Control of Pore Sizes in Mesoporous Silica Templated by Liquid Crystals in Block Copolymer−Cosurfactant−Water Systems

Pingyun Feng,*,[†] Xianhui Bu,[‡] and David J. Pine*,[†]

Departments of Chemical Engineering and Chemistry, University of California, Santa Barbara, California 93106

Colloidal silica has been polymerized in the aqueous domain of lyotropic liquid crystal phases in ternary surfactant (Pluronic F127 or P123)−cosurfactant (butanol, pentanol, or hexanol)−water systems to create optically transparent mesostructured surfactant−cosurfactant−silica monoliths. The use of ternary systems enriches phase diagrams of aqueous surfactant systems, which in turn introduces more flexibility and diversity into the designed synthesis of mesoporous materials. Lyotropic surfactant liquid crystal phases are preserved throughout the inorganic polymerization and gelation processes and directly template the formation of inorganic mesophases. The cosurfactant chain length and the cosurfactant/surfactant mass ratio have been used to control the pore size. The large shrinkage of mesopores during calcination can be reduced with hydrothermal treatment prior to calcination. Highly ordered mesoporous silica samples with identical pore sizes, but very different wall thickness, can be prepared. The removal of surfactants and cosurfactants gives periodic hexagonal mesoporous silica with excellent thermal and hydrothermal stability.

Introduction

Because of their high specific surface areas and large uniform pore sizes, mesoporous oxides have many potential applications in shape-selective heterogeneous catalysis, biomolecular separation, and immobilization.[1−6] Thin films of porous silica are also potential candidates for use as ultralow dielectric constant materials in the semiconductor industry.[7−9] In most cases, mesoporous oxides are synthesized from micellar solutions with low surfactant concentrations; small micrometer-sized powders are usually precipitated from starting mixtures.[10,11] In solutions with low surfactant concentrations, surfactant liquid crystal phases and mesoporous silicates are formed in a cooperative manner driven by charge density matching between surfactant assemblies and inorganic precursors.[12] The synthesis products of such a cooperative self-assembly process are in general unpredictable because the interaction between inorganic precursors and surfactant assemblies can significantly alter phase behavior of traditional water/surfactant systems.

An alternative and potentially more predictable approach for the synthesis of mesoporous oxides is the direct templating by preformed lyotropic liquid crystal phases prepared under relatively high surfactant concentrations (usually >20 wt %).[13−16] Since a rich literature exists of phase diagrams of various surfactant systems,[17−19] such an approach would allow one to design structural features of inorganic mesophases by controlling in advance the structure of templating lyotropic liquid crystal phases. Another advantage of templating with preformed lyotropic liquid crystal phases is the possibility to fabricate large transparent monoliths for optical, electronic, or other advanced applications.[20−23] Furthermore, because liquid crystals can be aligned macroscopically by shearing, or in electric and magnetic fields,[24] the approach described here opens up the possibility of synthesizing highly oriented, single-crystal-like, optically transparent silica monoliths. The potential applications of these oriented monoliths can be extended to even more diverse areas if they can be made with a large range of pore sizes. In this paper, we focus our effort on how to achieve the continuous adjustment of pore sizes in these silica monoliths.

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Until now, the templating of periodic mesoporous materials with preexisting liquid crystal phases has been restricted to only a few surfactants in the surfactant/water binary system.[13] The pore size of mesophases obtained so far is limited by surfactant lengths and the restricted range of compositions.[13] Attempts to expand to other compositions and to tune pore sizes usually lead to the loss of long-range ordering.[14] Here we report the room temperature synthesis of periodic mesoporous silica by templating with liquid crystal phases prepared from ternary systems consisting of amphiphilic triblock copolymers such as Pluronic F127, cosurfactants such as butanol or pentanol, and water. The triblock copolymer−alcohol−water ternary system exhibits a rich phase behavior including micellar (L1), reverse micellar (L2), cubic (I1), hexagonal (H1), and lamellar lyotropic liquid crystalline phases.[25] But until now, no success has been reported of directly using these liquid crystals as templates for the synthesis of periodic mesoporous silica.

