Notes

An Intriguing Morphology in Crystallizable Block Copolymers

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The complex and important structures formed by assembly of amphiphilic molecules result from a delicate balance between competing intermolecular forces. In the simplest example, soap molecules surround and divide oil droplets in water. In biological systems the intricate function of selective membranes and cellular structures is determined by such forces. The variety of phases formed by polar lipids are notable for their sensitivity to the intermolecular forces dictating their curvature.[1-3] In polymeric systems, the length of the chain molecules exacerbates this balance of forces, often producing new and unique topologies.[4] While the influence of crystallization of one of the components has been known for some time,[5] we have discovered that the unique interplay between hydration and ordering can produce new morphologies, namely, cylindrical structures coexisting with spheres and lamellae. These new structures provide a visual display of the intricate balance between ordering and curvature in self-assembling polymers.

We have previously shown[6-9] that micelle formation in poly(ethylene oxide)/polystyrene (PEO/PS) diblock copolymers in cyclopentane is very sensitive to trace amounts of water. Due to the affinity of PEO for water and the incompatibility of water with the other components, the addition of water to a PEO/PS solution promotes the formation of more micelles, each containing more chains. The water concentration has an even more dramatic effect in systems having very little water where unusually large stable nonspherical aggregates with semicrystalline domains are formed.

Our first indication of the presence of crystalline aggregates came as we investigated the associative behavior of PEO/PS with dynamic light scattering. We dissolved a dry solid-state PEO/PS diblock (purchased from Polymer Laboratories having a molecular weight of 11 140 and 65 EO/80 S repeat units) in cyclopentane at concentrations around 1 wt % and measured size distributions between additions of water. In dynamic light scattering the decay of an intensity–time autocorrelation function is related to rates of molecular motions. We find the relaxation times corresponding to the motion of the associated structures by Laplace inversion of the correlation function.[10] In systems having very little water, we resolve three distinct particles, shown in the intensity distribution in Figure 1 and identified as aggregates, micelles and single chains. The effective hydrodynamic radius of the aggregates ranges from 40 to 110 nm, while the spherical micelles are 10–14 nm and single chains are 2 nm.[6] The addition of water promotes the formation of spherical micelles with cores of hydrated poly(ethylene oxide) at the expense of both single chains and aggregates. The aggregates, when present, always coexist with micelles, as illustrated in Figure 1. Similar observations were made with a larger PEO/PS, M_w = 187 000 (170 EO and 1730 S); however, these solutions must be dehydrated further to form crystalline aggregates. The aggregates are stable for periods longer than a year, and their presence is very reproducible. We can remove aggregates by adding water and produce them by dehydrating solutions having spherical micelles. There is a large window of polymer and water concentrations where spherical micelles and aggregate coexist.

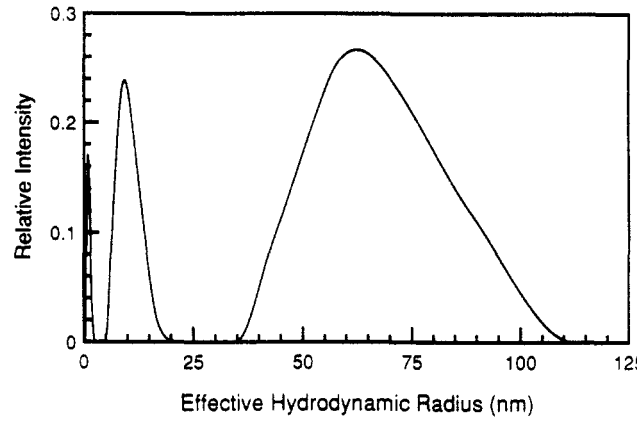

Figure 1. Typical intensity-weighted size distribution for dry (25 ppm water) solutions of a PEO/PS = 65/80 block copolymer at 1300 ppm size distributions measured at an angle of 90°. The peaks represent single chains, spherical micelles, and large aggregates in ascending order.

