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PS-*b*-PEO/SILICA FILMS WITH REGULAR AND REVERSE MESOSTRUCTURES OF LARGE CHARACTERISTIC LENGTH SCALES PREPARED BY SOLVENT EVAPORATION-INDUCED SELF-ASSEMBLY

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Introduction

Since the discovery of surfactant-templated silica by Mobil scientists in 1992, mesostructured silica has been synthesized in various forms including thin films, powders, particles, and fibers.[1] In general, mesostructured silica has potential applications, such as in separation, catalysis, sensors, and fluidic micosystems. In respect to these potential applications, mesostructured silica in the form of thin films is perhaps one of the most promising candidates.

The preparation of mesostructured silica films through preferential solvent evaporation-induced self-assembly (EISA) has recently received much attention in our laboratories[2]. However, no amphiphile/silica films with reverse mesophases have ever been made through this EISA procedure. Furthermore, templates employed to date have been either surfactants or poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers, such as Pluronic P-123, both of which are water-soluble and alcohol-soluble. Due to their relatively low molecular weight, the templated silica films with mesoscopic order have been limited to relatively small characteristic length scales.

In the present communication, we report a novel synthetic method to prepare mesostructured amphiphile/silica films with regular and reverse mesophases of large characteristic length scales. This method involves evaporation-induced self-assembly (EISA) of amphiphilic polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers. In the present study, the PS-*b*-PEO diblocks are denoted as, for example, PS(215)-*b*-PEO(100), showing that this particular sample contains 215 S repeat units and 100 EO repeat units. This PS(215)-*b*-PEO(100) diblock possesses high molecular weight and does not directly mix with water or alcohol. To our knowledge, no studies have reported the use of water-insoluble and alcohol-insoluble amphiphilic diblocks as structure-directing agents in the synthesis of mesostructured silica films through EISA. It is believed that the present system is the first to yield amphiphile/silica films with regular and reverse mesophases, as well as curved multi-bilayer mesostructures, through EISA. The ready formation of the diblock/silica films with multi-bilayer vesicular mesostructures is discussed.

Experimental

The synthesis began with a dilute homogeneous solution containing a PS-*b*-PEO diblock copolymer, tetraethoxysilane (TEOS), hydrogen chloride (HCl), tetrahydrofuran (THF), and water (Milli Q). In a typical synthesis, a diblock copolymer was dissolved in THF at 2wt.% to obtain a molecularly dispersed and homogeneous solution. Subsequently, a certain amount of TEOS, HCl, and water were added to the copolymer THF solution. The quantity of TEOS added was such as to achieve a final volume ratio of the copolymer to silica ranging from 40 : 60 to 70 : 30, under the assumption that TEOS converts completely to silica. The total amount of HCl and water added was such as to achieve mole ratios of 1TEOS : 0.004HCl : $5H_2O$. After 30 minutes of sonication, a diblock/silica film was obtained by casting the homogeneous solution. This film was calcined at 450°C for three hours in air to remove the diblock copolymer, resulting in a mesoporous silica film.

Mesostructures of the as-prepared and calcined films were directly observed on a JEOL 2010 transmission electron microscope (TEM) using an acceleration voltage of 200kV. The samples for TEM were prepared by scratching the films with tweezers and directly dispersing the film fragments onto holey carbon copper grids.

Results and Discussion

Figure 1 shows representative transmission electron microscope (TEM) images of PS(215)-*b*-PEO(100)/silica films prepared with the volume ratios of the diblock to silica of 40 : 60 (**1A** (calcined)), 50 : 50 (**1B** (uncalined)), and 70 : 30 (**1C** (uncalcined) and **1D** (calcined)). The mesophase shown in **Figure 1A** is a regular one and reveals appreciable mesostructural order. The circular regions, with an increased brightness compared with that in their surroundings, are hollow spheres and have nearly rectangular or hexagonal arrays. The sizes of these spots are very uniform. As directly measured from the TEM micrograph, the diameter of the spots is of the order of 18nm, while the average wall thickness is ca. 9nm. Before calcination, these bright spots are enriched with the PS blocks. The size of the pore regions changes little before and after calcination.