Pluronic F127 is a unique surfactant because it has a high molecular weight with a large hydrophilic volume. The long hydrophilic chain offers the possibility of synthesizing mesoporous oxides with thick walls that may lead to an increased thermal and hydrothermal stability. Recently, a cubic mesophase (SBA-16) was synthesized over a narrow range of dilute F127 concentrations (3−5%) in a precipitation process.[26] The hexagonal phase, however, could not be prepared by similar low concentration procedures. Here, it is demonstrated that by using preformed liquid crystals as templates in ternary systems, it is not only easy to synthesize highly stable hexagonal mesoporous silica from F127, but a high degree of control over the pore size can also be achieved.

Experimental Section

Synthesis. Surfactants were obtained from BASF and used as received. The approximate chemical formula is $EO_{106}PO_{70}EO_{106}$ for Pluronic F127 and $EO_{20}PO_{70}EO_{20}$ for Pluronic P123, where $EO = -CH_2CH_2O-$ and $PO = -CH_2(CH_3)CHO-$. Tetramethoxysilane (TMOS) was used as the silica source. All syntheses for composite silica−surfactant−cosurfactant mesophases are performed at room temperature. These composite mesostructures can be calcined directly or treated hydrothermally at 100 °C before calcination in order to reduce the extent of shrinkage during calcination. In a typical synthesis, the colloidal silica was prepared by mixing an aqueous dilute HCl solution with TMOS followed by removal of methanol under vacuum. The homogeneous mixture of the colloidal silica, Pluronic F127, and pentanol was then placed on a centrifuge to remove bubbles. The mass ratio was water (2.89):TMOS (3.83):F127 (1.00):pentanol (0.72).

The birefringent H1 phase was immediately observed upon complete mixing of all components. The fluid mixture usually turned rigid within a few hours. But gel shrinkage could continue for days as shown by the decreasing *d* spacing. The optically transparent monolithic gel took the shape of the reaction vessel. The long-range ordering of the mixture persisted throughout these processes as monitored by X-ray powder diffraction. Mesoporous silica were obtained by calcination of as-synthesized samples at 450 °C for 6 h or by repeated extraction with ethanol at 60 °C.

Characterizations. Low-angle powder X-ray diffraction (XRD) patterns were recorded on a Scintag X2 (or Scintag PAD X) powder diffractometer using Cu Kα radiation operating at 35 kV and 25 mA. A Peltier cooled Si (Li) solid-state detector was used so that no filter or monochromator was necessary to remove the Cu Kβ radiation. The distance between the sample stage and the detector was 25 cm.

Nitrogen sorption isotherms were measured on a Micromeritics ASAP 2000 system at 77 K with samples outgassed at 180 °C under vacuum for at least 6 h. The typical sample mass was about 150 mg. Pore sizes, specific surface areas, and pore volumes were calculated using a modified Broekhoff−de Boer method.[27] Transmission electron micrographs (TEM) were recorded on a JEOL 2000FX microscope operating at 200 kV using copper grids.

Results and Discussion

Synthesis. The direct liquid crystal templating approach employed here uses high surfactant concentrations (usually >20 wt %) and is performed at mildly acidic pH conditions. The surfactant concentration needs to be high enough to form lyotropic liquid crystals. Several factors such as desired mesophases and pore sizes, surfactant types, and types and concentrations of cosurfactants dictate the selection of the surfactant concentration. This method is in contrast with previous synthetic approaches involving triblock copolymers as templates. Stucky et al. reported the synthesis of mesoporous silica using triblock copolymers under strongly acidic conditions (pH < 1) and dilute surfactant concentrations (usually less than 6 wt %) while Pinnavaia and co-workers performed their syntheses near neutral pH conditions with surfactant concentrations usually below 0.1 mol/L.[26,28]

The criteria for selecting proper synthetic conditions for direct liquid crystal templating differ from those for indirect liquid crystal templating at low surfactant concentrations. At low surfactant concentrations, surfactant molecules usually exist in micellar forms, and no long-range organized surfactant structures exist. Thus, it is advantageous to use strongly acidic or basic conditions to enhance interactions (electrostatic, hydrogen bonding, etc.) between silica oligomers and surfactant assemblies. These inorganic−organic interactions serve to induce long-range ordering of surfactant species that can act as templates to help organize inorganic polymerizing species.[12]

For direct liquid crystal templating, surfactant concentrations are high enough to form long-range ordered assemblies even in the absence of silica−surfactant interactions. Thus, it is neither necessary nor advantageous to create strong interactions between surfactant arrays and inorganic species because such interactions may disrupt the already existing long-range ordering of surfactant arrays. Therefore, our experiments are usually performed at the isoelectric point of silica to minimize possible electrostatic interactions. For the same reason, nonionic Pluronic surfactants are likely to be more suitable for use in direct liquid crystal templating than charged surfactant molecules.

