Tuning the Dimensions and Periodicities of Nanostructures Starting from the Same Polystyrene-*block*-poly(2-vinylpyridine) Diblock Copolymer**

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The controlled tuning of the characteristic dimensions of two-dimensional arrays of block-copolymer reverse micelles deposited on silicon surfaces is demonstrated. The polymer used is polystyrene-*block*-poly(2-vinylpyridine) (91 500-*b*-105 000 g mol^{-1}). Reverse micelles of this polymer with different aggregation numbers have been obtained from different solvents. The periodicity of the micellar array can be systematically varied by changing copolymer concentration, spin-coating speeds, and by using solvent mixtures. The profound influence of humidity on the micellar film structure and the tuning of the film topography through control of humidity are presented. Light scattering, atomic force microscopy, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy were used for characterization. As possible applications, replication of micellar array topography with polydimethylsiloxane and post-loading of the micelles to form iron oxide nanoparticle arrays are presented.

1. Introduction

The creation and control of surface structures on a nanoscale level is essential for the development of surfaces with novel and useful properties. Using self-assembly of macromolecules to form surface nanopatterns is emerging as a promising and flexible technique.[1–7] The key advantage of such "bottom-up" processes is that large surface areas can be treated quickly and at low cost. Block copolymers are frequently used, since they readily self-assemble to form a rich variety of nanoscale periodic patterns. First real-world applications of such nanoscale patterning are beginning to be reported; for example, for use in flash memory devices and metal oxide semiconductor (MOS) capacitors.[8–11]

For many potential applications the dimensions of the nanostructures need to be optimized experimentally. Tools to continuously vary the dimensions of the nanopatterns in a predictable and simple manner are required. For microphase-separated thin films, tuning of morphology and size of the nanoscale patterns formed is conceptually most-easily achieved by changing the molecular weights and/or the block ratio of the polymers used. This approach, however, demands the synthesis and characterization of a large number of different block copolymers and can therefore mean a major experimental effort. A similar, more practicable approach that has shown promising results is the swelling of the microphases by admixture of homopolymers corresponding to one or both of the polymer blocks.[12–16]

As part of our efforts to assemble a flexible and general toolbox for the creation of a wide range of surface nanostructures, we are investigating the possibilities offered by block-copolymer micelles. Such aggregates form from block copolymers when they are dissolved in a selective solvent—i.e., a solvent that dissolves only one of the blocks well—and are spherical, wormlike, or cylindrical with at least one dimension in the range 10 to 200 nm.[17] Deposition of such micelles onto surfaces as monolayers leads to chemical and topographical nanopatterns.[18–21] A potentially very useful application is their ability to act as nanocontainers for the organization of other building blocks, for example, nanoparticles, biomolecules, or other functional units.[22] These patterns frequently show responsive 'smart' behavior and can also be replicated in other materials.[21,23–25] Being able to tune the size and spacing of the micelles translates into controlling the surface density and the mean distance of organized functional units in a straightforward manner.

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Earlier work on the tunability of micelle dimensions and the periodicity of micellar arrays has focused on the use of copolymers with different molecular weights and/or block ratios.[26–36] Cogan and co-workers have shown the possibility of increasing the aggregation number of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) reverse micelles from cyclopentane through inclusion of water in the PEO core.[37,38] Ouarti et al. describe tuning of size and morphology through addition of core-forming homopolymer.[39] Cho et al. have reported PS-*b*-P2VP (P2VP: poly(2-vinylpyridine)) reverse micelles with quarternized P2VP blocks exhibiting different aggregation numbers in toluene and methyl ethyl ketone.[40] Earlier researchers have shown that the nature of the solvent can influence the interfacial surface tension between the corona and core, and this can influence the micelle aggregation number.[41,42] Some of the theoretical treatments on the micellation process show that the coronal block can also exert a strong influence on the micellar characteristics, especially when the solvent is very good for the outer block.[43] This indicates the possibility of obtaining differently sized micelles by simply changing solvents.

