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Cavitated Block Copolymer Micellar Thin Films: Lateral Arrays of Open Nanoreactors

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ABSTRACT: We report the formation of novel self-assembled ultrathin (ca. 20 nm) films comprising in-plane arrays of nanoscale surface cavities. The original micellar thin films, formed by casting kinetically stable reverse micelles from a solution of a styrene (PS)−acrylic acid (PAA) diblock copolymer in toluene onto silicon nitride substrates, consist of lateral hexagonal arrays of spherical PAA microdomains in PS matrix. Upon aqueous treatment to load metal ions into the PAA domains, cavitation of the individual PAA micelle cores occurs, leading to the formation of cavities in the center of the micelles and exposing the PAA domains to the film's surface. Experimental evidence reveals that cavitation takes place as a result of hydration and swelling of the PAA micelle cores during sample treatment in an alkaline solution. The use of these cavitated, metal-loaded PAA domains as arrays of open nanoreactors for inorganic nanocluster synthesis is demonstrated.

Introduction

Amphiphilic block copolymer molecules, similar to low-molecular-weight surfactants, aggregate to form micelles in selective solvents above a certain critical micelle concentration (cmc). In particular, block copolymers are known to assemble into spherical reverse micelles in organic solvents, with the insoluble polar blocks collapsing together to form the core and the soluble nonpolar blocks forming the corona which extends into the solvent environment.[1−3] Such spherical aggregates are generally very monodispersed in size; it is commonly believed that they are formed via closed association of a fixed number of macromolecules per micelle.

At the next level of self-organization, micelles assemble to form highly ordered structures owing to superior size uniformity and high kinetic stability of the individual micellar building blocks. Of relevance to this current report is the laterally ordered hexagonal array of deposited micelles formed upon casting spherical micelles into an ultrathin film on a flat solid substrate, which has been the subject of recent investigations by several research groups.[4−6] Since the dimensions of block copolymer micelles fall in the approximate 10−100 nm range, the self-assembly of micelles into ordered patterns is of interest in terms of potential applications in nanotechnology. For example, the polar cores of laterally ordered micelles have been employed as templates in which 2D arrays of inorganic nanoclusters can be created.[7,8]

Previously, our research group has employed an aqueous-based approach to synthesize in-situ inorganic nanoclusters within carboxylic acid-functionalized microdomains of microphase-separated bulk block copolymers.[9,10] The initial objective of our current investigation was to apply the same aqueous-based approach to synthesize 2D arrays of nanoscale inorganics using templates of in-plane microphase-separated, carboxyl-containing block copolymers. As such, we employed laterally ordered templates of deposited poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) micellar thin films, in which the carboxyl-functionalized cores could serve as the nanoreactors.

In addition to the successful use of PAA micelle cores as in-situ templates, we also report here a structural transformation of the micellar thin films which occurs upon cavitation of the individual deposited micelles. Such a process takes place during the aqueous treatment employed to selectively load metal ions (nanocluster precursors) into the PAA microdomains and leads to the creation of unique hexagonal arrays of nanoscale surface cavities. Via experimental evidence, we demonstrate that the cavitation of the individual micelle is a result of swelling of PAA micelle cores and rupture of PS shells during the treatment of micellar thin films in aqueous solution of NaOH—the first step of the two-step metal loading technique.[10] Finally, interesting observations associated with the use of these cavitated micelles as open nanoreactors are presented.

Experimental Section

Materials. Polystyrene-*block*-acrylic acid (PS-*b*-PAA) (M_n 16 400-*block*-4500, with a 1.05 polydispersity) from Polymer Source, Inc., was used as received. The following chemicals were also used as received: sodium hydroxide (98.9%) obtained from Mallinckrodt; calcium hydroxide (95+%), lead(II) acetate trihydrate, silver(I) acetate, cadmium(II) acetate dihydrate (98%), and tetraaminepalladium chloride from Aldrich; copper(II) acetate monohydrate (98+%) from Strem. All aqueous solutions were made with deionized water. The silicon nitride membrane substrates were purchased from Structure Probe, Inc. Each TEM-grid-sized substrate (total size 3 mm) consists of a 100 nm thick amorphous, low-stress Si_3N_4 membrane supported on top of a 0.2 mm thick silicon wafer that has been back-etched in the center to create a see-through square window of size 0.46 mm. Each substrate was rinsed with toluene prior to film casting.

