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Ordering of Block Copolymer Micelles in Confined Two-Dimensional Solutions

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In this paper the structure of thin films of a solution of diblock copolymer micelles in a confined two-dimensional environment will be addressed. The films are made of diblock copolymer micelles dissolved in an organic solvent (toluene) and are studied by means of transmission electron microscopy (TEM). This is possible due to the very low temperature used (cryo-TEM), a technique applied only very recently for organic solvents.[1,2]

The diblock copolymer consists of styrene and 2-vinylpyridine, one block of deuterated polystyrene (dPS) with a molecular weight of 75 000 and one of poly(2-vinylpyridine) (P2VP) with a molecular weight of 102 000 or 32 000 (75–102 and 75–32, respectively). The diblock copolymers were dissolved in toluene, a good solvent for PS and a poor solvent for P2VP, yielding a 2% (w/v) solution. The block copolymers form micelles already at low concentrations.[3] The core is densely filled by the P2VP blocks, while the dPS blocks form the corona.[2]

Using TEM, it is necessary to have a very thin film of the material of interest. Here we use so-called "holey" carbon grids, having a noncontinuous support film, looking like a spider web (see Figures 1 and 2). The holes determine to a large extent the confinement imposed on the micelles (as explained below). The "holey" grids were covered with a thin layer of the solution and cooled to −196 °C in order to prevent evaporation of the toluene. TEM micrographs were recorded while the specimen temperature was kept at −170 °C. (For more details, see ref 2.)

Figures 1 and 2 show micrographs of films of block copolymers 75–102 and 75–32, respectively. The holes on the grid are spanned by a thin film of frozen solution. The micelles are visible only because of phase contrast.[4,5] They are confined to a small volume limited by the toluene/air interfaces and the carbon support surrounding the toluene film. The thickness of the film is apparently comparable to the size of the micelles.[2] The core diameter determined from the micrographs is $D \approx 45 \pm 5$ nm for 75–102 and $D \approx 30 \pm 5$ nm for 75–32. Typical intermicellar distances are $D_2 \approx 60 \pm 5$ nm and $D_2 \approx 45 \pm 5$ nm, respectively. D_2 can be interpreted as a total micellar diameter (including core and corona).

Inside the smaller holes and in the vicinity of the edges of the larger holes, the micelles tend to arrange themselves in lines locally parallel to the boundary with equidistant spacing. On a global scope the lines are closed and envelope one another. In the inner parts of the larger holes a hexagonal ordering of micelles is obvious. This phenomenon is also observed in biological systems.[6] Note that micelles are ordered even in those cases where the concentration is too low to cover the whole area of the hole (Figure 2). In these cases micelles form hexagonally ordered clusters, leaving some parts of the area uncovered. This behavior (ordering and clustering) implies that there are attractive forces between the micelles and between the micelles and the confining boundary. Because micelles in the bulk of the toluene solution repel each other, this must be a consequence of the two-dimensional nature of the situation. Here, the film surface tension apparently induces an effective attraction between the micelles. In fact, the surface area is larger in the case where micelles

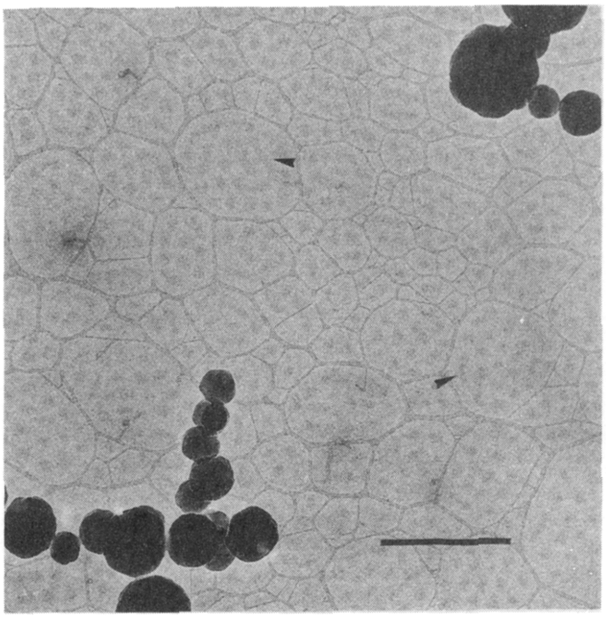

Figure 1. Cryo-electron micrograph of 75–102 dPS–P2VP diblock copolymer in toluene. Indicated are areas where the micelles start agglomerating: the first step in the formation of thin diblock copolymer films. (The bar indicates 500 nm.)