We found that under suitable experimental conditions the typical dimensions of the ensuing arrays of micelles are also strongly dependent on the deposition conditions, which in turn form a convenient handle for tuning. We could achieve the tuning of characteristic dimensions over relative ranges of several tens of percents without changing the molecular weight or the block ratios of the copolymer, and without chemically modifying the polymer or including any foreign species.

Reverse micelles of PS-*b*-P2VP are formed when the copolymer is dissolved in solvents such as toluene and xylenes that are selective for the PS block. These micelles have a swollen PS corona and a condensed P2VP core. Monolayer films of packed micelles are obtained by spin-coating onto silicon surfaces. We observed that the morphology and the behavior of the micelles obtained from toluene differ significantly from the micelles obtained from the xylenes. Micelles obtained from toluene tend to pack closely together to form arrays with constant periodicities that are not sensitive to change of solution concentration or the spin speed in the coating process, i.e., their packing resembles the packing of hard particles. In contrast, the micelles coated from xylenes show a different behavior. The mean distance between the individual micelles in these films, i.e., the array periodicity, was very susceptible to the spin speed and to the solution concentration used, thus providing a very convenient handle to systematically tune the array characteristics.

In addition, we report the influence of humidity on the micelle film structure. The micelles deform when deposited on a surface and the extent of this deformation is observed to vary as a function of humidity of the coating environment during film formation. In analogy to the much higher responsiveness of micelles coated from xylene to concentration and spin speed,

we also find a higher responsiveness of micelles from xylenes towards changing humidity. There are some earlier reports that describe the influence of humidity on the phase separation of homopolymer blends.[44,45] We are not aware of any earlier observation of the influence of the humidity on the structure of block-copolymer-micellar thin films. This observation made it necessary for us to prepare all micellar films in a humidity-controlled environment. Unless otherwise stated, all measurements and images in this report correspond to a relative humidity of 15–20 %. The possibility of changing the periodicity in a systematic way with convenient handles is attractive for several applications. We present two examples where the ordered micellar arrays with tunable dimensions and periodicities could be put to use: The replication of the topographies in polydimethylsiloxane (PDMS) to obtain nanostructured PDMS surfaces; and the use of micelles after deposition as nanoreactors to create arrays of particles with tunable spacing.

2. Results and Discussion

The PS-*b*-P2VP reverse micelles were prepared separately in toluene and *o*-, *m*-, and *p*-xylenes, with the solution concentration in the range 0.3–1.5 wt %. The micellar solutions were characterized with laser light-scattering measurements to determine the hydrodynamic radius, aggregation number, the ρ parameter, and the solvent quality. The micelles were drop-coated on a transmission electron microscopy (TEM) grid and the morphology and the diameters of the micelles were obtained from the TEM measurements. A monolayer of micelles on a surface was obtained by spin-coating the micellar solution on freshly piranha-treated silicon substrate. The topography of the micelle thin film was determined using tapping-mode atomic force microscopy (AFM). The average particle heights and the array periodicities were determined using histograms obtained from the image-analysis functions within the AFM Digital Instruments software. The reverse micellar solutions of PS-*b*-P2VP from toluene, *o*-, *m*-, and *p*-xylene were characterized with both dynamic and static light scattering. The results are summarized in Table 1. The micelle aggregation numbers obtained from light-scattering measurements were higher in xylenes than in toluene. The micelles partly collapsed on the surface during film formation, forming a continuous residual layer ca. 5–10 nm thick due to partial fusion of the coronal blocks of adjacent micelles (Fig. 1).

The thickness of this layer was determined using AFM. The micellar films coated from toluene exhibited micellar bump

Table 1. Results from light scattering experiments in different solvents. *Rg*: radius of gyration; *Rh*: hydrodynamic radius.

