Self-Ordering of Diblock Copolymers from Solution

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Spontaneous self-assembly of macromolecules is an important area of current research since it provides the opportunity for nanoscale patterning otherwise inaccessible by lithographic procedures.[1−3] In this regard, attention has been focused on long-chain block copolymers, which are macromolecules composed of blocks of two different monomer units covalently linked. These diblocks are usually incompatible, and when annealed as thin films, they segregate into lamellae arranged such that one of the blocks uniformly covers the substrate surface as the other is localized at the vacuum/polymer interface.[4] We report here the spontaneous self-assembly of symmetric diblock copolymers into surface micelles, which occurs during adsorption onto a solid surface from a concentrated solution employing a selective solvent. These micelles form a two-dimensional (2D) superlattice with a high degree of in-plane ordering, apparent in microscope images. Significantly, a circular-to-ribbon phase transition is observed with increasing polymer concentration. These 2D structures are shown to be the equilibrium configuration of the diblock copolymer in the presence of a selective solvent. The observed morphologies are analogous to those which arise from phase transitions previously observed[5] in three-dimensions when a lamellar diblock copolymer phase is swollen by low molecular weight homopolymer. The films deposited on solid surfaces by the passive dipping technique used here have been shown to form chemical, as well as topographical, nonhomogeneous patterning masks with structure length scales or pattern distances in the nanometer range.[6] Consequently, understanding the physical principles governing the pattern formation enables one to control the scale, morphology, and chemical composition of the polymer aggregates themselves.

Table 1. Characterization of the Micelles at the Circular-to-Ribbon Transition[a]

$N_{PS}-N_{PVP}$	h (Å)	L_{min} (Å)
800−870	80	750
730−580	60	710
510−540	57	540
520−380	30	580
200−200	25	400

[a] Height (h) of the core (measured by AFM) and minimum spacing (L_{min}) between cores are given.

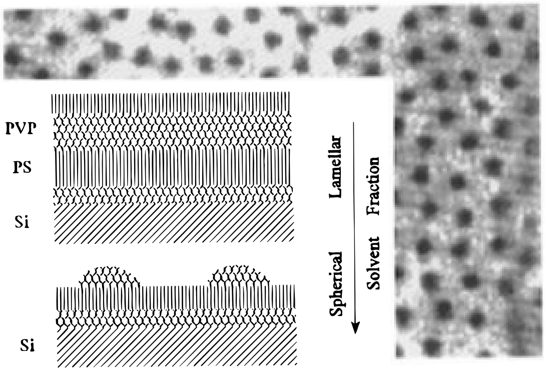

Figure 1. Bright field TEM image of the adsorbed micellar structure formed from a diblock copolymer/toluene solution of 2 mg/mL for $PS_{800}-PVP_{870}$. The micelles are 80 Å high (measured by contact atomic force microscopy) and are 1000 Å apart. The ordered micelles are formed on an SiO-coated grid. Dark cores correspond to PVP aggregates. The inset shows the phase transition from lamellae to circular micelles as the solvent swells the PS blocks.

Formation of the surface micelles is very simple. A clean substrate (i.e., Si) is immersed in a beaker containing a toluene solution of polystyrene(PS)-*b*-poly-2-vinylpyridine(PVP) diblock copolymer (Table 1). Immersion times varying from a few seconds to 24 h resulted in no discernable difference in the structure observed using microscopy. The substrates were rinsed for a few seconds in pure toluene to remove any loosely attached residues following the solvent evaporation process and were examined using contact mode atomic force microscopy (AFM). Figure 1 is a transmission electron microscopy (TEM) image of the pattern obtained by dipping an SiO-covered grid in a $PS_{800}-PVP_{870}$ toluene solution. The TEM sample was stained with I_2 vapor, which adsorbs only in the PVP domains and renders them opaque to the electron beam. In the figure, the protruding circular cores are dark (i.e., are composed of the PVP blocks). Since toluene is a good solvent for PS and is a nonsolvent for PVP, the PVP block collapses to minimize the unfavorable interaction with the toluene. The spaces between cores, which appear light in the TEM image, are composed of stretched PS blocks. This pattern, clearly an inverted phase, has the same dimensions as those formed when the polymer is spread at the air/water interface.[7] From the dimensions of the surface micelles in Figure 1, one can estimate that they contain approximately 40 copolymer chains. In toluene solution, the cores of the 3D micelle are also composed of the PVP block, while the PS chains form the corona which extends into the good solvent. Three-dimensional micelles, however, contain only six chains per micelle, as determined by light scattering, and are significantly smaller than the 2D micelles observed in Figure 1. Consequently the observed structures are not due to a direct adsorption of spherical micelles from solution, but form after significant reorganization of the chains on the adsorbing surface. In this case, the silicon surface is first covered by a lamellar layer, approximately 40 Å thick, with the PS at the solution interface and the micelles then order on top of this layer (Figure 1, inset). Neutron reflectivity and ellipsometry studies[8] have confirmed the existence of this layer and verified theoretical predictions that the excluded volume interaction causes the PS block to form a stretched brush in a toluene

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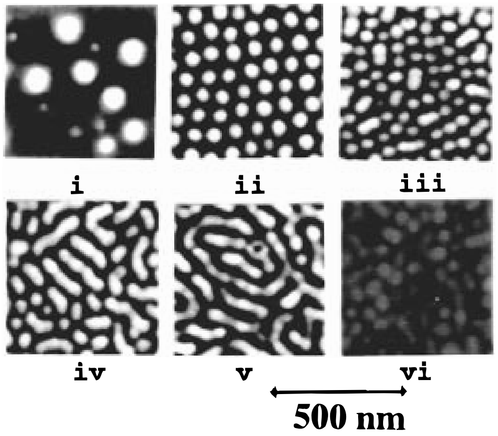

Figure 2. Patterns obtained from PS$_{800}$−PVP$_{870}$ toluene solutions of concentrations of 0.5, 2, 7, 9, 11, and 13 mg/mL respectively.

solution.[9] This excluded volume interaction can also swell the PS coronas, minimize the overlap between adjacent micelles, and induce the long-range hexagonal order observed in Figure 1.