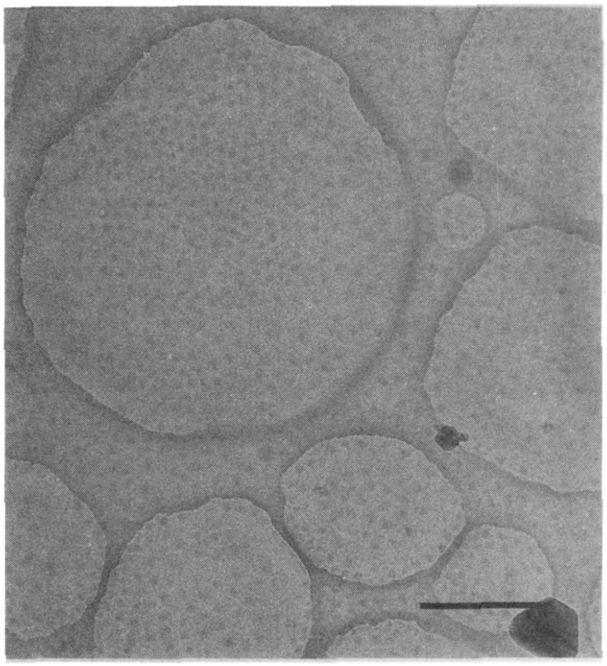

Figure 2. Cryo-electron micrograph of 75–32 dPS–P2VP diblock copolymer in toluene. In the bigger holes, not always completely filled, the micelles are hexagonally closed packed. (The bar indicates 500 nm.)

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Figure 3. Schematic drawing of diblock copolymer micelles in a thin film of amorphous toluene showing the difference in surface area when the micelles are apart from each other (a) and when they are close together (b).

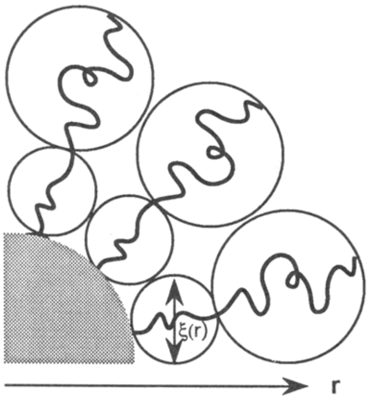

Figure 4. Schematic drawing of a micelle showing the dilute polystyrene chains emerging from the dense poly(2-vinylpyridine) core.

are apart from each other (Figure 3a) than in the case where the micelles are close to each other (Figure 3b). This attraction favors the formation of a 2D ordered structure, hexagonal ordering being the most natural.

As has been argued before, the micelles observed have been formed during the preparation of the solution.[3] Since the electron micrographs give detailed information about the average size of the micelles, it is of some interest to compare it with theoretical predictions. The formation of *equilibrium* micelles is an extremely slow process (refs 7 and 8) and usually takes much longer than the time of the experiment. Therefore, the size of the micelles is controlled by dynamics. Small micelles can be formed relatively fast, and this process is enhanced by the strong incompatibility between the P2VP blocks and toluene. At first, the micellar size increases with time primarily due to a fusion of smaller micelles into larger ones

$$Q_1 + Q_2 \Rightarrow Q \tag{1}$$

where Q is the number of block copolymer chains in a micelle. The fusion is an activation process. The activation state corresponds to the situation where the cores of two micelles just come into contact, implying severe deformation of the coronas. The activation energy, U, the energy of "elastic" deformation of PS blocks, is on the order of the elastic energy of a chain stretch in an undeformed corona (cf. ref 7). The size of the micelles observed is determined by