At high surfactant concentrations, the formation of silica−surfactant−cosurfactant mesophases undergoes several distinct periods including the initial sol, gelation, and aging. Typically a strong low-angle diffraction peak is observed throughout these stages (Figure 1). For samples synthesized under certain conditions, e.g., in the P123−butanol−water−silica system, high-order diffraction peaks such as (110) and (200) peaks can also be observed (Figure 2). During the gelation and aging periods, the *d* spacing gradually becomes smaller (Figure 1), and the long-range ordering of the sample improves as evidenced by the increasing scattering intensity. A

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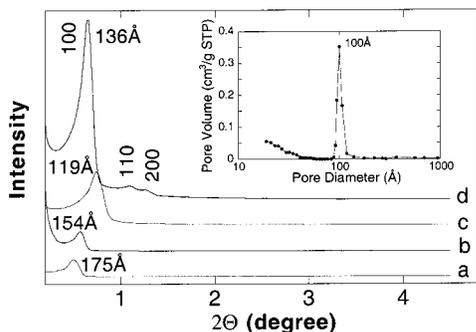
Figure 1. XRD patterns of as-synthesized and calcined hexagonal mesophases prepared from the F127/pentanol/water system. The mass ratio between pentanol and F127 is 0.59. (a) the freshly prepared liquid crystal phase; (b) after gelation; (c) after calcination; (d) hydrothermally treated at 100 °C for 24 h and then calcined. Inset: the BdB−FHH pore size distribution curve from the adsorption branch for sample "d".
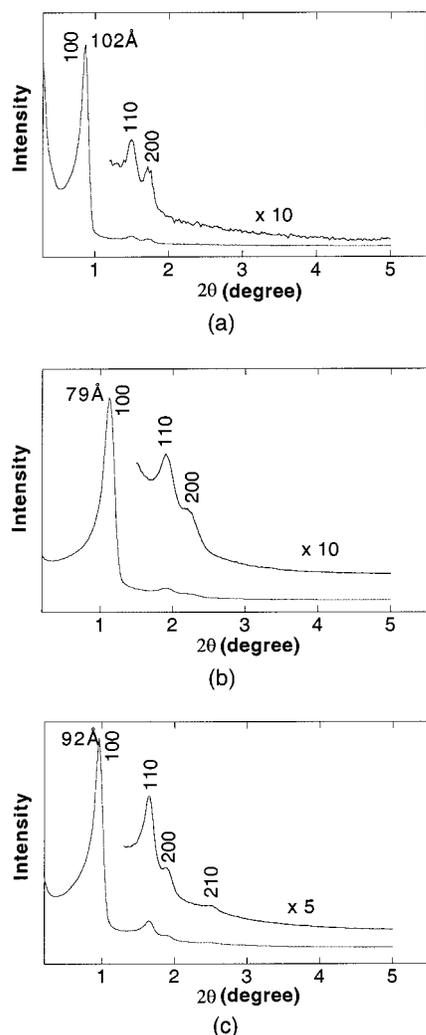
Figure 2. XRD patterns of as-synthesized and calcined hexagonal mesophases prepared from the Pluronic P123/ butanol/water system. The mass ratio between butanol and P123 is 0.15. (a) as-synthesized silica−surfactant−cosurfactant mesophase without hydrothermal treatment; (b) calcined and then hydrothermally treated at 100 °C for 24 h; (c) hydrothermally treated at 100 °C for 24 h and then calcined.

significant decrease (as high as 23%) in the d spacing occurs when samples are calcined (Figures 1 and 2).

Hydrothermal Treatment. Since direct liquid crystal templating is typically performed at room temperatures

and under weakly acidic conditions, there should exist a much higher concentration of unreacted silanol groups in silica−surfactant−cosurfactant mesophases as compared to those prepared under strongly basic or acidic conditions.[10,11] Thus, there is an unusually large shrinkage in the d spacing during calcination of mesophases prepared by direct liquid crystal templating (Figures 1 and 2). For example, the d spacing for one mesophase prepared from the F127−pentanol−water system is decreased from 154 to 119 Å, and the shrinkage is nearly 23% (Figure 1). In comparison, the d spacing of the cubic mesophase (SBA-16, also prepared from F127) is reduced from 124 to 118 Å upon calcination, and the shrinkage in the d spacing is less than 1%.[26] Note that despite the large shrinkage for mesostructures reported here, long-range ordering is still maintained (Figures 1 and 2).

