Ion-Stabilized Block Copolymer Micelles: Film Formation and Intermicellar Interaction

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ABSTRACT: Thin films of poly[styrene-*block*-(2-vinylpyridine)] with equally long blocks were prepared by casting micellar toluene solutions on a mica or carbon substrate. The structure of the films was studied by scanning force microscopy and transmission electron microscopy. Structural variations were observed depending on the concentration of the solution from which the films were obtained and depending on the neutralization of the pyridine units by $HAuCl_4$. Scanning force microscopy as well as dynamic light-scattering experiments demonstrated an increasing stability of the inverse micelles upon ionization of the poly(2-vinylpyridine) core. While the micelles of polystyrene block poly(2-vinylpyridine) transformed into wormlike and lamellar structures upon film formation, the micellar structure was preserved when the poly(2-vinylpyridine) block was partly or fully neutralized by the gold acid. Scanning force microscopy revealed formation of an adsorbed, brushlike first layer on which the micelles assembled to form the following layers. The kinetic stability of the block ionomer micelles is reflected in the scanning force micrographs by the fact that surface coverage of the adsorbed block copolymer brush was reduced when the toluene solution was diluted directly before film preparation. During the given time, the concentration of the free chains (critical micelle concentration) could not recover by dissociation of micelles. Increasing degrees of neutralization, i.e., increasing loading of the micelle core by $AuCl_4^-$, resulted in growing diameters of the core as well as of the polystyrene shell, which is explained by the enhanced segregation parameter $\chi_{\mathrm{core-shell}}$ and stretching of both blocks. Remarkable repulsion between the micelles was observed in monolayer films at high degrees of ionization which is temptatively explained by electrostatic repulsion caused by transfer of $AuCl_4^-$ ions to the substrate-bound brush.

Introduction

Block copolymers with one ionic block may be considered block ionomers as long they are in bulk or a nonpolar solvent and form only tight ion pairs which are strongly interacting dipoles.[1] In this case the ionic blocks agglomerate and reverse micelles are formed. Like nonionic block copolymers, block ionomers follow the concept of a closed association. Below the critical micelle concentration (CMC), the molecules are dissolved in their unimeric form. Above the CMC they begin to form micelles and the concentration of unimeric molecules remains fairly constant upon further increase in the total concentration.[1−4] Due to the strong interactions of the dipoles in the ionic block, the stability of the micelles is typically higher than in the core of nonionic block copolymers. Thus, light-scattering and size-exclusion experiments have demonstrated very small critical micelle concentrations, and it was shown that the association of block ionomers in nonpolar solvents does not change over weeks if small amounts of a polar solvent are added.[3] The structure of block ionomer micelles has been described by different theoretical approaches based on the balance of the interfacial energy between the core block and the hydrophobic corona and on the stretching energy of the chains in the core and the corona.[5−8]

While block copolymers in solution generally tend to form spherical micelles if one block is preferentially dissolved by the solvent, the bulk structure can vary from a dispersion of spherical domains to lamellae depending on the length of the constituent blocks.[9] As the equilibrium bulk structure often differs from the thermodynamically stable structure in dilute solution, the equilibrium pathway from a block copolymer solution to a bulk film is usually accompanied by complicated structural transformations. Long relaxation times of the block copolymer structures require extensive annealing or lead to metastable, often disordered morphologies.[9−11] Particular long relaxation times of block ionomer micelles and their corresponding long term stability may, however, offer a possibility to obtain total kinetic control on the structure of solution cast films.

In the present work, we explore the possibilities to obtain films of dry micelles from a symmetrical poly[styrene-*block*-(2-vinylpyridine)] block copolymer which will not form spherical micelles in the solvent free equilibrium state.[12] The stability of the micelles formed in dilute solution was increased by neutralization with $HAuCl_4$, thus converting the poly(2-vinylpyridine) block into a polyionic block. Formation of thin polymer films has been studied by scanning force microscopy. Transmission electron microscopy has been used as a complementary method in order to depict the gold-stained core of the micelles in the thin films. Besides the advantage in contrast enhancement for the electron microscopy experiments, the gold salt was also chosen because it can serve as a precursor for nanoscopic gold particles. Formation of a particulate film of monodisperse regularly distributed gold crystallites will be the subject of a following report.[13]

