Mesosized Crystal-like Structure of Hexagonally Packed Hollow Hoops by Solution Self-Assembly of Diblock Copolymers

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Mesosize crystal-like aggregates with an internal structure of hexagonally packed hollow hoops (HHH) in a polystyrene matrix have been prepared in solution by self-assembly of asymmetric polystyrene-*b*-poly(acrylic acid) diblock copolymers. Most of the aggregates are cylindrical or in the shape of truncated cones. The external surface of the aggregates and the internal surface of the hollow hoops are lines with short poly(acrylic acid) chains. The hoop morphology is imposed because the end-capping energy of a rod on this size scale is more important than the curvature energy. A strong interdependence between the external shape and the internal structure in these mesosize particles is demonstrated. [S0031-9007(97)04815-1]

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The organization of mesoscale self-assembled structures is an active area of research in materials chemistry, structural biochemistry, and other disciplines [1]. Molecular self-assembly gives rise to a wide variety of complex biological structures; also, self-assembled systems have potential applications, for example, as vehicles for drug and gene delivery, and as matrices or templates from which new structural materials can be made [2]. Block copolymers with well characterized compositions have received much attention in this context [3,4]. A number of ordered structures have been identified in bulk [5]; more recently, a wide range of morphologies has also been prepared in dilute solutions [6–8]. In this Letter, we report on the formation of mesoscale aggregates from polystyrene-*b*-poly(acrylic acid) diblock copolymers with a highly regular, nearly crystalline internal structure. The preparation involves first the formation of individual vesicles and a subsequent assembly of the vesicles induced by added NaCl ions. Driven by the minimization of surface energy and chain stretching, as well as the strong interdependence between the external shape and the internal structure of the particles, the aggregated vesicles collapse and rearrange ("crystallize") gradually to form aggregates with a crystalline hexagonally packed array of hollow hoops, which are lined on the inside with the poly(acrylic acid) blocks. The size of the aggregates imposes the crystal morphology, which, in turn, modifies the external shape of the particles. On this size scale, the end-capping energy of a microdomain is more important than the curvature energy in determining the structure of the aggregates.

The copolymer used in this study is a diblock of polystyrene and poly(acrylic acid), PS(410)-*b*-PAA(13), where the numbers in parentheses represent the number of average degrees of polymerization of the blocks. To prepare the mesoscale aggregates in aqueous solution, deionized water is added dropwise with stirring to a solution of 2 wt. % copolymer in N,N-dimethylformamide (DMF, a common solvent for both the PS and the PAA blocks). Self-assembly of the copolymers starts at about 3.5 wt % of water to yield vesicles. When the water content reaches about 6 wt %, a small amount of NaCl (aqueous solution) is added to the solution to induce aggregation of the as-formed vesicles. Subsequently, the solution, at that water content, is stirred for one day (or for varying times for the kinetic studies) to allow PS wall fusion and rearrangement. Finally, the structures of the aggregates are fixed by adding more water which extracts DMF from the PS domain. The resulting solution is dialyzed against distilled water for 3 days to remove all of the DMF. The structures of the aggregates are observed on a Phillips EM410 transmission electron microscope (TEM). A more detailed description of the TEM sample preparation techniques can be found in previous publications [6].

Figure 1 shows a micrograph of relatively small mesosize aggregates, which are chosen for display since the dimensions permit observation of the internal structures by TEM. Larger structures are more opaque. From the dimensions of the shadowed regions (not seen because exposure time was such as to optimize the visibility of the internal features), these particles are clearly three dimensional. Dark regions represent the block copolymer, while the white regions represent hollow spaces (the spaces were filled with an aqueous solution, but the water was removed during the TEM sample preparation). The aggregates, on first sight, appear to have several different internal structures. For example, aggregates labeled A in Fig. 1, which are typical of many, appear mainly cylindrical; some others resemble truncated cones; near the outer regions one sees a hexagonal array of hollow spots; the center regions appear lamellar. The brightness of the spots decreases toward the center of the aggregates. Some of the aggregates show a structure of concentric circles (indicated by B in Fig. 1). The very high degree of regularity suggests that a process akin to crystallization may be operative.