As shown in **Figure 1B**, in the ringed regions of the two upper species, brightness alternates (around their spherulite centers); the average width of the lighter and darker regions is ca. 21nm and ca. 11nm, respectively. The rings with higher transmission are enriched with PS while the rings with lower transmission are enriched with silica and PEO. Since the diameter of the rings is much larger than the width of the lighter and darker regions, the domain curvature is very small; consequently, these multi-rings are essentially lamellar in nature: either multi-bilayer lamellae or multi-bilayer vesicles.

The mesostructures shown in **Figure 1C** reveal noticeable order. In particular, the brightness in the circular regions is relatively low compared with that in their surroundings; this pattern of contrast, with dark spots in a light background, is different from that shown in **Figure 1A**. These dark spots of the circular regions result from enrichment with silica and the PEO blocks. Therefore, the mesophase is a reverse one. The sizes of the spots, which have nearly rectangular or hexagonal arrays, are very uniform. As directly measured from the TEM micrograph, the diameter of the spots is of the order of 13nm, while the average edge length of the rectangle or hexagon is ca. 23nm. Calcination removes PEO and the continuous PS matrix, resulting in partially sintered silica particles with a quite uniform size of ca. 12nm in diameter, as shown in **Figure 1D**.

It is necessary to point out that small-angle x-ray scattering (SAXS) studies were performed at the University of New Mexico/Sandia National Laboratories SAXS facility. Also, nitrogen (N_2) adsorption/adsorption isotherms of the prepared mesoporous films were measured by a surface acoustic wave (SAW) technique. This technique is described elsewhere.[2] For the hollow spheres (shown in **Figure 1A**), the SAXS diffraction pattern may suggest a mixture of both hexagonal-close-packed (hcp) and face-centered cubic (fcc) structures, and the SAW measurement shows that the pores are connected.

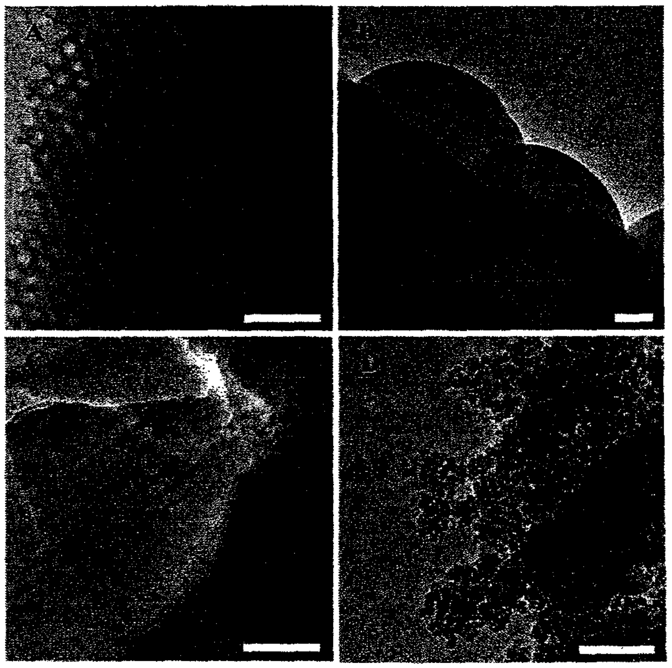

Figure 1. TEM images of the PS(215)-*b*-PEO(100)/silica films prepared with the diblock to silica volume ratios of 40:60 (A), 50:50 (B), 70:30 (C-D) (A and D calcined; B and C uncalcined). Scale bars (A-D) are 100 nm.

We also studied another two diblock samples with the volume ratio of the diblock to silica of 40:60. **Figures 2A and 2B** show TEM images of calcined silica films templated by PS(35)-*b*-PEO(109) and PS(563)-*b*-

PEO(705), respectively. As directly measured from the TEM micrographs, the diameters of the spots in **Figures 2A** and **2B** are of the order of 6nm and 23nm, respectively. In addition, the average wall thicknesses are ca. 5nm and 10nm, respectively.