Experimental Section

Block Copolymer/Ionomer Solutions. Poly[styrene-*b*-(2-vinylpyridine)] (PS-*b*-P2VP) with $D_{\mathrm{PS}}/D_{\mathrm{P2VP}} = 190-190$ was obtained by sequential anionic polymerization as described elsewhere.[12] A stock solution of the block copolymer was prepared in absolute toluene (5 mg/mL). Tetrachloroauric acid was added in amounts related to the 2VP units, i.e., $HAuCl_4$/2VP = 0, 0.01, 0.1, 0.3, 0.5, 0.7, and 1.0. The solutions were stirred for 48 h. Solutions of very low concentration were

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obtained by dilution with toluene and additional stirring for 48 h.

Thin Film Preparation. A freshly cleaved piece of mica was dipped into the particular solution. Typically, the substrate was kept inside the solution for 20 min. Shorter or longer times did not yield different structures. The mica plate was taken out of the solution and immediately brought into contact with a piece of filter paper in order to remove the adhering liquid and dry the surface rapidly.

Scanning Force Microscopy. This was performed with a Nanoscope III instrument (Digital Instruments, St. Barbara) in tapping mode.[14] The oscillation frequency was ca. 360 kHz depending on the Si-cantilever which had a spring constant of about 50 N/m. The optimal operating point for the tapping frequency was chosen as far as possible on the low-frequency side of the noncontact resonance curve.[15] The tip radius was checked by a calibration standard[27] and was typically 8 nm for good tips and 15 nm for bad ones.

Transmission Electron Micrographs. These were taken of films which were obtained by putting a small drop of the $HAuCl_4$-treated PS-*b*-P2VP toluene solution with a block copolymer concentration between 1 and 5 mg/mL onto a carbon-coated copper grid. The liquid was immediately removed by means of a soaking tissue. The films were studied by transmission electron microscopy (bright field images, PHILIPS EM400T instrument, 80 kV). For minimizing the destruction of the polymer by the electron beam, the electron beam intensity was kept as low as possible (second condenser lens, 50 Pt; objective lens, 30 Au).

Dynamic Light Scattering. Studies on micellar solutions were carried out using a submicron particle analyzer (System 4700c, Malvern, 64 channels) and an argon-ion laser from Spectra Physics operating at 488 nm at a scattering angle of $\Theta = 90°$. The sampling time was 2 μs and the experimental time at least 2 h to ensure a statistic where the χ^2 parameter was smaller than 5×10^{-6}. Samples were filtered with a nominal pore size of 0.4 μm before the experiment. Solutions were in the concentration range 0.02−5 mg/mL. In all cases, the diffusion coefficient did not depend on the concentration. The normalized time correlation function of the electric field of scattered light, $g(q,\tau)$, was approximated by a cumulant expansion,

$$g(q,\tau) = \exp(-\Gamma\tau)^*[1 + (\mu/2)\tau^2 + ...]$$

where only the first, Γ, and the second, μ, moments were calculated. The effective translational diffusion coefficient (D_T) was calculated according to

$$D_T = \Gamma/q^2$$

where q is the absolute value of the scattering vector $\mathbf{q}$,

$$\mathbf{q} = (4\pi n/\lambda)\sin(\Theta/2)$$

n is the refractive index of the medium and λ is the wavelength of the incident light. The hydrodynamic radius of the particle, R_h, was calculated from the translational diffusion coefficient, D_0, at zero concentration, using the Stokes−Einstein relationship:

$$R_h = k_B T/6\pi\eta D_0$$

where k_B is the Boltzmann constant, $T = 302$ K is the absolute temperature, and $\eta = 0.585$ Ns/m (toluene at $T = 302$ K) is the viscosity of the solvent medium.