In order to identify the three-dimensional structure from two-dimensional projected images, a tilt series of

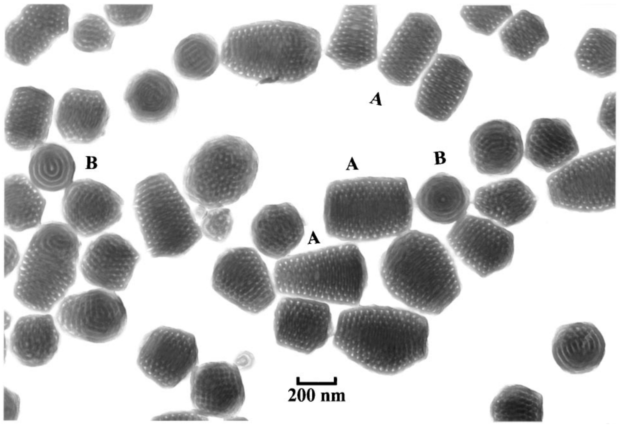

FIG. 1. Mesosize aggregates with regular hollow internal structures made from a 2 wt% solution of PS(410)-*b*-PAA(13) in DMF/H_2O (94/6) mixture by the addition of NaCl to a final concentration of 11 mM.

micrographs is very useful. Figure 2 shows a set of TEM images of the same aggregates but viewed from different angles. In general, the appearance of the aggregates changes somewhat as a function of the tilt angle. Specifically, when the angle changes from $-45°$ to $+45°$, particle A shows a change from hexagonally packed bright spots to dark spots, while the dimensions remain the same; particle B, somewhat smaller in size, does not appear to change appreciably in either dimensions or internal structure. Most interestingly, particle C shows a concentric circle structure at a tilt angle of $-45°$, which changes to hexagonally packed white spots when it is viewed at an angle of $+45°$. These features suggest that the internal structures of most of the aggregates may be very similar in spite of difference in their appearance. These differences may be merely a result of our viewing the aggregates from different directions, since the aggregates are more or less random in their orientation on the EM grid. These results also suggest that the aggregates are either cylindrical or in the shape of truncated cones with a highly cylindrically symmetric internal structure. This structure appears hexagonally symmetric viewed from some directions, but to consist of concentric circles when viewed from other directions.

Block copolymers in bulk usually phase separate because of the incompatibility of the different blocks. Microdomains resulting from the aggregation of the minor component can form different ordered structures in the matrix composed of the major component blocks; examples are spheres on a cubic lattice, hexagonally packed cylinders, ordered bicontinuous gyroids, hexagonally performated lamellae, and simple lamellae [5]. We find that none of these well-known structures can describe the morphology of the aggregates found in the present system. A new structure of hexagonally packed hollow hoops (HHH) is suggested, which does satisfy the observations.