Solvent	Aggregation number	Rg [nm]	Rh [nm]	ρ [a]
Toluene	101	57	68	0.84
o-xylene	934	74	108	0.69
m-xylene	1160	91	128	0.71
p-xylene	594	84	125	0.67

[a] $\rho = Rg/Rh$, is indicative of the morphology of the micelles. For an ideal sphere, this value is 0.75.
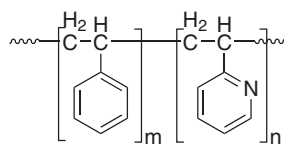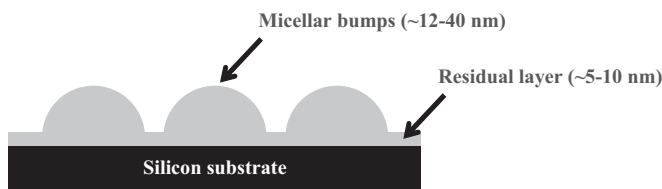
Figure 1. Schematic illustration of the as-coated micellar film, showing a continuous residual layer below the micellar bumps.

heights of 11 nm and a residual layer thickness of 10 nm (Fig. 2). The array had a periodicity of 72 nm, which did not change as a function of concentration or the spin speed.

The micelles obtained from the xylenes behaved quite differently from the ones obtained from toluene with respect to changes in coating conditions. When the micelles were coated from a less-concentrated solution, the micellar bumps were spaced farther apart than when coated from a more-concentrated solution. It was possible to systematically vary the periodicity of the micellar array by changing the concentration of the micellar solution used for coating (Fig. 3). However, when

solutions were too dilute (< 0.4 wt %) the micellar films were no longer homogenous but exhibited patchy coverage on the surfaces. When the concentration was too high (> 1.3 wt %) the micelles tended to form multilayers. We show the periodicity change in the range 140–90 nm for the micelles from *o*-xylene, working between 0.5 and 1.0 wt % at 5000 rpm spin speed (Fig. 3). We observed 7 nm changes in periodicity per 0.1 wt % change in concentration. The decrease in periodicity was also accompanied by an increase in the micellar bump heights and the residual layer thickness, in such a way that the total polymer volume per micelle was conserved.

A similar tuning of periodicity was also achieved by varying the spin-coating speeds, while keeping the copolymer solution concentration constant (Fig. 4). At higher spin speeds, the micelles were spaced farther apart than at lower speeds. The micelle heights and residual layer thickness responded to the periodicity as in the previous case.

Solutions of reverse micelles were also prepared in *o*-xylene/ toluene solvent mixtures of varying compositions. We observed that the periodicity could be changed between the values that correspond to micelle arrays prepared from toluene (72 nm)
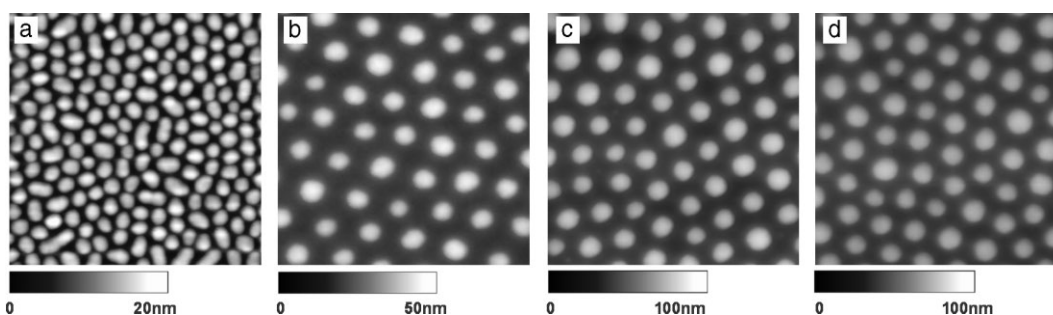