Results and Discussion

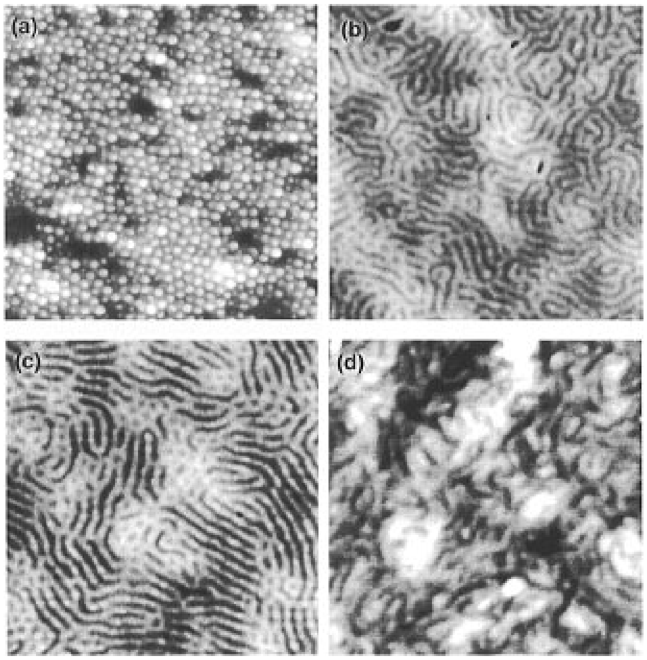

Figure 1. SFM images of micelles formed of a symmetrical block copolymer in a selective solvent and the transformation into wormlike structures upon casting: (a) 1, (b) 2, (c) 2.5, and (d) 5 mg/mL total block copolymer concentration. The length of the image corresponds to 1 μm.

Formation of micelles and their assembly within thin films was studied by scanning force microscopy, SFM, and transmission electron microscopy, TEM. As a solvent we used toluene which is known to be selective for the polystyrene block and to promote association of poly[styrene-*block*-(2-vinylpyridine)], PS-*b*-P2VP, to micelles.[1,12,16,18] Thin films were deposited from the micellar solution either on a freshly cleaved mica substrate (for SFM) or on a carbon-coated copper grid (for TEM). Either the substrate was dipped into the polymer solution and kept there for some time to allow adsorption (for SFM), or a drop was left on the substrate (for TEM) and then immediately freed from the wetting liquid by bringing it into contact with a soaking tissue. Actually, the film formation process presents a combination of adsorption under liquid and casting because some evaporation of the solvent is inevitable when the solution is removed.[16]

Figure 1 shows a series of SFM pictures of films prepared from differently concentrated solutions of a symmetrical polymer PS-*b*-P2VP where each block had a length of 190 monomer units. Figure 1a depicts a layer of rather uniformly packed spherical micelles formed from a solution of 1 mg/mL. The micelles were formed in dilute solution but were of sufficient kinetic stability to keep their original shape after evaporation of the solvent and not to transform to a thermodynamically favored layered structure.[9−11] The coverage of the surface is not complete, and the holes in the layer can be used to evaluate the height of the micelles. The 15 nm thickness of the layer is consistent with the diameter of a dry micelle of 18 ± 2 nm, as can be estimated according to eq 1 where the weight of a micelle is defined by

$$M_{\text{micelle}} = \frac{p^* M_w}{N_A} = \rho_{\text{micelle}} {}^* \frac{4}{3}\pi^* R^3 \qquad (1)$$

It can be assumed that the interaction with the substrate causes some horizontal deformation of the micelle, resulting in a height value smaller than the diameter of the corresponding sphere. Lateral dimensions are difficult to evaluate from the scanning force micrographs because of the convolution with the tip

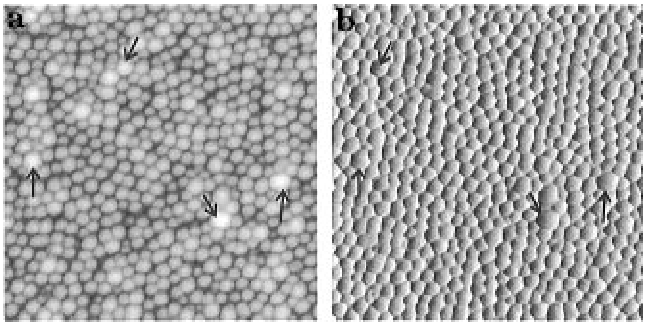

Figure 2. SFM images of ion-stabilized micelles (loading ratio $HAuCl_4/2VP = 0.5$, total block copolymer concentration = 5 mg/mL): (a) topography and (b) amplitude image (0.9×0.9 μm^2), showing that the shells of adjacent micelles interact strongly; however, the micelles keep their individual integrity.

apex. The micelle density, $\rho_{micelle}$, was taken to be constant in the micelle volume and equal to the bulk density of PS and P2VP, $\rho_{PS} = \rho_{P2VP} = 1.1$ g/cm^3. On the basis of light-scattering experiments, we assumed 50 block copolymer molecules/micelle, i.e., $p = 50 \pm 20$. M_w is the molecular weight of the block copolymer and N_A the Avogadro number. The uncertainty of ±2 nm is estimated from a moderate variation of $p = 50 \pm 20$.

