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Letters

Syntheses of Silica/Polystyrene-*block*-Poly(ethylene oxide) Films with Regular and Reverse Mesostructures of Large Characteristic Length Scales by Solvent Evaporation-Induced Self-Assembly

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Silica/diblock films with various mesostructures of large characteristic length scales were synthesized through evaporation-induced self-assembly (EISA). The structure-directing agents used were amphiphilic polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers of high molecular weights. The synthesis process began with a dilute homogeneous solution of a silica precursor and the diblock copolymer in a mixture of tetrahydrofuran (THF) and water. After this dilute solution was cast, THF preferentially evaporated; accordingly, the species in the depositing film increasingly concentrated and the solvent quality for the diblock progressively decreased. At some critical point, cooperative self-assembly of both the PS-*b*-PEO diblock and the silicate started. Subsequently, liquid-crystalline mesophases were obtained. The present study indicates that silica/diblock films with different mesostructures can be synthesized by using one identical diblock; as the volume ratio of the diblock to silica increases, mesostructures change progressively from regular to inverted (reverse) via lamellar. For the silica/diblock films with regular mesophases, copolymer removal produces mesopores; highly ordered mesoporous silica films with different pore sizes result from using diblocks with different molecular weights. Particularly noteworthy is the ready formation of the silica/diblock multi-bilayer vesicular mesostructures. The present system is believed to be the first to use high glass transition temperature ($T_g \approx 373$ K), PS-based amphiphilic diblock copolymers to prepare silica/diblock films with regular and reverse mesophases, as well as multi-bilayer vesicular mesostructures, through solvent evaporation-induced self-assembly.

Introduction

The discovery of surfactant-templated silica mesophases in 1992 has led to a great deal of attention on the synthesis of mesoporous inorganic oxides to extend applications of

microporous zeolitic materials (pore size less than 1.2 nm in diameter) toward larger pore sizes.^{1–6} Mesostructured

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inorganic oxides with large pores and thick walls are important for the systematic fundamental study of structure–property relationships and are much in demand for their technologically promising and diversified applications such as selective synthesis and separations involving large molecules, miniaturized electronic and magnetic devices, fluidic circuits, and photonic crystals with tunable band gaps. However, the classical techniques for the synthesis of mesoporous silica rely on the use of low-molecular-weight amphiphiles as structure-directing agents; the pore sizes of the resulting inorganic nanostructures are usually less than 3 nm. The use of inert oils as swelling agents to enlarge pore sizes, if necessary, makes mesostructural control difficult, because of the phase transitions of the amphiphiles, and can also cause the inorganic network to be mechanically unstable because of the thinness of the walls between pores. With respect to the potential applications such as in separation, catalysis, sensors, and fluidic microsystems, mesostructured silica in the form of thin films is perhaps one of the most promising candidates.

Recently, the preparation of mesostructured silica films through preferential solvent evaporation-induced self-assembly (EISA) has received much attention in our laboratories;⁷ to date, the structure-directing agents employed have either been 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. Because of their relatively low molecular weight, the templated silica films with mesoscopic order have been limited to relatively small characteristic length scales. It is generally acknowledged that the synthesis process begins with a dilute homogeneous solution of soluble silica and a surfactant in ethanol/water solvent. When the solution is cast or coated onto a substrate, preferential alcohol evaporation induces cooperative self-assembly of the surfactant and silicates. Finally, silica/surfactant films with regular liquid-crystalline mesophases are obtained. Surfactant removal yields silica films with mesopores. No silica/surfactant films with reverse mesophases have previously been made through this EISA procedure.

It is necessary to point out that, in the research field of self-assembly of amphiphiles in solution, self-assembled micelles or aggregates are usually termed as “regular” or “reverse, or inverted”, depending on the polarity of the solvent.^{8,9} When the solvent is polar, such as water, the associates are referred to as *regular* with the core formed

by the hydrophobic part of the amphiphiles. When the solvent is apolar or of low polarity, the associates are referred to as *reverse (or inverted)* with the core formed by the hydrophilic part of the amphiphiles. In the present study, when silica is the matrix, the mesophase is referred to as “regular”; when silica is not the matrix, the mesophase is referred to as “reverse”.