To further investigate aggregate stability and reversibility, we studied the effect of changing temperature with a sealed solution containing PEO/PS = 65/80 aggregates. The sample was heated to 40 °C and cooled to 23 °C without structural changes. Upon heating to 68 °C, above the melting temperature of poly(ethylene oxide), dynamic light scattering on the sealed sample revealed only single chains. Subsequent cooling to 23 °C resulted in the formation of very large aggregates over a period of 24–48 h. Eventually, the aggregates became so large that they settled out of solution. These temperature experiments indicate that dispersed aggregates must be melted to approach their equilibrium structure; the dependence on the preparation method indicates the kinetic influences on morphology.

These aggregates were large enough to investigate with an optical microscope when sealed in precision square glass capillary tubing with a path length of 1.0 mm and wall thickness of 0.2 mm. Figure 2 reveals a polydisperse collection of square platelets several microns on a side with poorly resolved edges. We envision the structure as a crystalline lamellar domain of poly(ethylene oxide) in between two brushes of solvated polystyrene.

We explored these structures with transmission electron microscopy at the Center for Interfacial Engineering at

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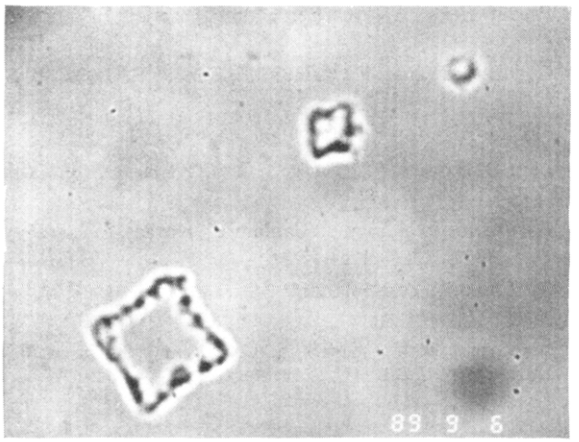

Figure 2. Optical micrographs of heat-treated aggregates illustrating a polydisperse collection of square platelets.

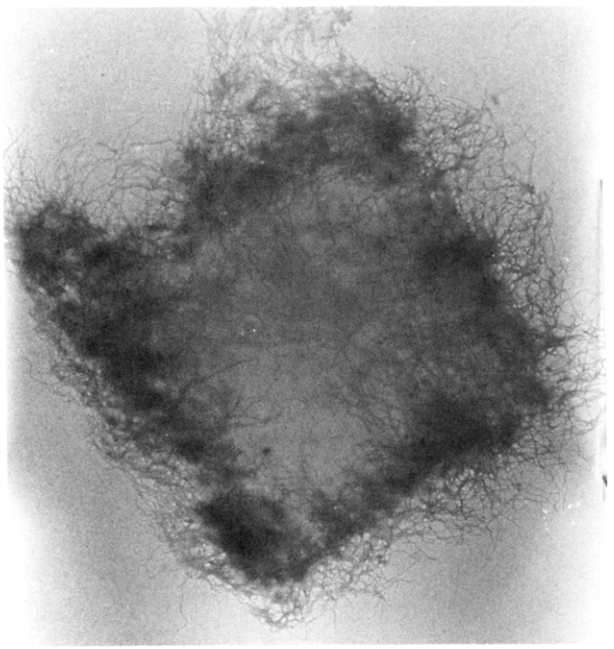

Figure 3. Electron micrograph of a heat-treated aggregate revealing a platelet structure with copolymer cylinders extending from the edges.