Sample Preparation. The block copolymer was mixed with toluene (HPLC grade, not anhydrous) at a 2.5 mg/mL concentration, resulting in a slightly cloudy, slightly viscous mixture. Heating the mixture to ∼140 °C yields a clear solution which

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remains optically clear when allowed to cool back to room temperature. Each thin film sample was produced by spin-casting: first covering the substrate with a small amount of the (room temperature) polymer solution, followed immediately by spinning the substrates at 1600 rpm for 1 min. Residual toluene was removed from samples under vacuum. AFM studies revealed film thickness in the range of 20 nm.

The two-step metal loading treatment[10] involves submerging samples first in a 0.04 M $NaOH_{aq}$ solution for 16−24 h, followed by a 1 min rinse in deionized water. Samples are then treated in their respective metal salt solutions (0.4 mM $PbAc_2$, 0.02 M $CdAc_2$, 0.04 M $CuAc_2$, 5 mM AgAc, and 5 mM $Pd(NH_3)_4Cl_2$, where Ac = CH_3COO) for 20−40 h, followed by a 2−4 min rinse. H_2S gas was generated for use in PbS nanocluster synthesis by adding a few drops of bis(trimethylsilyl) sulfide (Aldrich) into ~10 mL of water. The $H_2S_{(g)}$ source vial and samples were then placed together in a closed jar for 30 h at room temperature. Afterward, residual $H_2S_{(g)}$ was removed from samples under vacuum.

Microscopy. Transmission electron microscopy (TEM) was performed on a JEOL 200CX operating at 200 kV. Atomic force microscopy (AFM) was performed on a Digital Instruments Dimension 3000 Nanoscope IIIA scanning probe microscope operating in Tapping mode using a silicon cantilever (nominal specified tip radius of 5−10 nm).

Results and Discussion

Each thin film sample was prepared by spin-casting the solution of PS-*b*-PAA diblock copolymer (M_w 16.4K-*b*-4.5K, equivalent to 158 and 62 repeat units for PS and PAA blocks, respectively) onto a 100 nm thick silicon nitride membrane supported on a silicon substrate, back-etched to create a window. The amorphous “TEM-transparent” silicon nitride membrane is featureless; thus, it allows for direct plan-view TEM observation through the thin film deposited on it without the need for potentially damaging flotation/transfer procedures. Researchers have successfully used silicon nitride membranes as substrates for matching TEM−AFM studies of block copolymer thin films.[11]

To load metals into the PAA domains of the thin films, we followed the two-step ion-exchange protocol described above. The technique yields selective loading of metal ions in the carboxyl-containing domains of block copolymers. The first step ($NaOH_{aq}$ treatment) neutralizes the COOH groups in the acid-functionalized domains to COO^-Na^+. The subsequent uptake of selected metal ions is facilitated[10] as the transition-metal ions replace the Na^+ ions which bind relatively weakly to the COO^- groups. The loaded metal also effectively provides contrast for TEM observations.

The casting solution’s concentration of 2.5 mg/mL PS-*b*-PAA in toluene is significantly above the critical micelle concentration generally observed for amphiphilic block copolymers in selective solvents. (For example, a cmc of 0.065 mg/mL for PS-*b*-P2VP in toluene[12] has been reported.) Therefore, formation of reverse micelles is expected. Initially, the mixture at room temperature is visibly cloudy and more viscous than pure toluene. This mixture was spin-cast onto silicon nitride substrates and loaded with $PbAc_2$ (“Ac” = acetate = CH_3COO) via the aqueous loading technique mentioned above. The plan-view TEM image (inset A of Figure 1) of such a film features cylindrical micelles in which the PAA cores, stained with Pb, appear dark. Heating the cloudy mixture transforms the elongated micelles into ones of lower aspect ratios. Heating at ~108 °C for 20 min (film casting is done after the solution has cooled back to room temperature) transforms the elongated micelles observed before heating into mostly elliptical aggregates. Further increase in the temperature of the heating cycle yields an increasing fraction of spherical aggregates. Heating above ~140 °C produces transparent solutions with a consistency similar to that of toluene; casting from such solutions yields only spherical micelles.