Increasing the block copolymer concentration (2 mg/mL) yielded films which covered the surface fully. However, the micelles started to transform and lose their spherical shape (Figure 1b). Wormlike structures were formed. Further increase of the total block copolymer concentration (2.5 mg/mL) promoted the transformation from spherical micelles to worms (Figure 1c).

Films which were obtained from even higher concentrated solutions (5 mg/mL) yielded blurry pictures with ill-defined details indicating transformation to another structure. It has been well established that phase-separated, symmetrical block copolymers tend to form lamellae parallel to the surface of the substrate upon approaching the equilibrium state.[10,11] Figure 1d may be regarded to present a lamellar structure which could not fully develop during solvent evaporation or where homogeneous coverage of the surface would result in a film thickness which does not correspond to an integer of the lamellae periodicity.[10,11]

The stability of the micelles can be enhanced if the polar core block is converted to an ionomer block. This is demonstrated in Figure 2 which shows coverage of the mica surface by several layers of micelles. The film was prepared from a micellar PS-*b*-P2VP toluene solution (5 mg/mL), which had been treated with tetrachloroauric acid. Upon neutralization of the pyridine groups, pyridinium ions are formed which bind the tetrachloroaurate as a counterion. Different than in the preparation shown in Figure 1d, the micelles could not transform to a less dispersed structure. Within the depicted layer, the micelles tend to arrange in hexagonal order. At some places in Figure 2a, marked by an arrow, additional micelles can be observed to be deposited on top of the surface layer.

Figure 2b shows the first deviation of the tapping mode SFM amplitude signal[14,15] resulting in shadowing of height features along a scan line (left to right) and giving a quasi-3-dimensional impression of the projection of the topography image into one plane. The pictures demonstrate a dense packing of the micelles, as the original spherical shape of the micelles is deformed to hexagons. The core interaction is however strong enough so that the integrity of the micelles is preserved. Even for much thicker layers, deposited from more highly concentrated solutions, we did not observe the transformation to wormlike or lamellar structures, as occurred in the case of the PS-*b*-P2VP films when the pyridine groups were not neutralized.

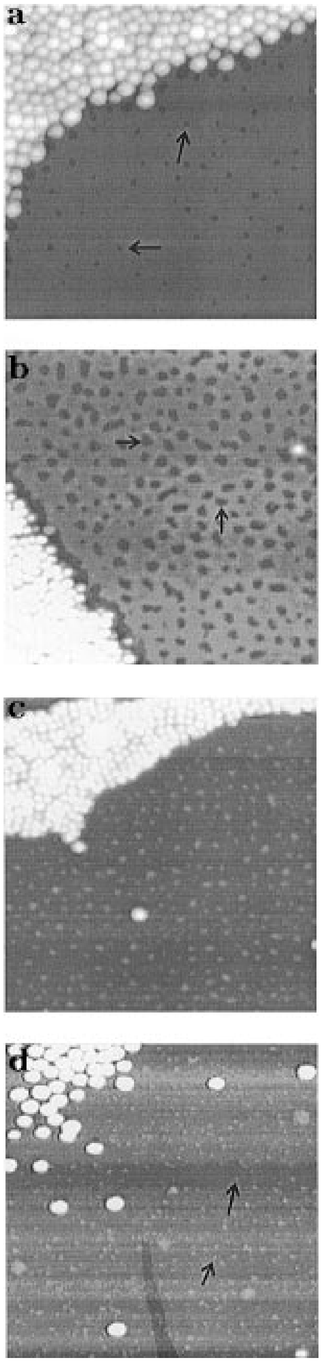

Figure 3. SFM images of ion-stabilized micelles (loading ratio $HAuCl_4/2VP = 0.5$): (a) solution of 2 mg/mL for casting the film. Micelles assemble on top of an adsorbed block copolymer brush. A series of dilutions shows the decreasing of the adsorbed polymer layer: (b) 1, (c) 0.1, and (d) 0.01 mg/mL. The critical micelle concentration was not restored during the time given for relaxation.