the University of Minnesota. Samples were prepared by placing a small drop of the liquid on a poly(vinyl formal) film coated with carbon and mounted on the surface of a standard TEM grid. The samples were dried via the rapid evaporation of cyclopentane and observed at 100 kV in a Phillips CM30 analytical electron microscope. We again observed square platelets (see Figure 3) now with the edges resolved. The surprising discovery is the cylindrical structures we find protruding from the platelet edges with diameters of 30 nm, the same size as the hydrodynamic diameter of PEO/PS = 65/80 spherical micelles. We propose that spherical micelles coexist with these lamellar platelets and cylindrical protrusions. The cylinders are thus micelles having ordered PEO cores with PS coronae; we illustrate the proposed structure in Figure 4. A number of such crystallites were observed, and the cylindrical structures correspond to the indistinct edges of the dispersed platelets observed with an optical microscope.

Crystallites of PS/PEO diblock copolymers were first observed in ethylbenzene through light scattering, birefringence, and dielectric measurements.[11] A lamellar structure was proposed for the crystals.[12] Lamellar structures have been seen in optical micrographs of dilute

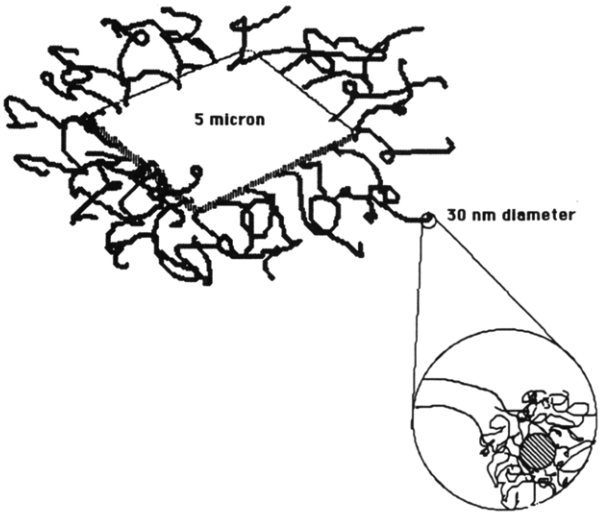

Figure 4. Schematic diagram of the semicrystalline micelles. The platelet comprises a crystalline layer in between two brushes of swollen blocks. Cylindrical micelles protrude from the edges of the platelet.

solutions of PS/PEO diblock copolymers in several solvents.[5] Electron diffraction patterns indicate that the PEO in the diblock structures has the same crystal structure as PEO homopolymer.[13] Studies of crystals composed of diblock copolymer or PEO homopolymer crystals seeded by copolymer crystals display structural variation, although the cylindrical micelles extending from the edges of platelets have not been seen previously. Polarized light microscopy of PS/PEO solutions in pentanedione by Kovacs and co-workers[14] reveals evidence for cylindrical mesophases having liquid-crystalline order. These structures may be related to the cylindrical micelles observed in this work; indeed optical evidence for kinking and undulation in these cylinders matches our picture of bent cylinders. While initial theoretical work has focused on the lamellar morphology,[15,16] these new structures serve to motivate additional investigations.

We have performed a preliminary study illustrating the competition between spherical micelles and semicrystalline aggregates as a function of water and copolymer concentrations. Spherical micelles coexist with aggregates over a wide range of copolymer and water concentrations. After annealing, we find aggregates with both cylindrical and planar geometries in coexistence with spherical micelles. The existence of crystallites in PS/PEO is clearly related to water content. Strong interactions among poly(ethylene oxide) blocks may promote a more ordered domain having less curvature. The addition of water disrupts the order in the crystalline domain, resulting in the spherical structure otherwise preferred by an amorphous block copolymer. We suspect that the spheres scavenge most of the water in the system, with decreasing amounts of water and enhanced order in the cylindrical and lamellar structures. In addition, despite the modest polydispersity of these polymers (M_w/M_n = 1.12), the formation of cylindrical structures may reflect a partitioning of polymers having larger polystyrene content. These observations illustrate the importance of ordering on the morphology of assembled block copolymers and serve to motivate further investigation into this phenomenon.

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