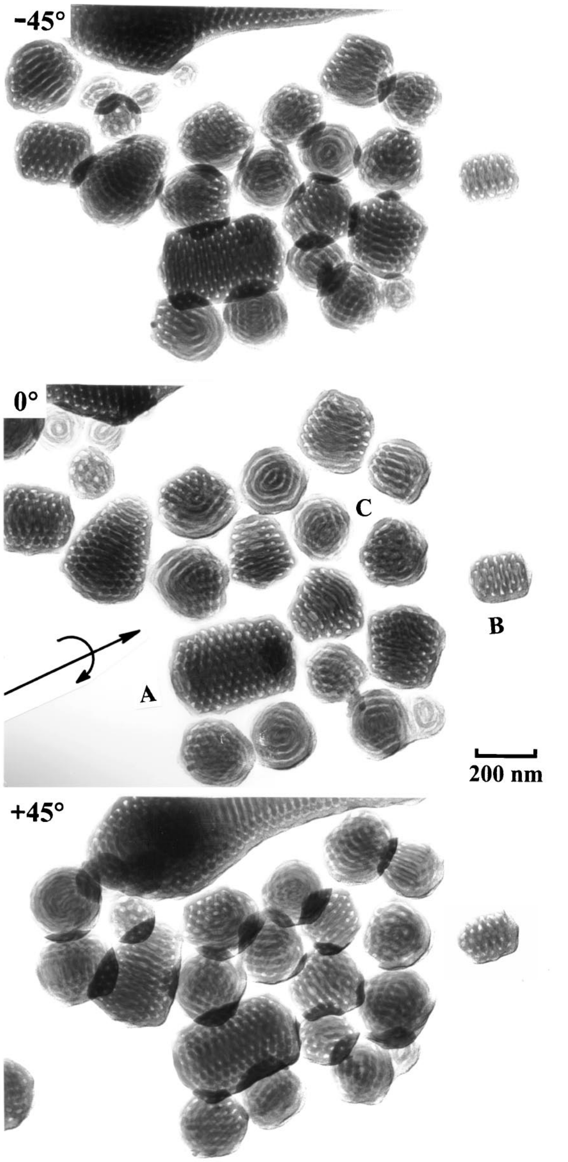

FIG. 2. TEM pictures of the same mesosize aggregates imaged after the aggregates have been tilted to different angles as labeled in the pictures. The axis along which the aggregates were rotated is indicated by the arrow in the 0° picture.

The HHH structure of the mesosized aggregates is confirmed by computer visualization. The appearance of the experimental micrographs was simulated by obtaining two-dimensional projections of the structure from different viewing directions. Figure 3(A) shows the arrangement of multiple-concentric hoops in a hexagonal pattern with the parameters (e.g., tube diameter and intertube distance) obtained from the TEM results. Figures 3(B) to 3(D) show the computer generated images by using the Linux version of Persistence of Vision Raytrancer, POV-Ray. The darkness at each pixel is a linear function of the thickness of the PS phase at that point. Multiple-concentric rings [Fig. 3(B)] are seen in the projection along the direction of the (principal) Z axis. Figure 3(C) is an image viewed along the Y axis (90° from the Z axis). Hexagonally packed bright spots are seen in the outer regions, while the center regions appear lamellar. Figure 3D shows a projection along a direction of 20° from the Y axis on the YZ plane.

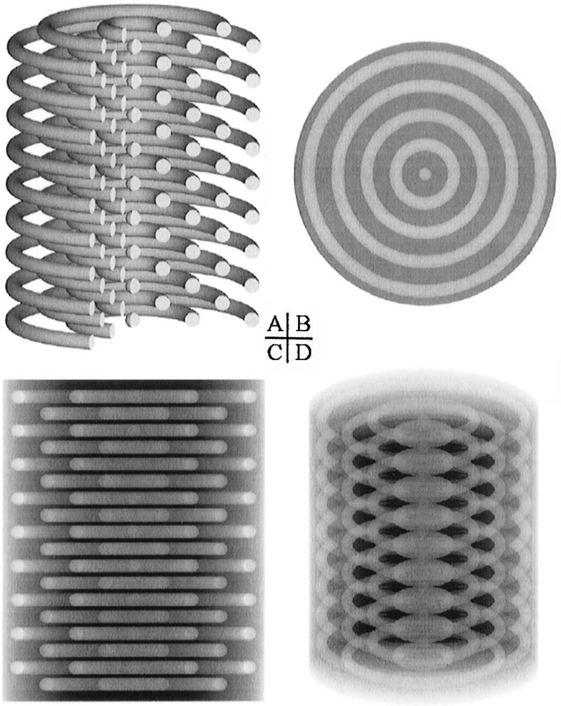

FIG. 3. The hexagonal arrangement of multiple-concentric hoops with a 110° angle cut to show the hexagonal packing pattern (A). Computer generated images obtained by confining the transparent hexagonally packed hoops (A) into a semitransparent cylindrical PS matrix and projecting along the direction of the (principal) Z axis (B), of the Y axis (C) and 20° from the Y axis on the YZ plane (D).