Figure 3 shows films which were prepared from solutions whose concentration was too low to obtain full coverage of the substrate by the micelles. The block copolymer was treated with 1 gold atom/2 2VP units, $HAuCl_4/2VP = 0.5$. The pictures demonstrate the presence of an interlayer between the substrate and the micelles. The observation is consistent with the generally excepted view that the amphiphilic block copolymer adsorbs by interaction of the polar block with the polar substrate (freshly cleaved mica) forming a hydrophobic brush.[19,20] Adsorption of the free block copolymer chains was also confirmed by SFM and XPS studies on ultrathin films of the same block copolymer without neutralization by $HAuCl_4$.[21,22] Thus, it can be concluded that the mica substrate was first covered with a brush of adsorbed free block copolymer, on which the micelles are deposited as a second layer.

Remarkable is the observation that the layer of adsorbed polymer is structured or does not cover the substrate completely. The sample shown in Figure 3a was prepared from a 2 mg/mL block copolymer solution. Clearly, the micelles are assembled on top of a polymer with small holes (marked by arrows). When the solution was diluted to 1 mg/mL and stirred for another 48 h, the amount of adsorbed block copolymer decreased (Figure 3b). Further dilution to 0.1 and 0.01 mg/mL yielded (after 48 h of stirring) films where the adsorbed block copolymer formed isolated clusters, partly covered by islands of the micelles (Figure 3c), even approaching the size corresponding to single macromolecules (partly marked by arrows in Figure 3d). Regarding the thermodynamics of micellar solutions, it had to be expected that the micelles act as a free chain reservoir restoring the critical micelle concentration. Obviously, this was not the case, which can be explained by the ultraslow dissociation process of block ionomer aggregates.[3] When the same solutions were, however, equilibrated for 2 weeks, the number of micelles was significantly decreased in the film prepared from the 0.1 mg/mL solution and no micelles were found in the preparation from the 0.01 mg/mL solution. From this, the critical micelle concentration can be estimated to be between 0.1 and 0.01 mg/mL, which is in agreement with the results from light-scattering experiments.

In summary, our observations indicate that the small CMC allowed only formation of a layer of adsorbed macromolecules full of holes as shown in Figure 3a,b. When the solutions were diluted, the concentration of free block copolymer chains dropped even in the presence of micelles below the CMC because of the ultraslow relaxation time of the block ionomer micelles,[3] and the surface coverage by adsorbed chains decreased even more.

Adsorption of free chains on the mica substrate could also be controlled by increasing the amount of gold acid incorporated into the micelles. A similar series of images as shown in Figure 3 has been obtained by keeping the polymer concentration at 0.1 mg/mL but varying the amount of loading from 0.1 up to 1.0 $HAuCl_4$/VP unit. Accordingly, the CMC of a PS-*b*-P2VP block copolymer can be shifted by controlling the degree of block ionization, i.e., amount of gold acid.

So far the SFM pictures gave information on the surface structure of the block copolymer films. As a complementary method, transmission electron microscopy allowed us to obtain a projection image through the film where the contrast was caused by the difference in electron density between the gold-loaded core and the corona of the block ionomer micelles.

Figure 4 shows high-magnification TEM images of micellar films where the P2VP core had been loaded with different amounts of tetrachloroaurate ions. The samples in Figure 4 had a tetrachloroauric acid content of $HAuCl_4/2VP = 0.1, 0.3, 0.5, 0.7$, and 1.0. The dark species have been identified as small gold particles, which formed upon electron irradiation in the TEM by reduction of the tetrachloroaurate. Clearly, the gold particles arranged in clusters where a cluster cor-