Here, we report on a novel synthetic method to prepare mesostructured silica/diblock films with regular and reverse mesophases of large characteristic length scales. The templating approach is through evaporation-induced self-assembly (EISA), and the structure-directing agents are amphiphilic polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers possessing high molecular weight. It is well-known that when PS blocks are long and PS volume fractions are high, the PS-*b*-PEO diblocks do not directly mix with water or alcohol. Furthermore, the glass transition temperature of the PS ($T_g \approx 373$ K) is high. To the best of our knowledge, no studies have been reported on making use of self-assembly of water-insoluble and alcohol-insoluble PS-based amphiphilic diblock copolymers as structure-directing agents in the synthesis of mesostructured silica films.

The present approach involves the use of tetrahydrofuran (THF) instead of alcohol because THF is a thermodynamically good solvent for both the PS and PEO blocks; furthermore, THF is water-soluble and evaporates faster than water. In addition, the magnitude of PS–THF interaction is relatively high compared with that of some other PS–solvent interactions, such as the PS–dioxane interaction, as judged from the solubility parameter (δ) and as confirmed experimentally.^{10,11} The solubility parameter of PS ($\delta = 15.6\text{--}21.1$ [MPa]^{1/2}) and the solubility parameter of styrene ($\delta = 19.0$ [MPa]^{1/2}) are close to that of THF ($\delta = 18.6$ [MPa]^{1/2}).¹⁰ Generally, the synthesis process begins with a dilute homogeneous solution of a silica precursor, namely tetraethoxysilane (TEOS), and a PS-*b*-PEO copolymer in a mixture of tetrahydrofuran (THF) and water. After the starting dilute solution is cast, preferential THF evaporation concentrates the species in the depositing film and decreases the solvent quality for the diblock. At some critical point, cooperative self-assembly of both the PS-*b*-PEO diblock and the silicate is driven, and silica/diblock films with liquid-crystalline mesophases are generated. From one diblock, the as-cast films with various mesostructures are synthesized by varying volume ratios of the diblock to silica. As the volume ratio increases, the observed mesostructures change from regular to reverse via flat and curved lamellae. For the silica/diblock films with regular mesophases, diblock copolymer removal yields mesopores. Highly ordered mesoporous silica films with different pore sizes are prepared by using diblocks with different molecular weights. The ready formation of the silica/diblock films with multi-bilayer vesicular mesostructures is worthy of notice. It is believed that the present system is the first to use high glass transition temperature ($T_g \approx 373$ K), PS-based amphiphilic diblock copolymers to synthesize silica/amphiphile films with regular and reverse mesophases, as well as curved multilamellar mesostructures, through solvent evaporation-induced self-assembly (EISA).

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Experimental Section

The synthesis began with a dilute homogeneous solution containing a PS-*b*-PEO diblock copolymer, tetraethoxysilane (TEOS, 98%, Aldrich Chemicals), hydrogen chloride (HCl), tetrahydrofuran (THF, HPLC grade, EM Science), and water (Milli Q). The PS-*b*-PEO diblocks used were prepared by sequential anionic polymerization of styrene monomer followed by ethylene oxide monomer; a detailed description is given elsewhere.^{12,13} The diblocks in the text are denoted as, for example, PS(215)-*b*-PEO(100), showing that this particular sample contains 215 styrene repeat units and 100 ethylene oxide repeat units. THF and TEOS were used as received without further purification.