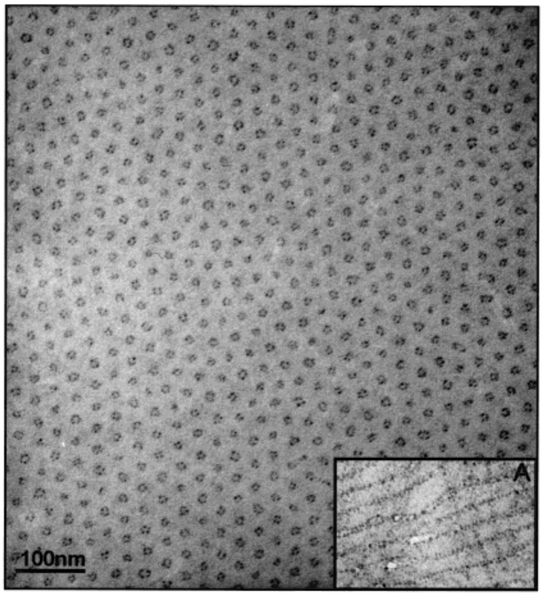

Figure 1. Plan-view TEM of PS-*b*-PAA thin film spin-cast onto silicon nitride membrane after heating solution at 150 °C for 20 min (and cooling to room temperature); PAA cores of deposited spherical micelles are stained with $PbAc_{2(aq)}$. Inset A: thin film spin-cast prior to heating the 2.5 mg/mL PS-*b*-PAA solution in toluene exhibits elongated micelles.

The main panel of Figure 1 shows a representative top-down morphology of thin films cast (at room temperature) after heating the solution at ~150 °C for 20 min. The film comprises a quasi-regular hexagonal array of circular features (sized 10−15 nm) which represent the Pb-stained PAA domains (cores) of the micellar aggregates. The spacing between adjacent stained PAA cores is approximately 33 nm. (Elemental Pb maps of the sample generated via scanning transmission electron microscopy, energy-disperse X-ray analysis, confirm that the dark staining of PAA domains seen in bright-field TEM is due to the loaded Pb.) In a similar fashion, we have successfully loaded the hexagonal PAA array with several other metal species, including Cu, Cd, Ag, and Pd. This thin film morphology is the focus of this current report.

A key morphological feature repeatedly observed in these metal-loaded samples is the fact that metal staining occurs around the perimeter of the roughly spherical PAA domains but is absent from the domain centers. A topological survey of the metal-loaded films via atomic force microscopy (AFM) reveals that their surfaces comprise hexagonal arrays of localized depression (to be referred to as “cavities” in this report), as shown in Figure 2A for a sample loaded with $CdAc_{2(aq)}$. The center-to-center spacing (~33 nm) and the quasi-hexagonal arrangement of the cavities seen in AFM correlate very well with the features observed via plan-view TEM. The existence of a cavity in the individual PAA core is responsible for the absence of metal loading at the center of the PAA microdomains shown in the TEM image of Figure 1. The 2D height profile associated with Figure 2B indicates a cavity depth of at least 7 nm—an underestimated value since the diameter of the AFM probe is comparable to the size of the PAA