The large shrinkage in the d spacing during calcination can be significantly reduced if as-synthesized samples are treated hydrothermally at 100 °C for 24 h prior to calcination. This is likely because hydrothermal treatment promotes the further cross-linking of the inorganic framework. For the sample mentioned above, after hydrothermal treatment, shrinkage during calcination is reduced by about half to approximately 12% (the d spacing after calcination is 136 Å, Figure 1). Such shrinkage is still considerably higher than that experienced by samples prepared at low surfactant concentrations. On the other hand, a high level of silanol concentrations may be desirable for postsynthesis functionalization of mesoporous wall structures. Thus, the materials reported here could provide new opportunities in the applications of mesoporous materials.

The pore size control by hydrothermal treatment is quite different from those reported earlier.[29−31] In those earlier works, there is a pore size increase during hydrothermal treatment of as-synthesized samples, which has been attributed to swelling effects of N,N-dimethylhexadecylamine generated in situ from cetyltrimethylammonium surfactant.[32] In our work, the pore size does not increase during hydrothermal treatment, and in fact a small decrease (<5 Å) is usually observed. The pore size difference between calcined samples with and without prior hydrothermal treatment is due to a different extent of shrinkage during calcination.

In addition to a reduction in shrinkage, precalcination hydrothermal treatment usually leads to an enhancement in mesoscopic ordering; as a result the intensity of the lowest diffraction peak is increased several times, and high-order XRD peaks become more easily observable. The ratio between the d spacings of the first three peaks is $1:3^{-1/2}:1/2$, which can be indexed with a hexagonal unit cell.

Mesoporous silica reported here have high thermal stability. The mesoscopic ordering is retained even after heating at 800 °C for a few hours. The hydrothermal stability is also excellent. For calcined samples, the hydrothermal treatment at 100 °C does not lead to any deterioration in the mesostructure (Figure 2b). Powder X-ray diffraction data show that hydrothermal treatment of calcined samples also has very little effect on the pore size. In comparison, calcined MCM-41 samples can be

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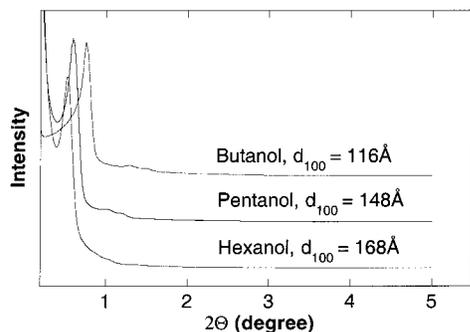
Figure 3. XRD patterns of calcined hexagonal mesophases showing the effect of different cosurfactants on the pore size. Each ingredient (surfactant, cosurfactant, water, and silica) has the same concentration (wt %). The cosurfactant/surfactant mass ratio is maintained at 0.72 for different cosurfactants.
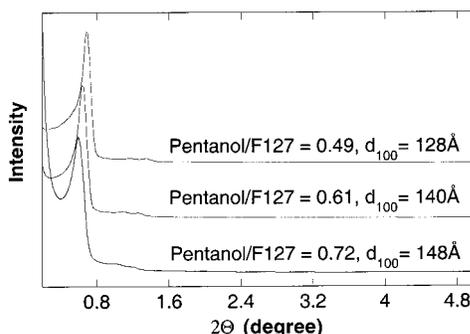
Figure 4. XRD patterns of calcined hexagonal mesophases showing the effect of different cosurfactant/surfactant mass ratios on the pore size in the ternary F127/pentanol/water system.

easily rendered amorphous by hydrothermal treatment at 100 °C.[29,33]

Cosurfactants and Pore Size. One important advantage of using cosurfactants is that it allows control of pore sizes. In particular, an increase in the carbon chain length of the cosurfactant leads to a significant expansion in the mesopore size (Figure 3). To exclude other possible factors, experiments with different cosurfactants are performed with the same weight concentration for each component in the initial mixture. The pronounced increase in the pore size is apparently due to an increased hydrophobic volume for cosurfactant molecules.