In a typical synthesis, a diblock copolymer was dissolved in THF at 2 wt % to obtain a molecularly dispersed and homogeneous solution. Subsequently, certain amounts of TEOS, HCl, and water were added to the copolymer THF solution. The quantity of TEOS added was such as to get a final volume ratio of the copolymer to silica from 40:60 to 70:30, under the assumption that TEOS completely translates to silica. The total amount of HCl and water added was such as to achieve mole ratios of 1 TEOS/0.004 HCl/5 H₂O; these ratios are the same as those indicated before.⁷ After 30 min of sonication, a thin film was obtained by casting the homogeneous solution. The silica/diblock film was calcined at 450 °C for 3 h to remove the diblock copolymer species.

Mesostructures of the films as-cast and after calcination were directly observed on a JEOL 2010 transmission electron microscope (TEM) with an accelerating voltage of 200 kV. The samples for the TEM were prepared by scratching the films with tweezers and directly dispersing scratched flakes onto holey carbon copper grids.

Results and Discussion

Previous studies of the mesophases of silica films templated through solvent evaporation-induced self-assembly (EISA) of low molecular weight amphiphiles demonstrated that a number of factors, and the interplay between them, influence the observed mesostructures.⁷ The variables include the nature of amphiphiles and silica precursors used, amphiphile/silica precursor mole ratios, as well as initial alcohol/water/amphiphile mole ratios. Furthermore, parameters such as pH and temperature, and the presence of additives such as organic swelling agents, have to be considered. In addition, the competition between drying and silica gelation during the sol-gel and self-assembly processes is critical in the formation of liquid-crystalline phases. In this preliminary report, we focus on the effect of the volume ratio of the copolymer to silica as well as copolymer compositions insofar as they affect the mesostructures of the silica/diblock films. The results are presented in the order of increasing the diblock to silica volume ratio. In view of the dynamic nature of the EISA preparation method, the films can possess some compositional nonuniformity at the mesoscopic level. For each sample prepared, the TEM study was performed carefully and extensively; the dominant mesophase observed is presented.

For the silica/diblock films prepared with a volume ratio of the diblock to silica of 40:60, representative transmission electron microscope (TEM) images of the calcined films are shown in Figure 1; the images reveal appreciable mesostructural order. Two diblock samples with very different PS block lengths are employed as the structure-directing agents; they are PS(215)-*b*-PEO(100) (A) and

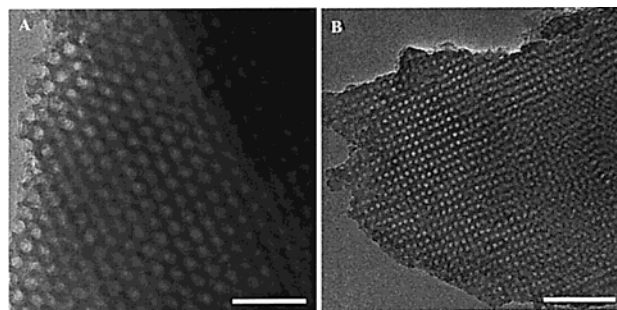


Figure 1. Representative TEM images of the calcined silica films templated by PS(215)-*b*-PEO(100) (A) and PS(35)-*b*-PEO(109) (B). The volume ratios of the diblock to silica are both 40:60. Scale bars are 100 nm.