Figure 2. Tapping-mode AFM images (1 μm × 1 μm scan size) of PS-*b*-P2VP (91 500-*b*-105 000 g mol⁻¹) reverse micelles coated from a) toluene (11 nm), b) *o*-xylene (18 nm), c) *m*-xylene (40 nm), and d) *p*-xylene (33 nm). The values in parentheses indicate the bump heights measured with the AFM.
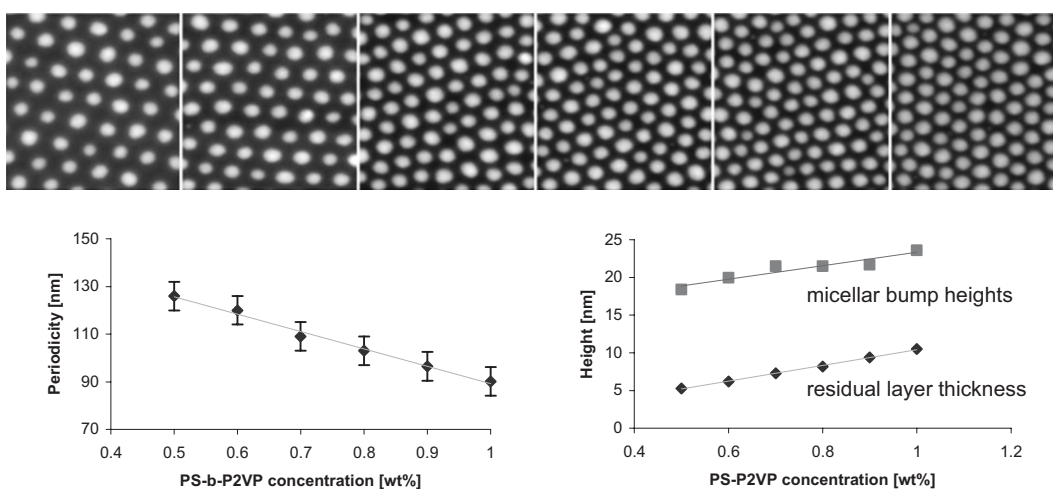

Figure 3. PS-*b*-P2VP (91 500-*b*-105 000 g mol⁻¹) reverse micelles spin-coated at 5000 rpm from *o*-xylene solutions of increasing concentration (from left to right) in the 0.5–1.0 wt % range. All AFM images are 1 μm × 1 μm scans with 50 nm *z* scale. The plots show the variation of the array periodicity (left) and residual-layer thickness with concentration (right).
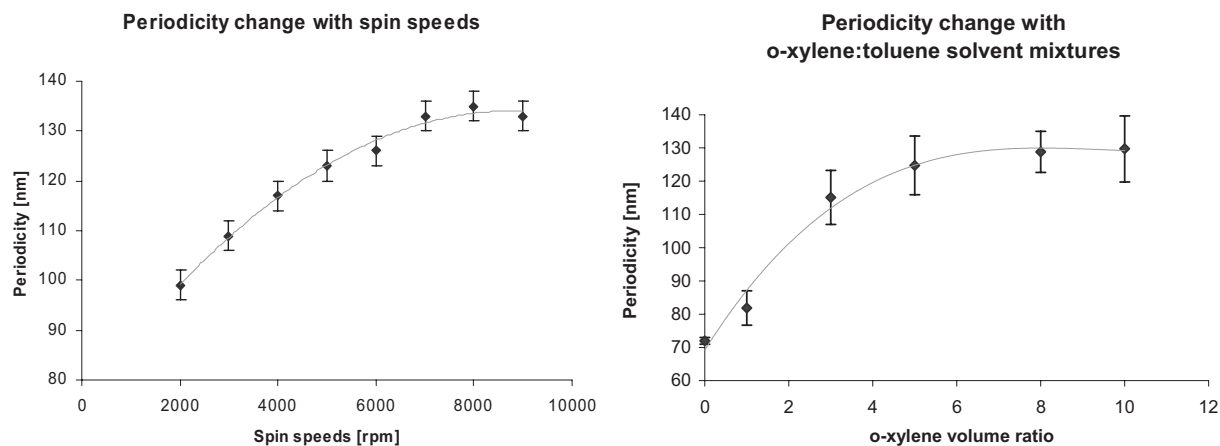
Periodicity change with spin speeds