$$wt_0 \exp(-U) \sim 1 \tag{2}$$

where w is the typical frequency of contacts between two micelles and t_0 is the preparation time. Conformations of PS blocks in a corona are similar to those for a star polymer in a good solvent (with functionality Q).[9–11] Using the picture of Daoud–Cotton blobs[9,10] (Figure 4), the free energy of the corona can be obtained. The result is $U_{\mathrm{cor}} \sim QQ^{1/2} \ln(D_2/D)$, where D_2/D is the ratio of the total diameter of the micelle to the diameter of its core. Absorbing the log factor in an unknown constant, κ (κ is weakly dependent on the solvent quality), we get the barrier for fusion

$$U = \kappa Q^{3/2} \tag{3}$$

(cf. ref 7). Equations 2 and 3 determine the number of block copolymer chains in a micelle:

$$Q \simeq \left[\ln \frac{wt_0}{\kappa}\right]^{2/3} \tag{4}$$

Hence, the aggregation number, Q, is predicted to be nearly independent of the molecular weights.

The aggregation number is connected to the diameter of the core. Assuming that the volume fraction of toluene in the P2VP core is small,[7] we obtain using the incompressibility condition:

$$Q = \frac{\pi}{6} \frac{D^3}{N_{\mathrm{P2VP}}\nu} \tag{5}$$

where $N_{\mathrm{P2VP}}\nu$ is the intrinsic volume of a P2VP block (ν is the volume per link). Using the observed values for D, we get $Q \approx 308$ for 75–102 and $Q \approx 290$ for 75–32. These aggregation numbers are similar, in agreement with the theoretical arguments given above.

The corona thickness can also be estimated using the Daoud–Cotton blob picture. The following relation between D_2 and D can be obtained as a result:

$$D_2^{1/\nu}\, D^{1/\nu} + \kappa' a^{1/\nu} N_{\mathrm{PS}} Q^{(1-\nu)/2\nu} \tag{6}$$

where κ' is a numerical constant, a is the statistical segment length of PS chains, and $\nu = 0.6$ is the Flory exponent.[12] With $\kappa' = 0.31$ we get the following from eq 6: $D_2 \approx 56$ nm for 75–102 and $D_2 \approx 41$ nm for the 75–32 system in reasonable agreement with the experimental data.

Only the cores of the micelles are visible because of the low PS corona density. The polystyrene blocks start from the surface of the core and are dissolved in toluene. This surface area is approximately equal to the area occupied by the first shell of blobs in contact with the core surface (Figure 4):

$$Q\frac{\pi}{4}\xi^2(r) \approx 4\pi R^2 \tag{7}$$

where $\xi(r)$ is the diameter of the blob at a distance r to the core center and R the radius of the core. The number of flexible segments per blob, $g(r)$, can be calculated by[9]

$$g^{3/5}(r)\, a = \frac{1}{2}\xi(r) \tag{8}$$

The dimensionless density can then be calculated from

$$\varrho(r) = \frac{6ga^3}{\pi\xi^3(r)} \tag{9}$$

Taking $a = 0.35$ nm results in a density of polystyrene blocks near the core surface of approximately 1–3%. According to eqs 7–9, this density continues to drop as $1/r^{4/3}$. It is obvious that the polystyrene corona is very dilute and will not be distinguishable from the amorphous toluene in the microscope.

In conclusion, the cryo-TEM technique was shown to be extremely useful for the study of thin films of diblock copolymer solutions. Self-assembly of copolymer micelles in 2D ordered structures inside micro holes of different sizes and shapes (corrals) was observed. The obtained results are in agreement with the theoretical predictions using the Daoud–Cotton blob picture. The method can be used to analyze the general effect of 2D confinement on the nature of ordering of macromolecular aggregates. The cryo-TEM technique can also provide useful information about the first stages of the formation of 3D micellar structures and the effect of surfaces on these structures.

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