PS(35)-*b*-PEO(109) (B). As shown in Figure 1, the circular regions, with an increased brightness compared with that in their surroundings, are hollow spheres and are in nearly hexagonal or rectangular arrays. The sizes of these spots are very uniform. As directly measured from the TEM micrographs, the diameters of the spots are of order 18 nm (A) and 5 nm (B). Before calcination, these bright spots are enriched with the PS blocks. Copolymer removal produces mesoporous structures with preservation of the mesostructural order; the maintenance of the order after calcination is worthy of notice. The pore size increases with the molecular weight of the diblock; thus, pore size can be rationally adjusted by choosing the appropriate diblocks. The mesophase shown in Figure 1 is regular. To the best of our knowledge, this regular silica mesophase prepared is a brand-new one, which consists of isolated spheres with a cubic array distributed in the silica matrix. Silica/diblock films with hexagonally arranged cylinders were prepared, from the same two diblock copolymers, at higher diblock to silica volume ratios (unpublished result). Under the TEM, we noticed that it is not easy to distinguish the spherical and cylindrical nature when the spheres overlap themselves very well in the very thin sample area; however, the spherical nature can be easily seen in the relatively thick sample area while the spheres do not overlap them very well. The latter case can be evidenced in Figure 1A. Additional information, such as cross section TEM images, 2-D grazing incidence small angle X-ray scattering (GISAXS) images showing that the film is macroscopically ordered and oriented in the direct normal to the substrate, and a surface acoustic wave (SAW) measurement showing no absorbing of nitrogen (N₂), about these isolated spheres with a cubic array distributed in the silica matrix will be presented in our forthcoming paper.

For the PS(215)-*b*-PEO(100)/silica film prepared with a volume ratio of this diblock to silica of 50:50, a representative TEM image of the as-cast film is shown in Figure 2A. In the ringed regions of the two upper species, brightness alternates (around their spherulite centers). As directly measured from this TEM micrograph, the average width of the lighter and darker regions is ~21 and ~11 nm, 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 structures are essentially lamellar in nature. For the PS(35)-*b*-PEO(109)/silica film prepared with a volume ratio of this diblock to silica of 60:40, a representative TEM image of the calcined film with curved multilamellae is shown in Figure 2B. The distance between the silica layers is not uniform. Without

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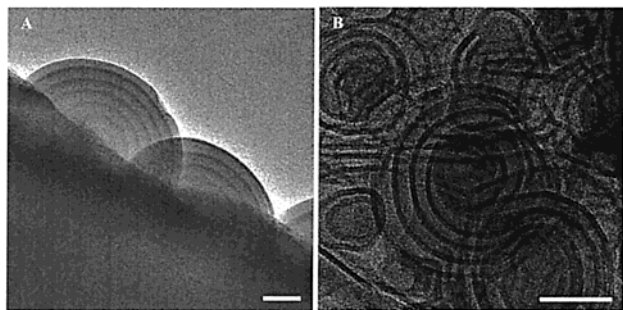


Figure 2. Representative TEM images of the as-cast PS(215)-*b*-PEO(100)/silica film with the diblock to silica volume ratio of 50:50 (A) and calcined silica film templated by PS(35)-*b*-PEO(109) with the diblock to silica volume ratio of 60:40 (B). Scale bars are 100 nm.

the diblock between the silica layers, the structure collapses or spreads apart after calcination because they are no longer separated by the polymer layers.

The ready formation of the silica/diblock films with multi-bilayer vesicular mesostructures in the present system is of interest. For silica/surfactant films prepared through the evaporation-induced self-assembly, multi-bilayer vesicular mesostructures have rarely been reported, although multi-bilayer lamellae have been documented.^{7b} Therefore, it is reasonable to comment that the formation of curved multi-bilayer lamellae, namely vesicles, in the present silica/diblock system is relatively easy compared to that in the silica/surfactant system. Furthermore, in dilute solution without silicates, it has been noted that block copolymer vesicles are relatively easy to prepare compared to small molecule amphiphile vesicles.^{13d,14,15} Thus, in both the silica/amphiphile and dilute solution systems, we speculate that the relative ease of formation of the silica/diblock vesicles and diblock vesicles can be argued to be due to the polydispersity of the copolymer chains. A detailed description of and discussion on the ready formation of multi-bilayer vesicular mesostructures in the present system can be found elsewhere.¹⁶

Multilayer lamellae and multilayer vesicles have been reported in some other systems, including blends of polystyrene-*b*-polybutadiene (PS-*b*-PB) and polystyrene (PS),^{17a} blends of polystyrene-*b*-poly(butyl methacrylate) (PS-*b*-PBMA) and poly(phenylene oxide) (PPO),^{17b} aerosol-generated particles,^{7c} as well as silica templated by liquid crystal phases of polybutadiene-*b*-poly(2-vinylpyridinium chloride) (PB-*b*-P2VP-HCl).¹⁸ However, the present system is believed to be the first to yield silica/diblock films with the multi-bilayer vesicular mesophase through the EISA procedure.