Periodicity change with o-xylene:toluene solvent mixtures

Figure 4. Plots show change in periodicity of the PS-*b*-P2VP (91 500-*b*-105 000 g mol^{-1}) reverse micelles from 0.6 wt % solution in *o*-xylene at varying spin-coating velocities (left), and tuning periodicity with varying composition of *o*-xylene/toluene solvent mixtures (right).

and *o*-xylene (130 nm) when coated at 5000 rpm spin speed and 0.5 wt % copolymer-solution concentration. The AFM measurements are indicative of a change in the aggregation number with the change in composition of the solvent mixture.

From the AFM measurements, it is possible to calculate the total volume of polymer per unit area of the surface. The volume per micelle is obtained by dividing the total volume per unit area by the number of micelles per unit area. The mass of a single micelle can be determined by assuming the density of micelles to be the same as the bulk polymer density. The number-average micelle aggregation number can be calculated from the micelle mass and the polymer molecular weight.

As the periodicity of the micellar array changes, the micellar aggregation numbers, as computed from the AFM measurements, remained constant in the solvents considered in this study. It was possible to systematically change the periodicities of the micelle arrays obtained from *m*- and *p*-xylenes as well. The changes in morphology and dimensions of the micelles due to changing the solvents and the tunability of array periodicity by varying coating conditions were not unique to the system under discussion, but were also observed in the case of PS-*b*-P2VP copolymers of other molecular weights (this study: (91 500-*b*-105 000 g mol^{-1}); 190 000-*b*-190 000 g mol^{-1} and 290 000-*b*-72 000 g mol^{-1} were additionally tested). As indicated above, block-copolymer micelles deposited from toluene behave in a qualitatively different manner. The periodicities of micelle arrays from toluene were observed to remain constant and were not affected by changing the spin-coating speeds from 2000 to 10 000 rpm or the solution-concentrations from 0.5 to 1.3 wt %. Our observations are compatible with a model in which micelles from toluene and from the xylenes become immobilized at their positions on the surface at different stages during the coating process. The reasons for this strikingly different behavior are at present not completely understood and are the subject of ongoing studies.

2.1. Influence of Humidity

The micelles from xylenes were found to be quite sensitive to the humidity of the environment while spin-coating. The micellar bumps were taller when coated in an atmosphere with higher humidity than when coated under low-humidity conditions. We observed almost a doubling of the micellar bump heights by changing the humidity (R_H) of the spin-coating environment from $R_H = 20$ to 50 %. The periodicity of the array did not change in response to the humidity variation. We therefore conclude that the influence of humidity manifests itself at a late stage of the film-formation process when the positions of the micelles, and with them the periodicity, have already been fixed. We speculate that the solvent evaporation from the surface during spin-coating leads to a reduction of surface temperature, favoring condensation of moisture on surface. Following the argument of Steiner and co-workers,[44] we believe this moisture would be preferably distributed within the hydrophilic P2VP cores, swelling them and also changing the interfacial surface tension between the PS and P2VP.[9] There are indications in the literature that the interfacial surface tension can influence the aspect ratio of micelles on surfaces.[46,47]

Comparing the polymer volume per micelle as determined from AFM measurements for samples coated under high- and low-humidity conditions revealed that the increase in the micellar bump heights was compensated exactly by a decrease in the residual layer thickness, thereby conserving the volume per micelle. This indicates that increase in the micellar bump heights is not due to the permanent inclusion of any foreign species, for example water, and that the humidity basically influences the degree of collapse of the micelles on the surface (Fig. 5). At a lower humidity, the micelles collapse more than at a higher humidity.