The structure consists of hexagonally packed dark spots. These computer-generated results duplicate the vast majority of the images obtained by TEM observations.

It is possible to study the kinetics of the formation of the structures all the way from the disordered to the ordered because of the low mobility (high viscosity) of the polymer chains in the self-assembled regions under the experimental conditions. Figure 4 shows the morphologies of the aggregates at different stages of the structural rearrangement or crystallization. The individual vesicles before the addition of NaCl are shown in Fig. 4(A). 5 min after the NaCl addition, the morphologies of the aggregates consists of large compound vesicles (LCVs) [Fig. 4(B)]. A bilayer shell around the periphery is clearly seen. An LCV is an aggregate of fused vesicles. 3 h after the addition of NaCl, the structures show some increased short range order [Fig. 4(C)]. It is also found that as the annealing time increases, the sizes increase gradually because of coalescence of the smaller aggregates. At 7 h [Fig. 4(D)], the outer regions become highly ordered, with the ordering moving towards the interior. After 12 to 24 h [Fig. 4(E) and 4(F)], the structures of some entire particles show long range order, which is akin to crystallinity. It is particularly noteworthy that crystallization also induces a change of the external geometric shapes of the aggregates from nearly spheroidal to near cylindrical or conical.

The causes of the formation of such structured mesosize aggregates are of interest from a fundamental point of view. Before the addition of ions, in spite of their high interface potential, the individual vesicles are stabilized in the solution through the interaction of the PAA blocks and the solvent. The PAA blocks are hydrated and partially ionized (charged) [7], which prevents small vesicles from adhesive contact and fusion into large vesicles. When a certain amount of NaCl is added, the screening of the PAA double-layer repulsion increases and the repulsion among the vesicles decreases. This decrease induces vesicles to come into adhesive contact and fusion, leading to the formation of LCVs.

The mechanism of morphogenesis in the mesoscale aggregates in the present system bears some resemblance to that of block copolymers in bulk [3,5]. The initial driving force appears to be mainly the interfacial tension between the solvent and the PS region. The original aggregates are bilayer vesicles, which means that the effective volume fractions of the PAA blocks (f_{PAA}) and of the PS blocks in solution are approximately equal. When NaCl is added, the effective f_{PAA} decreases because electrostatic screening by NaCl results in decreases to some degrees both in coil dimension of the PAA blocks and in the strength of repulsive interactions among the PAA segments. As a result, the surface area per PAA segment at the interface of the solvent and the PS region decreases. However, the minimization of the surface energy is eventually balanced by a newly established repulsion among the still solvated PAA blocks. In parallel with the phase behavior of block copolymers in bulk, as the effective volume fraction decreases, the structure of the self-assembled domains changes from lamellar to rodlike.

The formation of the HHH structure provides an excellent example of the relative importance of end-capping energy vs curvature energy for rods in mesosized particles. There are two ways of packing rods into a cylindrical space. One involves hexagonal packing of straight rods along the direction which is parallel to the principal axis of the cylinder. This type packing is subject to an energy penalty resulting from the formation of hemispherical caps on both the ends of the rods. The other way involves the formation of hoops to avoid the end-capping energy penalty; however, a curvature energy penalty is encountered in this type of packing. The first method of packing rods is well known in block copolymers in bulk. Because the aspect ratio of each rod is very high, the energy penalty for the end capping is relatively unimportant. However, in the present system, the dimensions of the aggregates are in the mesoscale range, e.g., several hundreds of nanometers. Under these circumstances, the end-capping energy becomes more important than the curvature energy. As a result, the hollow rods form rings, but the hexagonal pattern still remains. A similar effect is probably involved in the formation of closed spherical lamellae rather than the flat sheetlike lamellae in the present system [see Fig. 4(A)] [6,7].