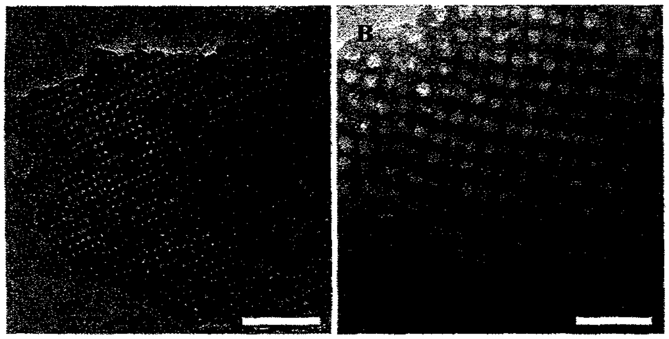

Figure 2. TEM micrographs of silica films (calcined). The diblocks used were PS(35)-*b*-PEO(109) (A) and PS(563)-*b*-PEO(705) (B). Scale bars (A-B) are 100 nm.

Therefore, it is reasonable to conclude that with an increase of the volume fraction of the diblock, mesophases of the as-cast films change from regular, to lamellar, and to reverse ones. In addition, the pore size increases with the molecular weight of the diblock. Thus, the pore size and wall thickness can be rationally adjusted by choosing the appropriate diblocks.

In the formation of the present liquid crystalline phases, both self-assembly and sol-gel processes function simultaneously. The self-assembly is driven by THF preferential evaporation; therefore, this self-assembly process not only involves both the copolymer and silicates but also goes through different concentration regions. Various morphologies have been observed in diblock copolymers in dilute solution[3,4] and in bulk[5]; especially, the formation of multiple morphologies, such as spheres, rods, bilayers and inverted aggregates, in dilute solution of PS-*b*-PEO has been investigated in some detail.[4] A comparison of the present system with the self-assembly of diblock copolymers in dilute solution and in bulk will be presented in a forthcoming paper,[6] in which a range of similarities, such as morphogenic effects of effective volume ratios of the two blocks, will be highlighted.

The ready formation of the diblock/silica films with muti-bilayer vesicular mesostructures in the present system is of interest. For small-molecule amphiphile/silica films prepared through the evaporation-induced self-assembly, multi-bilayer vesicles have rarely been reported, although multi-bilayer lamellae have been documented.[2] In dilute solution without silicates, it has been noted that block copolymer vesicles are relatively easy to prepare compared to small molecule amphiphile vesicles. The reason for the relatively easy formation of diblock copolymer vesicles in both systems compared to that of small molecule amphiphile vesicles may be argued to be the polydispersity of the copolymer chains.

This argument is supported by two experimental results. When two diblocks with the same PS block length but different PEO block lengths are mixed, both in dilute solution of mixtures of THF and water[4d] as well as in the present system, the formation of vesicles of blends occurs more ready than that of one diblock copolymer. Therefore, it seems reasonable to argue that the PEO polydispersity favors the formation of vesicles, in some degree. Further information and discussion will be presented in a forthcoming paper.[6]

Multi-layer lamellae and multi-layer vesicles have been reported in some other systems, including blends of polystyrene-*b*-polybutadiene (PS-*b*-PB) and polystyrene (PS),[5a] blends of polystyrene-*b*-poly(butyl methacrylate) (PS-*b*-PBMA) and poly(phenylene oxide) (PPO),[5c] areosol-generated particles,[2c] as well as silica templated by liquid crystal phases of polybutadiene-*b*-poly(2-vinylpyridinium chloride) (PB-*b*-P2VP·HCl).[7] However, the present system is believed to be the first to yield diblock/silica films with multi-bilayer vesicles through the EISA proceduce.

Finally, we would like to point out the possibility for multi-bilayer vesicles to be hosts for a mixture of guest species. Because of the differential curvature of each succeeding layer, multi-bilayer vesicles would selectively position different species to their optimum radial positions. Therefore, the present approach of the preparation of diblock/silica films with multi-bilayer vesicles could facilitate encapsulation with a high degree of control.[1d]

Conclusion

Diblock/silica films with various mesostructures of large characteristic length scales were synthesized through evaporation-induced self-assembly of PS-*b*-PEO. The prepared mesophases include regular, flat and curved lamellar, as well as reverse ones. By using one identical diblock but different volume ratios of the diblock to silica, diblock/silica films with different mesostructures are synthesized. As the volume ratio increases, morphologies of the mesostructures change progressively from regular to inverted mesophases, through lamellae. For the diblock/silica films with regular mesophases, copolymer removal produces mesopores; the pore size is controlled by the molecular weight of the diblock. The present system is believed to be the first to yield diblock/silica films with regular and reverse mesophases, as well as curved multi lamellae, through solvent evaporation-induced self-assembly (EISA).

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