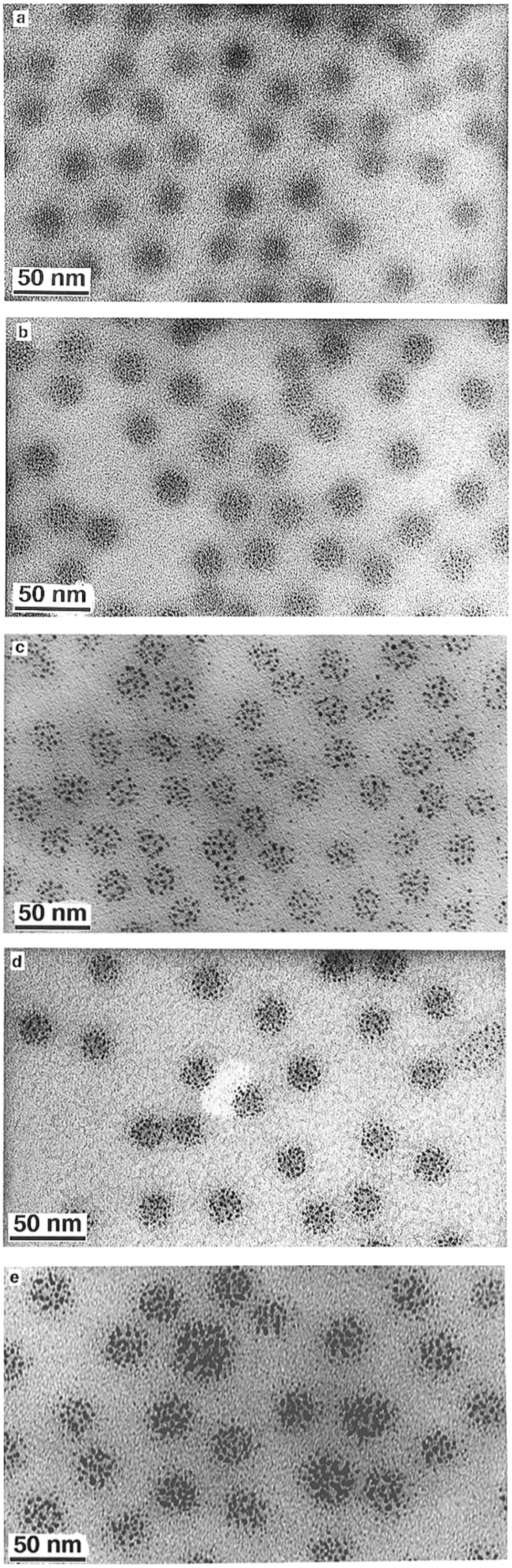

Figure 4. TEM images of a monolayer of micelles with a ratio of $HAuCl_4/2VP = 0.1, 0.3, 0.5, 0.7$, and 1.0 for a−e, respectively.

Table 1. Micelle Parameters Determined by SFM (Diameter), TEM (Core), and Dynamic Light Scattering (Agglomerated Chains) of a Block Copolymer Micelle Where the Specific Solution Has Been Treated with Different Amounts of $HAuCl_4$

$HAuCl_4$/2VP	micelle diameter (nm) ± 2 nm	core diameter (nm) ± 2 nm	corona thickness (nm) ± 4 nm	hydrodynamic radius (nm) ± 2 nm
0	15			19
0.01	18			23
0.1	21	18	3	26
0.3	25	21	4	26
0.5	31	23	8	26
0.7	32	23	9	26
1.0	33	25	8	27

responded to the core of a micelle. Increasing the amount of loading, the small particles increased in size, while the number of particles in each core remained about constant, indicating that the particle size depended on the density of incorporated precursor component and the average diffusion length of Au in the core.

The mean diameter of the gold-containing core was determined by evaluating at least 50 different micelles (Table 1). The estimated error of a ±2 nm considers the uncertainty from the blurred border between core and corona and the size distribution of the cores. The table also lists the mean micelle diameter which was determined from scanning force microscopy by measuring the height of at least 50 different micelles. The diameter of the micelles increased by more than a factor of 2 depending on the degree of neutralization. The error of ±2 nm is based on the size distribution of the micelles and the uncertainty in the height measurement, due to the elasticity of the scanned micelles which can differ depending on the amount of incorporated gold.[15]

The corona thickness values in Table 1 were obtained by subtracting the core diameter from TEM from the micelle diameter determined by SFM. Upon increasing the degree of neutralization from 0.1 to 1.0 $HAuCl_4$/2VP, the corona thickness increased from 3 to 9 nm.

Dynamic light-scattering experiments showed an increase of the hydrodynamic radius, R_H, upon small degrees of ionization. However, above 0.1 equiv of ion content, the hydrodynamic radius remained apparently constant which is in contrast to the increase of the dry micelles.