The effect of humidity was much less pronounced on the topography of the micellar films prepared from toluene. In the toluene case, micelles of 9.8 nm heights with 11.8 nm residual layer thickness, at R_H of 40 %, and of 12.1 nm heights and
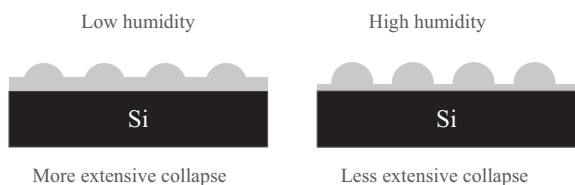
Figure 5. Schematic illustration of the change in micellar structure with humidity of the spin-coating environment.

10.6 nm residual layer at R_H of 20 % were obtained. Our experiments strongly emphasize the need for controlling the humidity of the environment during the formation of micellar thin films. It was possible to tune the micellar bump heights by systematically varying the humidity of the coating environment (Fig. 6). The heights were tunable between 16.8 and 41.5 nm and the heights reached saturation at 41.5 nm for the micelles from *o*-xylene.
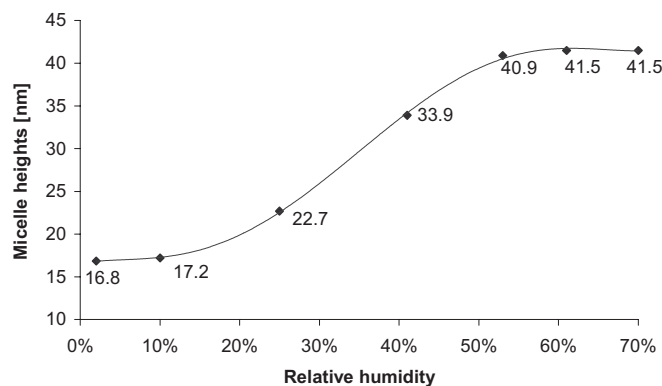
Figure 6. Variation of the amplitude of micellar bumps with humidity.

2.2. Micelle-Structure Replication with PDMS

The micelle-coated surfaces have a uniform chemistry of PS with nanoscale topography due to the micelles. Such substrates are suitable masters for replication in PDMS to obtain a complementary topography. Silicon substrates coated with PS-*b*-P2VP micelles from *o*-xylene were used as the masters. A PDMS prepolymer mixture with the curing agent was poured onto the micelle-coated substrate and cured at 65 °C for 3 h. The PDMS replica could be peeled off easily from the master and the topography of the replicated face was characterized with tapping-mode AFM. An array of pits of depth ca. 7 nm was observed on the PDMS, which corresponds to less than half of the micelle bump heights (~ 18 nm) in the master

used (Fig. 7). The periodicity of the micelle array was preserved in the replica. We believe the loss of amplitude in the replica to be a result of the surface tension of the PDMS. This is supported by the observation that the replication of micelle arrays with smaller spacing resulted in smaller pit depths in PDMS. This method offers an elegant and easy way to realize PDMS stamps with nanoscale features, which could be useful for further nanofabrication through microcontact printing or nanoembossing.

It was possible to scale this process up to 4 in. wafers with good homogeneity of replication over the entire surface. Although the replication of block-copolymer thin-film structures by PDMS to make PDMS pillars has already been reported,[48] our method has the additional advantages of tunability in lateral spacing, in addition to an experimentally simple procedure. The flexible and biocompatible properties of PDMS make it a promising material for applications such as bioactive bandages. We are currently investigating the influence of surface nanostructures on PDMS towards cell adhesion and growth. The influence of tunable PDMS nanostructured surfaces on human stem-cell culture is the subject of a forthcoming publication.[49] Further experiments are in process using a harder variety of PDMS to improve the faithfulness of the reproduction.