The pattern of surface micelles on Si was found to depend strongly on the solution concentration, which was varied between 0.5 and 13 mg/mL. As shown in Figure 2, at low concentrations the chains adsorb into large isolated micelles with scattered regions where short-range order has begun to nucleate. At higher concentrations, long-range, quasi-hexagonal order is established. With a further increase in concentration, the surface micelles become smaller and closer packed. The unfavorable interaction between PS and PVP limits the amount of PS/PVP interfacial area and determines the minimum circular micelle size and micelle−micelle distance.[10] Further increase of concentration causes the micelle cores to fuse into ribbons which are several micrometers long with the same minimum separation distance as spherical micelles. The ribbon or cylindrical micelle configuration, whose energy is normally higher than the circular micelle,[10] becomes the ground state of the system since it can accommodate more material while keeping both the micelle core and corona dimensions constant. Once the circular-to-ribbon transformation is complete, a further increase in concentration produces a second disordered layer of circular micelles lying above the first. The continual change in micelle size and morphology are governed solely by the solution concentration.

The minimum micelle spacings at the circular-to-ribbon transformation are listed in Table 1. The minimum micelle−micelle distance is seen to scale as $5R_g^{PS}$, where R_g^{PS} is the radius of gyration of PS in a good solvent, confirming that the micellar corona chains are highly stretched. The height of the PVP core scales as R_g^{PVP}, the melt radius of gyration. The diameter of the core, as measured from the TEM micrograph in Figure 1b, scales approximately as $3.5R_g^{PVP}$, suggesting that the micelle core is stretched laterally into a pancake configuration.

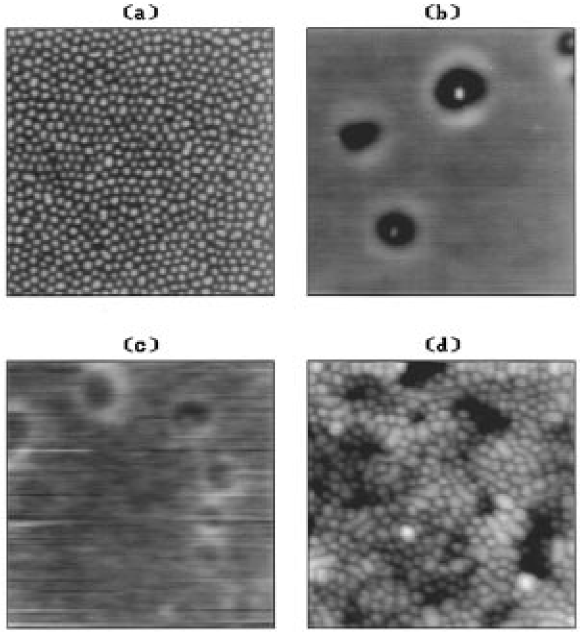

Figure 3. The four 2 × 2 micrometer images describe the reversibility of the micellization process. (a) The source sample dipped from a 3 mg/mL solution of PS$_{800}$−PVP$_{870}$ copolymer; (b) after annealing for 2 h at 180 °C; (c) after exposure for 10 min in toluene vapor; (d) after exposure for 3 h in toluene vapor.

In order to determine whether the observed morphologies are equilibrium structures or artifacts of the evaporation process, they were studied under solvent conditions in a glass AFM liquid cell. No micelles were detected on the silicon surface in the toluene solutions typically used for the dipping experiments described above. Spontaneous self-assembly on Si was only observed in situ as the solution became very concentrated (∼10%). When the micelle structures were annealed in vacuum at 180 °C, the surface became flat and the melt equilibrium configuration (lamellar) was obtained (figure 3). The samples were then placed in an enclosed vapor cell where a thin layer of toluene could be adsorbed onto the substrate from a warmer solvent reservoir. The equilibrium liquid layer thickness, as measured with ellipsometry, was approximately one micrometer, which is equivalent to spreading a 1% concentrated polymer solution. The surface of the film was then subjected to in situ contact AFM measurement in a toluene atmosphere. The circular micelle structures were recovered after approximately 3 h. The rearrangement in the presence of toluene vapor is much slower than the initial adsorption from the concentrated solution, since the diblock copolymers become strongly associated with the silicon surface during the annealing process.

These experiments conclusively show that the formation of two-dimensional micelles on a solid substrate is a reversible equilibrium process in very concentrated polymer solutions. The micelles form rapidly in the dipping process when the equilibrium concentration is reached. As long as the solvent is present, the polymer chains are mobile and can organize into the specific micelle structure that minimizes the total free energy. Once the solvent has completely evaporated, the polymer becomes glassy and the micelle structures are frozen. The lamellar−cylindrical−spherical transition, upon selectively swelling one of the blocks with low molecular weight homopolymer, is qualitatively similar to the results reported by Hashimoto using bulk diblock copolymers and was explained in terms of balancing the gain in conformational free energy with the cose of bending the interface.[5,10] A similar mechanism seems to be the driving force in the thin films reported here, except that in this case one must also consider the adsorption energies acting at the liquid and solid interfaces in order to obtain a quantitative description.

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