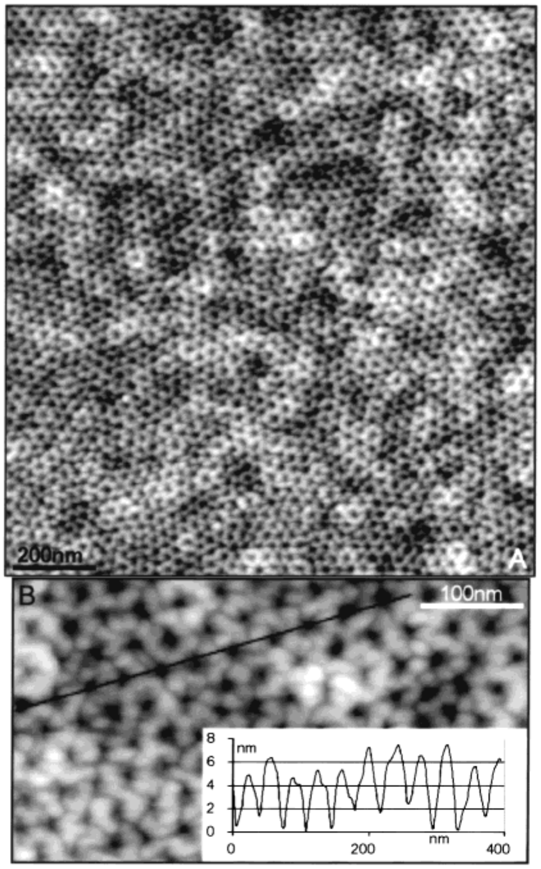

Figure 2. AFM height images of cavitated micellar thin film treated with $CdAc_{2(aq)}$.

domains. Analysis of AFM profiles near edges of deposited thin films yields an average deposited film thickness of ∼22 nm. Similar surface topography has also been observed in samples loaded with other metals.

It is important to note that the hexagonal arrays of cavities observed in metal-loaded thin films do not occur upon film casting, nor due to sample degradation on exposure to electron beam (in TEM), but rather during the aqueous metal loading process described earlier. The AFM height image of a representative block copolymer thin film before any aqueous treatment (Figure 3A) shows that the "as-cast" sample consists of protruding spherical features rather than cavities. The as-cast film topography reflects the structure of deposited reverse micelles[4,5] (where PS block forms the corona and PAA block the core). Similar to the metal-loaded PAA domains seen via TEM and AFM, these as-cast spherical micelles also assemble into hexagonal arrays, with the same center-to-center spacing (33 nm).

Direct adsorption of whole block copolymer micelles from organic solvents onto solid substrates[13] is made possible by the kinetic stability of the micellar aggregates. Relatively slow dissociation and exchange kinetics of aggregated block copolymer molecules in selective solvent[5,14] enables direct transfer of micellar structures into dry films during rapid casting processes. In addition, it has been shown that, upon film casting, toluene-swollen (PS) corona/shells of adjacent micelles fuse together to form a continuous film matrix, while the cores of the individual micellar aggregates maintain their integrity[6]—also evident in our system.

This solvent-free structure is not the thermodynamically stable morphology for our diblock copolymers thin films. Annealing of the micellar films above the glass transitions of both blocks (170 °C for 2 days under vacuum) yielded a morphology of in-plane cylinders of PAA embedded in PS matrix. We note that THF-cast free-standing films of the block copolymer revealed a bulk morphology containing hexagonal PAA cylinders in a PS matrix.

As mentioned above, the transformation of the film structure, from that of as-cast micelle array to the array of cavities, takes place during the aqueous NaOH treatment (first step of the two-step metal loading process). Figure 3B shows the topography of a micellar film after treatment in 0.04 M $NaOH_{aq}$ solution (26 h). The hexagonal arrangement and spacing between the NaOH-induced cavities match those of the as-cast spherical micelles (Figure 3A). Therefore, we conclude that the cavities are created at the centers of the individual micelles. We attribute the observed structural transformation primarily to the strong tendency of PAA to swell in the presence of base and the fact that the PAA domains are confined by thin shells of glassy polystyrene.

To consider the swelling of PAA core, we refer to the swelling behavior of carboxyl-containing polymer latex particles in alkaline solutions.[15−18] Upon exposure to a basic medium, carboxylic acid groups, incorporated into latex particles to stabilize them against flocculation, become negatively charged. This neutralization leads to the hydration and the associated volume increase as the particles become increasingly hydrophilic. Wiese and Rupaner[15] observed "alkali swelling" of poly(*n*-butyl acrylate) latex containing 15 wt % methacrylic acid monomer above pH 8. A maximum volume increase by a factor of 30 exhibited by the swollen particles occurs at pH 10.2. In other instances, subsequent removal of water from swollen latex leads to the formation of voids inside the particles.[16,17] The degree of alkali swelling is known to increase with the amount of carboxylic acid groups incorporated into the latex.[18]