Neutralization, i.e., conversion of the P2VP block to an ionic block, is expected to influence the size of the micelles (i) because of an increased volume fraction incorporated and (ii) because of increasing the interfacial energy, $\chi_{\mathrm{core/toluene}}$, between the ionic species and the nonpolar solvent.[9] The free energy of block ionomer micelles can be minimized by an optimum balance between the agglomeration number of chains and by stretching of the core block is order to minimize surface contacts to the inert PS block. A high extension of the core block was theoretically predicted in the superstrong segregation limit yielding a linear variation of the core diameter with the number of monomers of the core block.[23] X-ray studies on block ionomer micelles showed that the core radius can approach the contour length of the ionic block.[3]

In our case the core radius was still smaller than the length of the extended ionic block. This is most likely to be explained by the rather high molecular weight of the core block, as the energy for complete extension increases exponentially with increasing chain length. The increase in the corona thickness can be explained because increasing the number of chains per micelle enforced a more dense packing of the PS chains, forming a densely packed brush which stretches away from the core because of the increased excluded volume.[24]

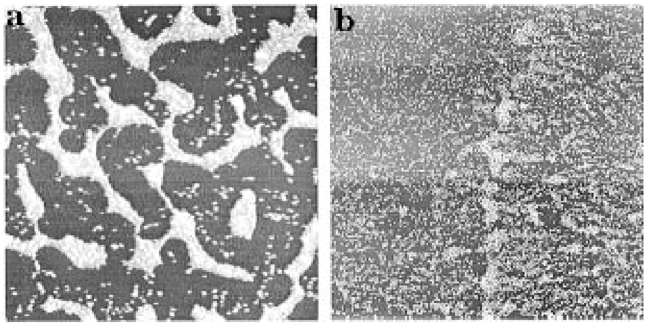

Figure 5. SFM topography of micelles cast onto mica, using a block copolymer concentration of 0.1 mg/mL with different amounts of incorporated tetrachloroauric acid cast onto a mica sheet: (a) $HAuCl_4/2VP = 0.5$ and (b) $HAuCl_4/2VP = 1.0$. Higher loaded micelles avoid agglomeration. Width of the image corresponds to 10 μm.

More difficult to rationalize is the observation that the hydrodynamic radius did not increase further at higher salt loadings of the micelles. However in the dissolved state, the corona chains are additionally extended because of the interaction with the solvent, and it can be argued that this effect is more pronounced for the smaller, less crowded micelles than for the larger micelles in which the chains are already extended so that the two effects cancel each other at least partly.

When we studied the film formation of PS-*b*-P2VP micelles at increasing loads of $HAuCl_4$, we made another quite striking observation. Figure 5 shows large scale images of a mica substrate which was only partially covered by micelles. Both samples were prepared by dipping the substrate into a toluene solution containing 0.1 mg/mL block copolymer. In the case of Figure 5a, the solution was loaded with 0.5 equiv of tetrachloroaurate acid. The sample shown in Figure 5b was obtained from the same solution to which, however, 1 equiv of the gold acid had been given, $HAuCl_4/2VP = 1.0$. In both cases, the substrate is covered by roughly the same numbers of micelles per unit area. While the less loaded micelles agglomerated to form monolayer islands, the more highly loaded micelles tried to avoid agglomeration and kept an average distance of about 15 nm between each other.

The same effect could also be observed in transmission electron micrographs for micelles which had been deposited on a carbon layer on a TEM grid, i.e., a less polar substrate. Figure 6a shows a micellar film which was obtained from a block copolymer solution treated with 0.5 equiv of the $HAuCl_4$. The distance between the centers of the micelles is equal to the diameter of the micelles as evaluated by SFM (Table 1). Thus, the micelles are densely packed corresponding to the situation shown in Figure 2 for a film cast on mica. Figure 6b presents an image of a sample obtained when the same block copolymer solution was treated with 1.0 equiv of $HAuCl_4$. In this case the average center to center distance was larger than 50 nm, demonstrating that the micelles did not agglomerate. The average separation distance is in the order of 15 nm and consistent with the SFM observations in Figure 5.