Unlike nonpolar oils that are located at the hydrophobic core of surfactant assemblies, the polar group (−OH group) of cosurfactants is believed to be located at the hydrophilic−hydrophobic interface to help in stabilizing liquid crystals and determining their surface curvatures.[19] The mesopore size is, to a large extent, determined by the volume of the hydrophobic core of surfactant arrays. Upon the addition of cosurfactants, the increase in the hydrophobic volume exceeds the increase in the hydrophilic volume. Thus, cosurfactants act as a special kind of swelling agent to allow an additional level of control over pore size.

In addition to the type of cosurfactants, the amount of a particular cosurfactant can be adjusted to achieve pore size control. When the amounts of surfactant, water, and silica are kept constant, the increase in the amount of cosurfactants such as butanol leads to an increase in the pore size (Figures 4 and 5).

(33) The stability of MCM-41 materials can be enhanced by following some special procedures. See, for example: Mokaya, R. *J. Phys. Chem. B* **1999**, *103*, 10204−10208.
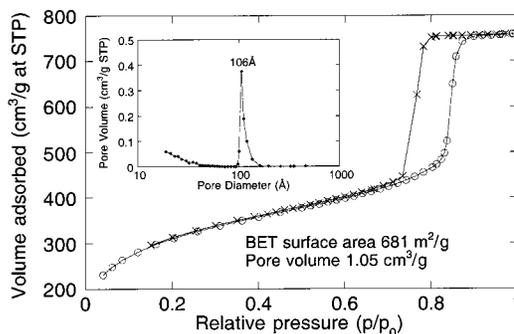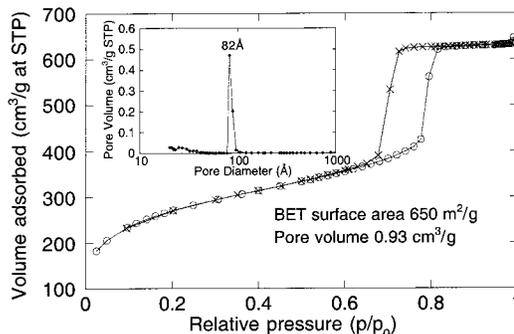
Figure 5. Nitrogen adsorption (○)−desorption (×) isotherms and the BdB−FHH pore size distribution curves from the adsorption branch showing a comparison between pore sizes for samples prepared at different cosurfactant/surfactant mass ratios: (a, top) at the pentanol/F127 ratio of 0.49; (b, bottom) at the pentanol/F127 ratio of 0.61.
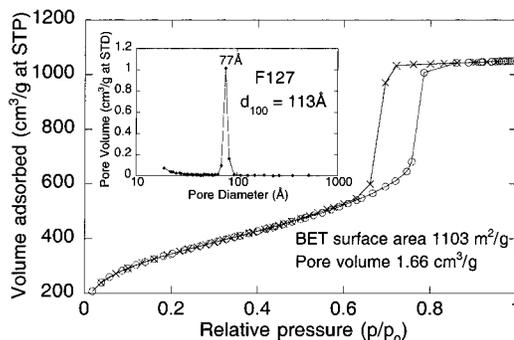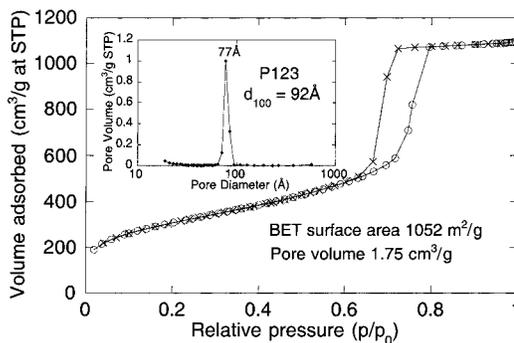
Figure 6. Nitrogen adsorption (○)−desorption (×) isotherms and the BdB−FHH pore size distribution curves from the desorption branch illustrating two materials with the same pore size, but very different wall thickness: (a, top) prepared from the P123/butanol/water system; (b, bottom) prepared from the F127/butanol /water system.