We believe that significant swelling of the PAA domains upon NaOH treatment (pH 12.6), employed in this work to facilitate metal loading, occurs in a manner similar to the swelling of carboxyl-containing latex. The fact that every repeat unit in the PAA micelle core is functionalized with a carboxylic acid group provides a strong driving force for the hydration of the PAA core upon neutralization; thus, substantial swelling can be expected. The volume expansion of the PAA domains leads to the rupture of the PS corona toward the film's free surface as indicated by the scheme in Figure 3. Our hypothesis relies on successful diffusion of aqueous reagents through the top PS-rich corona layer. This appears to be justified on the basis of our observations of metal loading without NaOH treatment, discussed later.

Alkali swelling of latex particles has been reported for several hydroxide bases of monovalent cations,[15,17] for example LiOH, NaOH, KOH, and NH_4OH. However, the swelling of particles is strongly dependent on the valency of the base's countercation. In contrast to monovalent bases, the use of divalent $Ca(OH)_2$ produces no swelling effect; latex particles maintain their original sizes independent of the solution pH.[15] Such absence of swelling is attributed to ionic cross-linking of neutralized acid groups within the matrix of the latex by the divalent Ca^{2+} ions which effectively inhibits volume expansion.

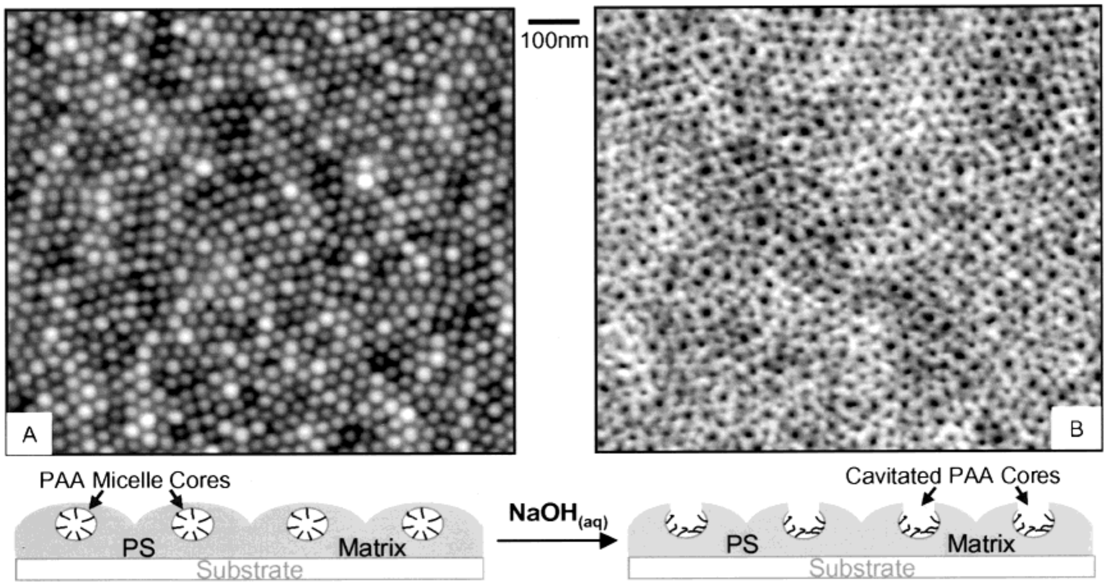

Figure 3. AFM height images of micellar thin films: (A) as-cast film; (B) film treated in 0.04 M $NaOH_{aq}$.