So far, we can only give a tentative explanation for the observed effect. The repulsive interaction between the micelles in Figure 5b is rather long range, like that

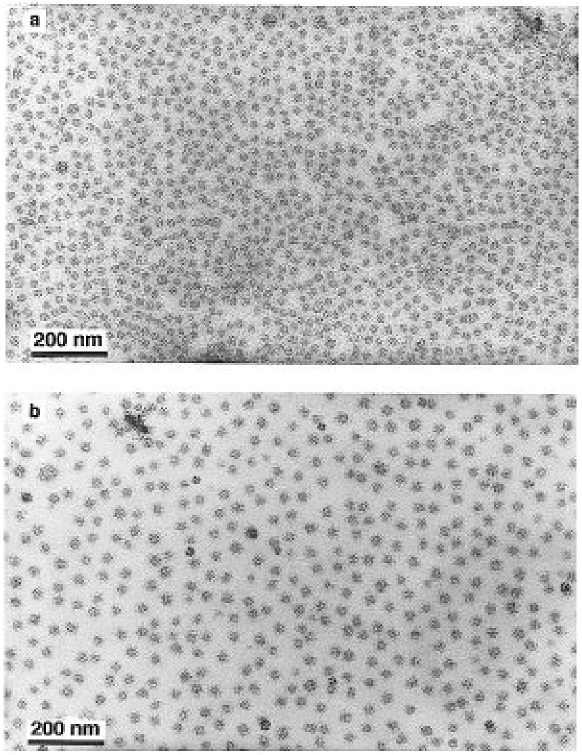

Figure 6. TEM micrographs. The core of a micelle is stained by different amounts of incorporated tetrachloroauric acid: (a) $HAuCl_4/2VP = 0.5$ and (b) $HAuCl_4/2VP = 1.0$. The images show the same effect on micelle organization as observed by SFM on mica in Figure 5.

observed for electrostatic interactions. When the $HAuCl_4$ acid protonates pyridine units, the $AuCl_4^-$ anion gets bound as a counterion. If, however, only a very small fraction of the anions can be released, the micelles will become positively charged and repel each other. Because of the low dielectric constant, the solvent cannot solubilize the anions, and the question arises to which location the anions may be transferred. On the other side, the nonpolar nature of the solvent also ensures that their is little screening of an electrical interaction between charged micelles. It has been calculated for poly[styrene-*b*-(vinylpyridine)] micelles in solution of organic solvents that there is a narrow window in concentration and dielectric constant where the micelles can adopt a net charge which is not sufficiently screened to surpress repulsive interaction.[25] Experimental evidence for a corresponding ordering of the micelles within a superlattice were found by light scattering.[25]

The situation described here cannot be compared to the electrostatic stabilization of colloids described by Derjaguin−Landau−Verwey−Overbeek (DLVO) theory using a Yukawa pair potential,[28] where the counterions transfer into solution and form a diffuse electric matrix. We assume the existence of some trap for a small amount of anions, either at the surface of the substrate, by free block copolymer chains adsorbed to the substrate, or by a small excess of the $HAuCl_4$ salt which was not taken up into solution. So far we found the same effect irrespectively whether mica or pyrrolitic graphite was used as a substrate. More systematic studies need to be done, taking into account effects which can be caused by traces of water and the surfaces with which the solutions were brought into contact.

Conclusions

It has been shown that films of densely packed spherical micelles with rather high structural regularity can be formed under stringent kinetic control from block ionomer micelles of poly[styrene-*block*-(2-vinylpyridinium$^+$$AuCl_4^-$)]. Micelles of the same block copolymer, which were, however, not neutralized, could only be deposited on a substrate as a monolayer full of holes. Attempts to increase the film thickness resulted in formation of a wormlike structure. In contrast, the block ionomer micelles could be packed densely without losing their structural integrity. Tapping scanning force microscopy revealed the formation of a brush of adsorbed boock copolymer chains on the polar mica surface as an interlayer between the substrate and the deposited micelles.

Low critical micelle concentration and the enormous kinetic stability of the micelles permitted the control of the coverage by adsorbed free block copolymer chains within wide limits. Furthermore, it was shown that the core diameter as well as the corona was increased up to 200% by neutralization of the poly(2-vinylpyridine) block which was explained by an increase in the association number and stretching of the block copolymer chains in order to minimize the total free energy of the surface.

Remarkable, yet not understood, repulsion effects between the $AuCl_4^-$-containing micelles were observed at high gold loads. Finally it may be noted that the regular partition of the gold salt within domains of equal size provides a potential route to more particulate films of the metals or semiconductors,[12,13,29] being of great current interest because of their peculiar electronic properties.[26]

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