F127−Cosurfactant−Water−Silica System. The introduction of cosurfactants such as butanol and pentanol to the binary surfactant/water system leads to a richer phase diagram. For example, the lamellar mesophase does

(a)

(b)

(c)

(d)

Figure 7. Transmission electron micrographs of as-synthesized and calcined samples prepared from the F127/butanol/water system: (a) as-synthesized silica−surfactant−cosurfactant composite phase; (b) after hydrothermal treatment at 100 °C for 24 h; (c) calcined sample "a"; (d) calcined sample "b".

not exist in the F127/water phase diagram at room temperature,[17] but the lamellar surfactant mesophase has already been reported in the surfactant/cosurfactant/water ternary system.[19] The use of cosurfactants can also create a larger single-phase domain for the hexagonal phase. For example, in the F127/water binary system the hexagonal phase is formed with ≈65−80 wt % of F127 whereas in the F127/butanol/water ternary system, much less surfactant (as low as ≈20 wt %) is needed to form the hexagonal mesophase.[19]

Because of the large phase domain for the hexagonal structure, hexagonal mesoporous silica has been synthesized with a relatively large range of cosurfactant/surfactant mass ratios. In the F127−butanol−water system, hexagonal phases can be prepared with cosurfactant/surfactant ratios from 0 to ≈0.8. The replacement of butanol by pentanol gives similarly ordered hexagonal mesoporous silica, but with larger pore sizes. Hexyl alcohol can also be utilized to synthesize hexagonally ordered mesoporous silica, but long-range ordering is in general not as good as that observed for samples prepared from

butanol or pentanol. For cylindrical hexagonal phases, the nitrogen adsorption−desorption isotherms typically show the expected type IV adsorption isotherm behavior with a type H1 hysteresis loop (Figures 5 and 6). The periodic hexagonal ordering for samples reported here has also been verified by transmission electron microscopy (Figures 7 and 8).

Because only one peak is usually observed in the X-ray powder diffraction pattern of as-synthesized samples, a question arises as to whether as-synthesized samples are disordered phases similar to wormhole type structures,[31] rather than periodic hexagonal structures. The images from transmission electron microscopy show that the hexagonal ordering is maintained for both uncalcined (with or without hydrothermal treatment) and calcined mesostructures (Figure 7). Such results also suggest that there is no phase transition during hydrothermal treatment or calcination. Preliminary experimental results show that the reason for the absence of high-order reflections for silica−F127−cosurfactant mesophases (not calcined me-
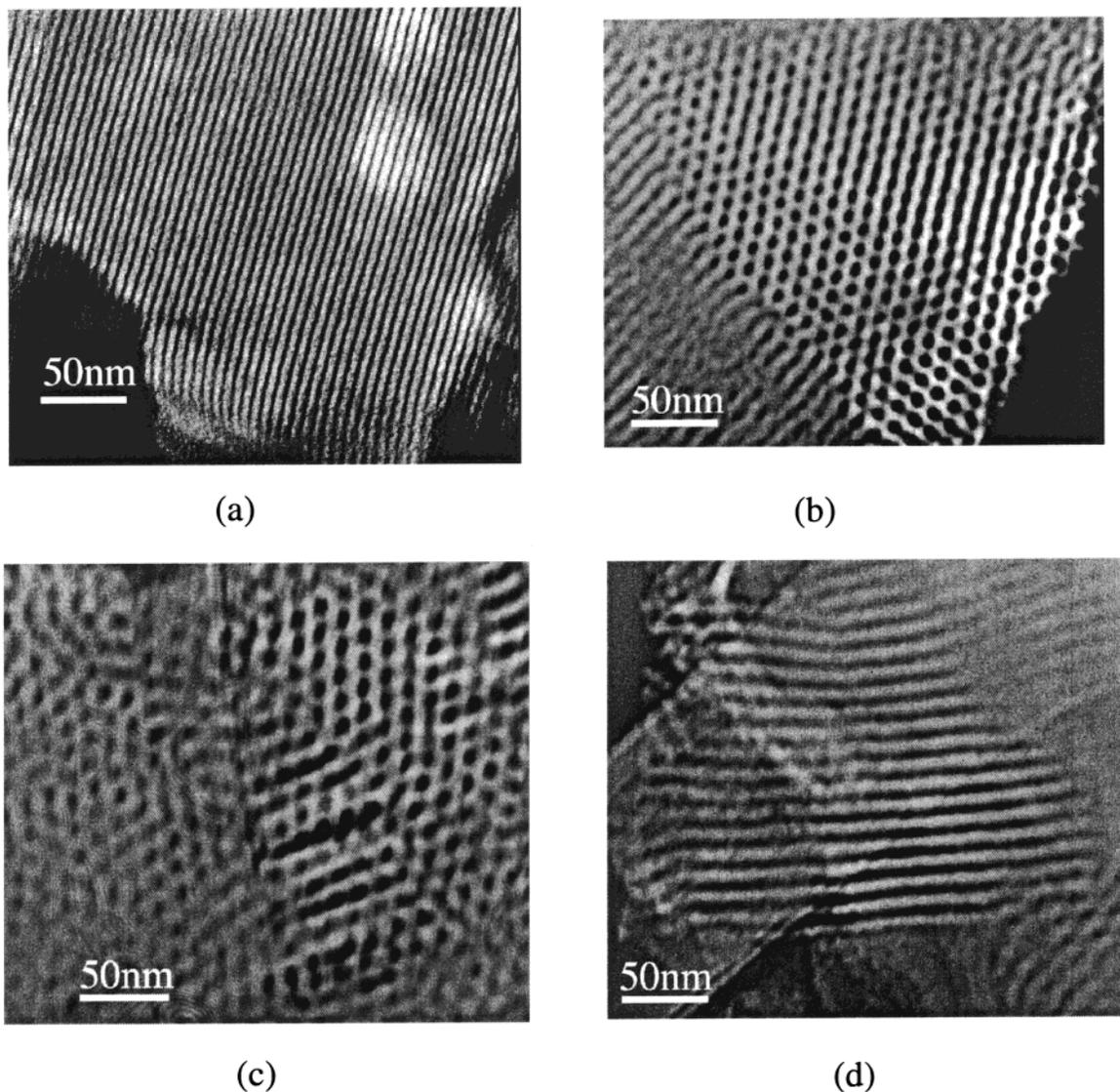
Figure 8. Transmission electron micrographs of calcined samples prepared under various conditions: (a) the side view of channels for a sample prepared from the P123/butanol /water system; (b) from the F127/pentanol/water system; (c) from the F127/hexyl alcohol/water system; (d) the side view of channels for a sample prepared from the F127/hexyl alcohol/water system.