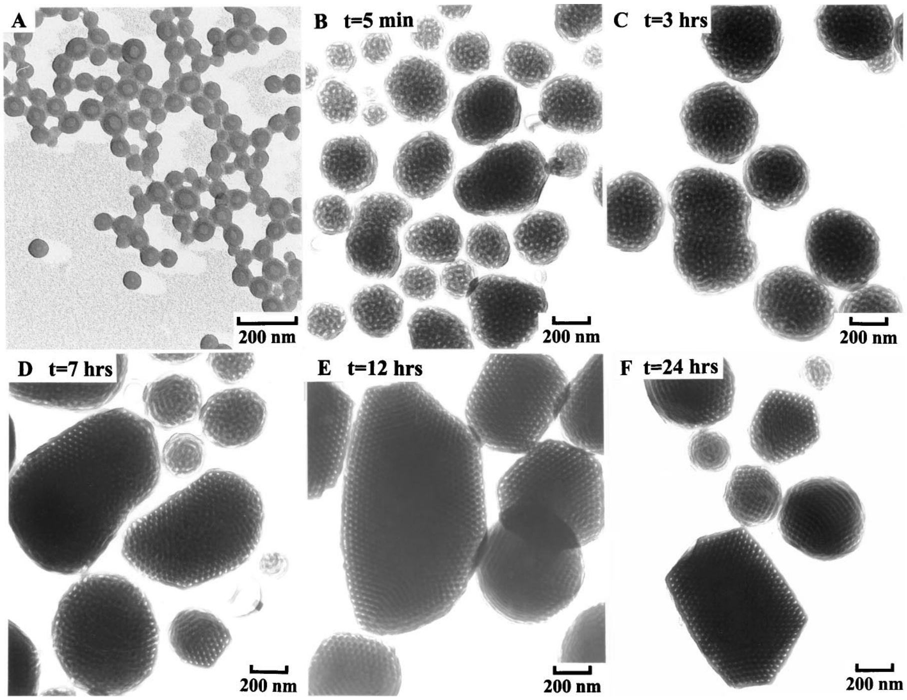

FIG. 4. Morphologies of the aggregates at different stages of crystallization: before NaCl addition (A), and 5 min (B), 3 (C), 7 (D), 12 (E), and 24 (F) h after the addition of NaCl to a final concentration of 9 mM at 6 wt % H_2O.

Although the aggregates are prepared from a dilute solution, the local polymer concentration within an individual particle is very high. Therefore, the formation of mesoscale aggregates with ordered internal hollow structures, from a viewpoint of self-assembly, bridges the gap between block copolymers in dilute solution and in bulk. Other "negative" morphologies are clearly possible, i.e., spherical holes and bicontinuous structures; size control of the hollow spaces should also be possible by manipulating, for example, the copolymer composition and molecular weight. The present system provides an excellent example of a strong interrelation mechanism between the external shape and the internal structure of mesoscale aggregates. Starting with nearly spherical assembled vesicles, the crystallization process leads to both the formation of a highly regular internal structure and a considerably increased regularity of the external shape. Simultaneously, the size of the particles imposes the morphology of hexagonally packed hoops in preference to hexagonally packed straight rods.

In terms of possible applications, it is conceivable that concentric rings may provide a timing mechanism in drug delivery. Another interesting possibility might be its use as a cylindrically symmetric diffraction grating or as materials for fabrication of electronic, conductive, and magnetic devices, if the internal hollow spaces could be packed with the appropriate materials. The use of the hollow cylinders as templates may also be of interest. Finally, the process of morphological change from aggregated vesicles to hollow rods is interesting in itself; a better understanding of the process may shed light on cell-cell interaction and their assembly.

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