2.3. Iron Oxide Dot Array Fabrication

Fabrication of inorganic nanoparticle arrays using block copolymers has been achieved by pre-loading or post-loading micelles with inorganic salts followed by additional process steps.[22,31,32,34,50] Post-loading implies that the inorganic salts are loaded after the formation of the micellar film, while pre-loading implies that the micelles are loaded in solution and
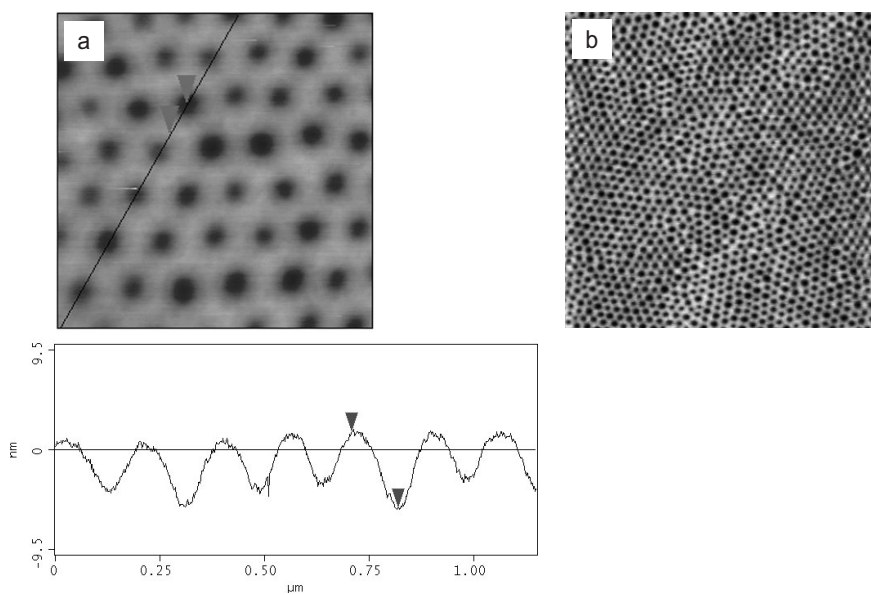

Figure 7. a) Periodic pits of depth ca. 7 nm in PDMS obtained by replication of micelle structures. b) 5 μm × 5 μm scan size of the pit array.

then deposited on the surface. Post-loading has the advantage that the deposition and the loading steps are independent of each other and that the aggregation number is not a function of the degree and type of loading. Thus the periodicity of the micellar array is preserved in the final nanoparticle array.[22] This advantage is particularly relevant in the context of the experiments reported in this article, since the tunability in periodicity achieved with the micellar array can be directly transferred to that of the inorganic nanoparticle array through postloading of the PS-b-P2VP micelles. We used an acidified solution of potassium ferrocyanide in water to load the P2VP core with iron species.

The acid protonates the basic cores, which are then capable of binding different anions (Fig. 8). In the subsequent step, the micelle arrays with the P2VP core loaded with ferrocyanide anions is exposed to an oxygen plasma, resulting in removal of the polymer and formation of iron oxide nanoparticles. (Fig. 9).

The Fe 2p spectra obtained from X-ray photoelectron spectroscopy (XPS) measurements show that the Fe is totally oxidized and is in the form of Fe_2O_3. The post-loading was also carried out with an acidified aqueous solution of potassium ferr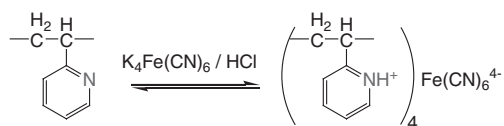icyanide. The nature and composition of the iron oxide particles obtained using ferro- and ferricyanide solutions were practically identical.

Since the periodicity of the nanoparticle array mirrors that of the micellar arrays, nanoparticle arrays of systematically varying periodicities can be obtained. The arrays of iron oxide particles are under investigation for their use as growth catalysts for carbon nanotubes. The process of post-loading of the micelles can be extended to obtain nanoparticle arrays of other metals, such as Au.