soporous silica) is likely related to the very unique structural feature of F127.

P123−Butanol−Water−Silica System. In comparison with the F127−butanol−water system, the phase diagram of the P123-butanol−water system shows a larger phase domain for the lamellar structure, but a much smaller domain for the hexagonal phase.[18] In this system the hexagonal phase is only favored at low cosurfactant/surfactant mass ratios (below ≈0.3). This is considerably smaller compared to that in the F127−butanol−water system. However, for the synthesis performed at low surfactant concentrations, the TMB/P123 (TMB = 1,3,5-trimethylbenzene) mass ratio beyond which a phase transition to mesocellular foams is also quite low (≈0.2).[34]

The synthesis for mesoporous silica was performed with a butanol/P123 mass ratio of 0.15. At this ratio, highly ordered hexagonal mesophases are prepared. The high-order reflection peaks (110 and 200) are easily observable even for the silica−surfactant (P123)−cosurfactant composite phase. In comparison, for samples prepared from F127, high-ordering reflections are usually only observable

after hydrothermal treatment or calcination. The nitrogen adsorption−desorption isotherm measurement shows that mesoporous silica prepared from the P123−butanol−water system has a high surface area and a well-defined pore size (Figure 6).

It is of interest to compare the wall thickness between samples synthesized from F127/butanol/water and P123 /butanol/water systems. The *d* spacings of the (100) peak for two different samples differ by as much as 21 Å, and yet pore sizes calculated from nitrogen isotherms are identical (Figure 6). This is apparently because the large hydrophilic volume of F127 gives rise to a much thicker wall in the F127-templated mesoporous sample. For these two samples, the calculated wall thickness for the F127-templated sample is 53 Å whereas the calculated wall thickness for the P123-templated sample is only 29 Å.

Conclusions. We have described a synthesis method that has extended the direct liquid crystal templating approach to ternary block copolymer−cosurfactant−water systems. The use of ternary systems enriches phase diagrams of aqueous surfactant systems, which in turn introduce more flexibility and diversity into the designed synthesis of mesoporous materials. This approach has

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allowed the synthesis of transparent silica monoliths whose pore sizes can be controlled by surfactant or cosurfactant types, cosurfactant/surfactant mass ratios, and precalcination hydrothermal treatment. Highly stable mesoporous silica have been synthesized in several ternary systems. The synthesis method described here is expected to be applicable to a diversity of chemical compositions because of its suitability to complex multicomponent systems.