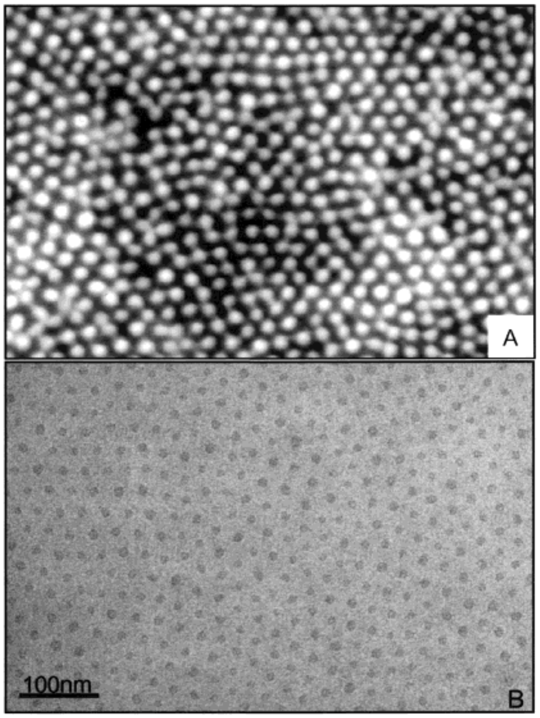

Figure 4. PS-*b*-PAA micellar thin film treated with $Ca(OH)_{2(aq)}$: (A) AFM height image; (B) TEM micrograph.

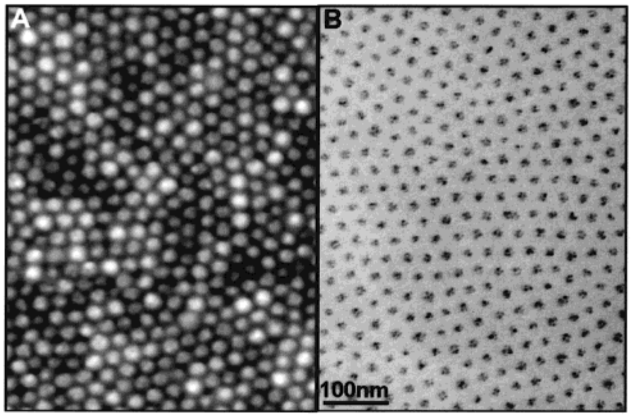

Figure 5. PS-*b*-PAA micellar thin film treated with $PbAc_{2(aq)}$, *bypassing NaOH*: (A) AFM height image; (B) TEM micrograph.

We performed an analogous experiment by treating our as-cast micellar thin films in a 0.0156 M (saturated) $Ca(OH)_{2(aq)}$ solution. AFM investigation of the samples, illustrated in Figure 4A, revealed a film topography with spherical micelles still intact (the micelle dimensions appear somewhat diminished, however) while cavities are clearly absent. TEM observation of the sample (Figure 4B) reveals dark staining of the PAA domains, confirming the successful loading of calcium from solution into the PAA domains. Thus, our results indicate that ionic cross-linking of PAA provided by the loaded Ca^{2+} ions successfully suppresses the swelling and subsequent cavitation of the PAA cores.

Wiese et al.[15] also reported that similar suppression of swelling due to ionic cross-linking can be achieved using other divalent cations (Zn^{2+} and Mg^{2+}). By the same token, we attempted additional loading experiments by treating samples directly in the aqueous loading solutions of $PbAc_2$ and $CdAc_2$ and bypassing the NaOH treatment. Similar to the results of $Ca(OH)_2$ treatment, we observed that swelling and cavitation of the micelles are again suppressed. The AFM profile of a sample treated with $PbAc_2$ (Figure 5A) exhibits spherical micelles resembling those of the as-cast sample. The corresponding TEM micrograph (Figure 5B) clearly shows that the selective sequestering of Pb into the PAA microdomains proceeded successfully. Essentially identical results were obtained from direct sample treatment in a $CdAc_{2(aq)}$ solution, bypassing NaOH.

Metal ions loaded into these samples in the absence of prior NaOH treatment impart relatively uniform staining contrast (Figure 5B) to the PAA domains, instead of the previously shown uneven (ring) staining characteristic of NaOH-treated, cavitated PAA cores (Figure 1). Such an observation represents additional evidence for the absence of void formation in the cores in these closed micelles. We note that the successful loading of the divalent cations into the PAA core in the absence of cavitation implies that aqueous reagents are indeed able to permeate through the PS-rich shell into the core of the closed micelle. It is our speculation that the diffusion of aqueous reagents, including NaOH, through the hydrophobic styrene-rich corona is possible