3. Conclusions

We have demonstrated convenient ways of tuning the dimensions of diblock-copolymer micelles and their 2D array periodicities by changing the preparation and coating conditions. PS-b-P2VP reverse micelles with differing morphologies, dimensions, and behavior can be obtained from different solvents. This was demonstrated with a copolymer molecular weight of 91 500-b-105 000 g mol^{-1}. The periodicity of the 2D micellar arrays can be varied systematically by varying the copolymer solution concentration and the spin-coating speed. The humidity had a significant influence on the degree of collapse of the micelles prepared from o-xylene. The micellar bump heights can be tuned by systematically varying the humidity of the spin-coating environment. This suggests a need for humidity control while preparing micellar thin films. The periodic topography offered by the micellar arrays was replicated with PDMS to obtain hole arrays of varying periodicities in PDMS. The post-loading of PS-b-P2VP micelles with iron salt to create iron oxide nanoparticle arrays of varying interparticle distances was demonstrated.

Figure 8. Schematic illustration of the inclusion of ferrocyanide anion into the P2VP core.
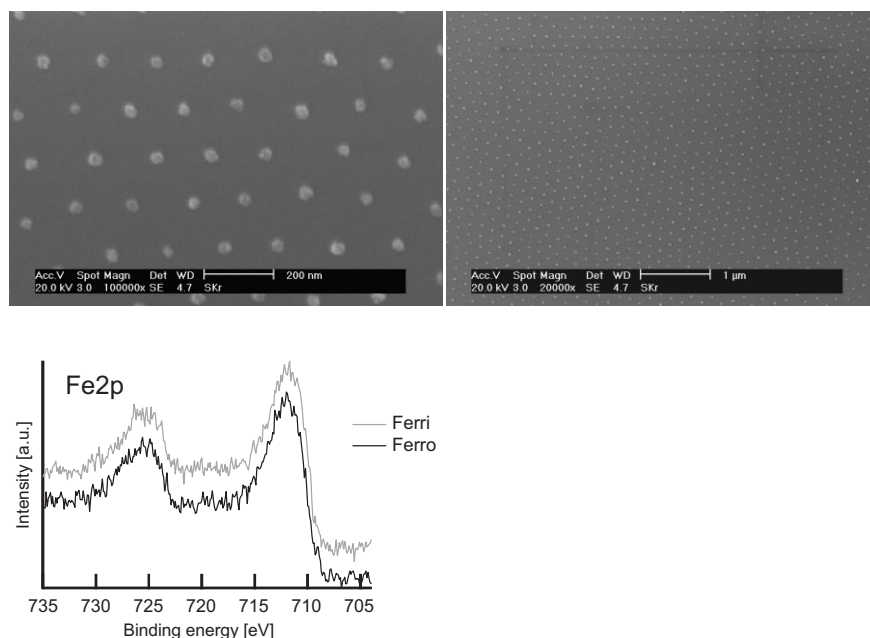
4. Experimental

Figure 9. Top: SEM images of iron oxide nanoparticles obtained through post-loading of the PS-b-P2VP micelles followed by oxygen plasma. Bottom: XPS characterization of the nanoparticle arrays prepared using acidified ferrocyanide (Ferro) and acidified ferricyanide solutions (Ferri) for loading.

steps. The AFM measurements were performed with a Veeco Dimension 3100 instrument and controlled by the Nanoscope software. For creation of iron oxide nanoparticle arrays, a silicon substrate coated with PS-*b*-P2VP micelles from *o*-xylene was dipped in aqueous loading solution containing 0.5 M ferrocyanide or ferricyanide salt and 0.1 M HNO$_3$ for 30 min, followed by oxygen plasma exposure (30 W, 50 mT, 3 min using Oxford Plasmalab 80). The loading solutions were used within an hour of preparation. PDMS reproduction was carried out with a 10:1 mixture of PDMS prepolymer (Sylgard 184) and curing agent poured on the micelle-coated substrate, followed by heating at 65 °C for 3 h.

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