It is recognized that chain stretching has an important effect on the entropy of the system; furthermore, the interactions in the PS layers, in the PEO layers, and at the interface are important contributions to the mesostructure. Thus, it is meaningful to study the degree of deformation (stretching) of both the PS and PEO chains

of the as-prepared mesostructures, shown in Figure 2A. Assume that a sharp interface exists between the PS and PEO layers and the composition in each layer is homogeneous. Hence, some of the PS and PEO chains should span the distance from the interface to the center of their layers. For the PS and PEO chains, the degrees of deformation (stretching), namely S_{cPS} and S_{cPEO} , are defined as the ratios of the radii of PS and PEO regions to the end-to-end distances of the PS and PEO chains in their unperturbed states ($R_{0\text{PS}}$ and $R_{0\text{PEO}}$), respectively. $R_{0\text{PS}}$ (nm) and $R_{0\text{PEO}}$ (nm) can be calculated from

$$R_{0\text{PS}} = 0.067 M_{\text{PS}}^{1/2} \quad (1)$$

$$R_{0\text{PEO}} = 0.075 M_{\text{PEO}}^{1/2} \quad (2)$$

while M_{PS} and M_{PEO} are the molecular weights of the PS and PEO blocks, respectively.^{10,11,13,15} In the present case, the radii of the PS and PEO regions are approximated to be half the thicknesses of the layers with higher and lower transmissions, respectively. Consequently, for the PS-(215)-*b*-PEO(100)/silica multi-bilayer vesicular mesostructures, as shown in Figure 2A, S_{cPS} is ~ 1.05 , while S_{cPEO} is ~ 1.11 . It is useful to point out that, for the PS-(215)-*b*-PEO(100) rods and bilayers made from THF/water dilute solution, the S_{cPS} of the rods is ~ 1.8 and that of the bilayers is ~ 1.2 .^{11b} A discussion of the importance of a decrease in the degree of stretching of the PS chains during the morphological transition in diblock aggregates can be found elsewhere.^{13,19} Therefore, the relatively small degree of stretching of the PS chains in the present mesostructure is worthy of notice.

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

For the PS(180)-*b*-PEO(120)/silica film prepared with a volume ratio of this diblock to silica of 70:30, a representative TEM image of the calcined film is shown in Figure 3A, which appears to be silica rods. Thus, the as-cast diblock/silica mesophase is a reverse one; calcination removes PEO and the continuous PS matrix, resulting in partially sintered silica rods with a quite uniform size of ~ 13 nm in diameter. For the PS(215)-*b*-PEO(100)/silica film prepared with a volume ratio of this diblock to silica of 70:30, two representative TEM images are shown in Figure 3B (calcined) and 3C (uncalcined). The mesostructures shown in Figure 3C 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 1. 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 on the order of 13 nm, while the average edge length of the rectangle or hexagon is ~ 23 nm. Calcination removes PEO and the continuous PS matrix,