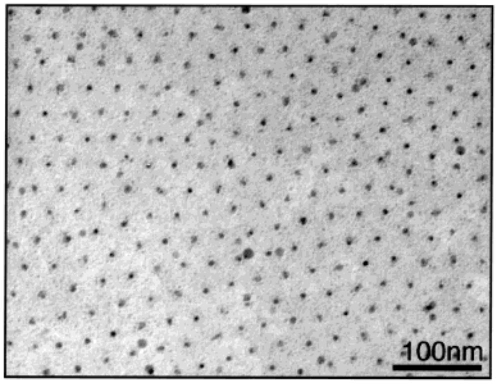

Figure 6. Plan-view TEM of PS-*b*-PAA micellar thin film containing Ag nanoclusters.

(within our experimental time frame) because the top PS corona layer that covers the PAA cores is very thin (most likely less than 10 nm since the film thickness is only ∼22 nm).

The selectivity of metal loading within the cavitated (open) micelles introduces a potential for utilizing these micellar thin films as templates for in situ synthesis of nanocluster arrays. We demonstrate this by loading a sample with silver (via $AgAc_{aq}$ solution, after $NaOH_{aq}$ treatment) followed by reduction in a hydrogen atmosphere (∼2 atm at 85 °C for 30 h). This resulted in a hexagonal array of silver clusters ∼4 nm in size within the thin film template as shown in Figure 6. The relatively uniform silver cluster size observed may be attributed to the inherent size monodispersity of the individual micelles and their PAA cores. Successful use of micelles as templates to achieve nanocluster size uniformity has been have demonstrated in a number of block copolymer micellar systems.[7,8,19]

Thus far, we have discussed the morphology observed in the thinnest regions of the micellar films in which only single layers of micelles have been deposited. In most samples, however, spin casting yields a variation in film thickness. An increase in thickness is generally accompanied by a transition in the observed plan-view morphology toward that of stacking multiple micelle layers. Shown via TEM in Figure 7 is the transition from a region of the familiar monolayer (upper-left corner) toward a bilayered region in which the two overlapping micelle layers assemble out-of-register (center) and in-register (lower-right corner) with each other. Occasionally, a transition from a bilayer to triple-layered deposited micelles has been observed in still thicker film regions.

We attempted to synthesize PbS nanoclusters within the micellar thin films by exposing samples loaded with Pb^{2+} ions to H_2S gas. However, we noticed during TEM observations that the resulting nanoclusters became unstable upon contact with the electron beam and appeared to “evaporate” from the micellar film template. This rearrangement of the nanocluster material led to the formation of larger aggregates on the film’s surface. We believe that these Pb-based surface objects of various sizes and shapes (rodlike, elliptical, rhombic, etc.) are crystals of PbS and its derivatives (e.g., $PbSO_4$).[20]

Figure 8 depicts the same transition region of the originally Pb-loaded sample (as Figure 7) after the sample has been exposed to H_2S and the electron beam (in TEM). Rearrangement of materials upon beam contact has effectively removed the PbS nanoclusters from the cavitated PAA domains. The depletion of cluster materials from the micellar monolayer area (thinner region, upper left) leaves behind mostly empty array of cavities (bright contrast) in the polymer matrix. In the bilayered region (lower right), the nanoclusters have been depleted from the open top layer of the overlapping micelles, while a hexagonal array of clusters remains in the covered bottom layer. We do not know the exact mechanism by which these nanoclusters become mobilized upon contact with the electron beam. Nevertheless, the above observation serves as an example of the unusual characteristics associated with our cavitated micellar thin films.

