCl concentrations of 0.05–1 mol/L, the same height as that for the salt-free solution was observed. Opposite to adsorption on the PEI-surface, only few small size aggregates could be observed on Mg^{2+} surfaces and also the density of adsorbed vesicles is reduced. This is due to a partial ion exchange of the K^+ ions with the Mg^{2+} ion during immersing in the solution.^{39,40}

Inspecting Figure 5a, it can be assumed that a part of the collapsed vesicles contains single micelles or even smaller vesicles. Most of the vesicles seem to be unilamellar. The micelles, adsorbed on MgCl_2 surface were of less height than that on HOPG and PEI surface (1 nm). Because of this considerable height difference, it can be expected that a thicker water layer on the hygroscopic MgCl_2 is embedding the micelles.

However, since the AFM measurements have been performed under atmospheric conditions, a deformation of the structures due the drying process cannot be excluded in this stage of experiments. Because of the hygroscopicity of the diblock copolymer micelles, a water film due to the air humidity will always be formed. Nevertheless, measurements under aqueous conditions are planned.

Conclusion

It could be shown that the direct visualization of micelles, vesicles and worm like micelles of diblock copolymers could be achieved by scanning force microscopy at temperatures over their glass transition temperature. Shape transitions of micelles to the rod like structures and spherical vesicles can be achieved in a reproducible way by varying the ionic strength of the solution. An important result of this work is that the adsorption structures on the substrate can be strongly influenced by the chemical nature of the surface. On strongly charged surfaces, the formation of structures, which are not existing in the solution, can be induced. The apparent heights measured are deviating

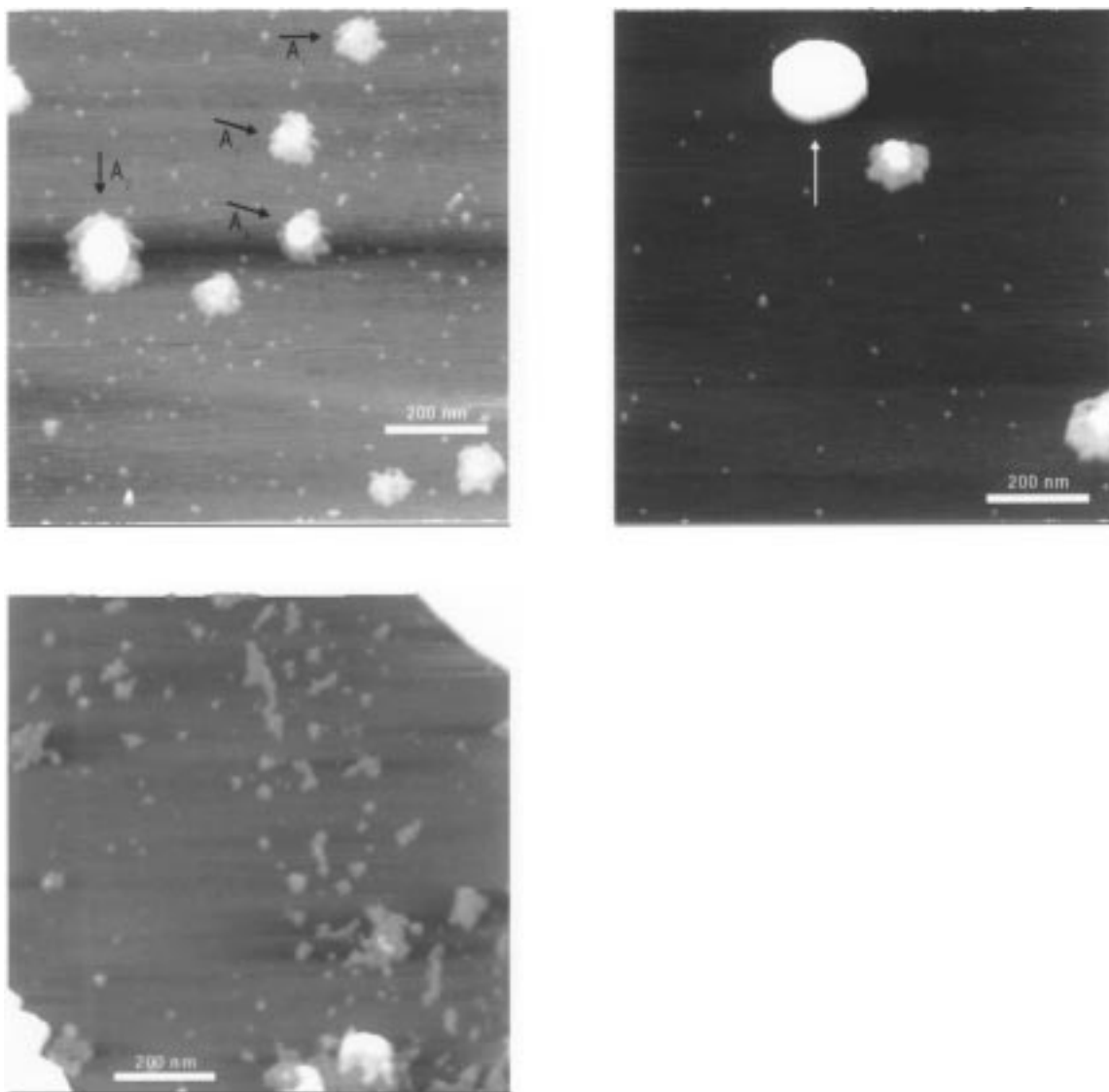


Figure 5. (a) SFM image (tapping mode, height) of PEE-PSSH aggregates on MgCl_2 -modified mica surface adsorbed from a solution without added salt. Arrow A_1 points at unilamellar vesicles. Arrow A_3 points at an unilamellar vesicle containing a spherical micelle. Arrows A_2 and A_4 point at multilamellar vesicles. (b) SFM image (tapping mode, height) of spherical micelles and unilamellar vesicles containing micelles on MgCl_2 -modified mica surface adsorbed from a solution containing a NaCl concentration of 0.05 mol/L. The arrow points at a cubic NaCl crystal that seems to be slightly deformed because of light tapping and a relative high scanning rate. (c) SFM image (tapping mode, height) of spherical micelles and wormlike structures on MgCl_2 -modified mica surface adsorbed from a solution containing a NaCl concentration of 1 mol/L.

strongly from the “true” dimensions in the solution as measured by scattering methods. Therefore, studies under aqueous conditions are necessary to verify and clarify the obtained results.

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