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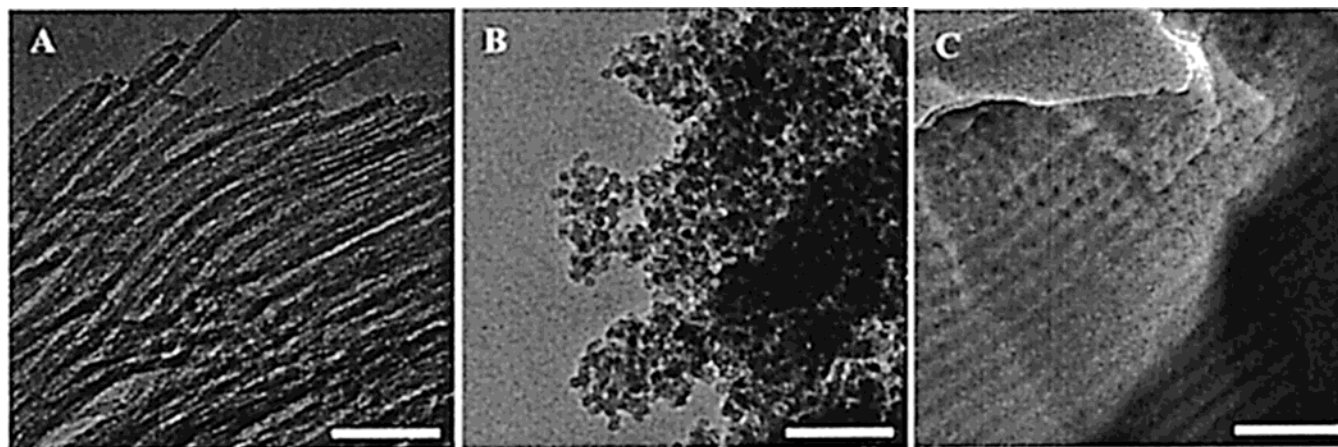


Figure 3. Representative TEM micrographs of silica templated by PS(180)-*b*-PEO(120) (calcined, A) and by PS(215)-*b*-PEO(100) (calcined, B; uncalcined, C). The volume ratios of the diblock to silica are both 70:30. Scale bars (A and B) are 100 nm.

resulting in partially sintered silica spheres with a quite uniform size of ~ 12 nm in diameter, as shown in Figure 3B.

Therefore, it is reasonable to conclude that mesophases of the as-cast diblock/silica films change from regular to reverse through lamellar, with an increase of the volume ratio of the diblock to silica. Thus, the morphogenic effects of the effective volume ratios of the hydrophobic to hydrophilic parts in the present system are similar to those in the three other systems, namely dilute, semidilute, and concentrated, and the bulk, with respect to the self-assembly of diblock copolymers. A comparison will be presented in a forthcoming paper.¹⁴ The present system is the first to use high glass transition temperature ($T_g \approx 373$ K), PS-based amphiphilic diblock copolymers to yield silica/amphiphile films with regular and reverse mesophases, as well as curved multilamellar mesostructures, through solvent evaporation-induced self-assembly (EISA).

Conclusions

Silica/diblock films with various mesostructures of large characteristic length scales were synthesized through evaporation-induced self-assembly (EISA); amphiphilic polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymers were the structure-directing agents. The prepared mesophases include regular, flat, and curved lamellae, as well as reverse ones. The synthesis process generally began with a dilute homogeneous solution of a silica precursor and a diblock copolymer in a mixture of tetrahydrofuran (THF) and water. After this starting solution was cast, THF preferentially evaporated; accordingly, the species in the depositing film increasingly

concentrated and the solvent quality for the PS block progressively decreased. At some critical point, cooperative self-assembly of both the PS-*b*-PEO diblock and the silicate started; liquid-crystalline mesophases were obtained.

By using one identical diblock but different volume ratios of the diblock to silica, silica/diblock films with different mesostructures are synthesized. As the volume ratio increases, the morphologies of the mesostructures change progressively from regular to inverted mesophases, through lamellae. For the silica/diblock films with regular mesophases, copolymer removal produces mesopores. Using diblocks of different molecular weight, highly ordered mesoporous silica films with different large pore sizes are prepared. The ready formation of the diblock/silica films with multi-bilayer vesicular mesostructures is noteworthy. By using high glass transition temperature ($T_g \approx 373$ K), PS-based amphiphilic diblock copolymers, the present system is the first to yield silica/amphiphile films with regular and reverse mesophases, as well as curved multi-lamellar mesostructures, through solvent evaporation-induced self-assembly (EISA).

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