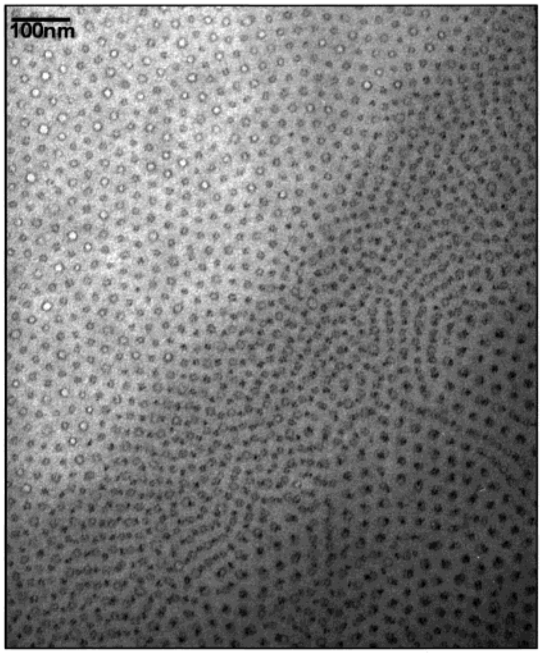

Figure 7. Transition in film morphology associated with increasing film thickness as observed in plan-view TEM. Film was exposed sequentially to $NaOH_{aq}$ and $PbAc_{2(aq)}$.

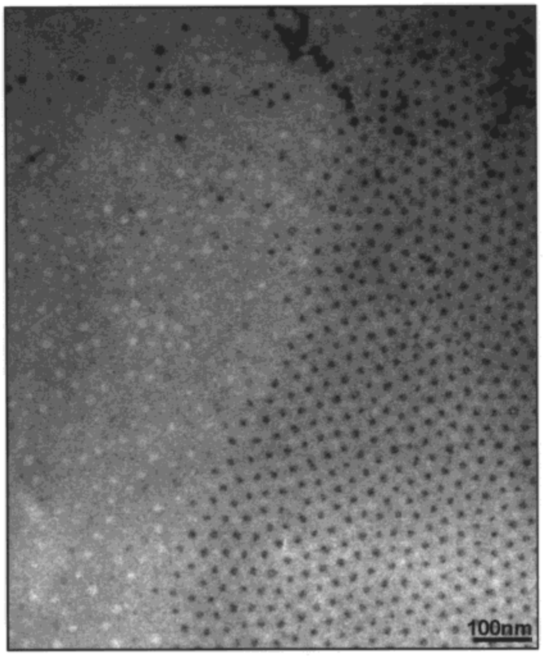

Figure 8. Plan-view TEM of cavitated thin film treated with $PbAc_{2(aq)}$ and exposed to $H_2S_{(g)}$: depletion of cluster material from open PAA domains on exposure to electron beam.

Similar structural transformation of the as-deposited (hexagonal) micelle to that of cavitated micelles has been successfully reproduced on other (more hydrophilic) substrates including glass and silicon wafer (with native oxides). Since the direct adsorption of micelles on both polar and nonpolar solid substrates appears to result in the same lateral ordering,[4,21] we anticipate the ability to generate such micellar thin films on many other surfaces as well.

There are possible applications for the cavitated micellar thin films. There is interest in the study of the influence of nanoscale substrate topography on the adhesion and behavior of biological cells.[22] The micellar thin films also offer the possibility of creating biospecific substrates via chemical tethering of cell-binding ligands to the carboxylic acid groups present through the cavitated PAA domains. Micellar thin film templates are potentially useful in the current efforts on miniaturization of devices. For example, the ability to selectively decorate the micelle cores with magnetic cobalt could contribute to enhancing data storage capacity in magnetic recording media,[23] owing to high areal density of the micellar self-assembly.

Conclusion

The deposition of styrene−acrylic acid block copolymer reverse micelles from toluene solution, and the formation of micellar thin films comprising laterally ordered arrays of PAA microdomains in the PS matrix, is demonstrated, along with successful use of such thin films as templates to synthesize corresponding arrays of inorganic (silver) nanoclusters. Upon exposure to the solution of a monovalent base, cavitation of the individual deposited micelles occurs due to hydration and swelling of the PAA cores, in analogy to swelling behavior of carboxyl-containing polymer latex particles in alkaline solution. The cavitation of the micelles transforms the as-cast film structure into in-plane surface cavities that are also arranged in the same hexagonal arrays. These cavities connect the PAA domains, originally covered by PS (corona) layer, to the free surface. Thus, the cavitated PAA domains serve effectively as open nanoreactors for nanocluster synthesis as demonstrated. Finally, the process presented here represents a facile method to create patterned surfaces comprising nanoscale carboxyl-functionalized (i.e., chemically reactive) sites.

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