

Triblock-Copolymer-Directed Syntheses of Large-Pore Mesoporous Silica Fibers

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There is currently intense interest in the topological construction of mesoporous materials both at the molecular and macroscale levels¹ because of the need for selective processing of mesoporous materials into forms suitable for applications in catalysis,² separations,^{3,4} chemical sensing, low-dielectric coatings,⁵ and optical communications.⁶ Mesoporous silica films have been grown under acidic conditions,^{7,8} at solid–liquid and liquid–vapor interfaces through an interfacial silica-surfactant self-assembly process,^{9–11} and more recently by sol–gel dip coating¹² and polymer templating.¹³ Liquid crystalline templating¹⁴ has been used for the fabrication of monolithic mesoporous silica with different macroscopic shapes.^{15,16} Oil-in-water emulsion chemistry has been employed to selectively create mesoporous hard and hollow spheres of controllable diameter.¹⁷ Highly ordered, optically transparent mesoporous silica fibers have been grown in a two-phase reaction system at room temperature.⁶ These fibers have been demonstrated to have potential as high-surface-area optical waveguides. Recently, it was reported that mesoporous spun fibers can be fabricated by a solvent-evaporation

technique using cetyltrimethylammonium chloride (CTAC) as the structure-directing agent¹⁸ in acidic media.^{7,8} This technique involved the addition of polymers, such as poly(ethylene oxide), to increase the viscosity for fiber spinning and is an extension of the traditional method of fabricating nonporous silica gel fibers.¹⁹ Under such circumstances, the polymers do not act as structure-directing agents and are incorporated homogeneously into the framework during synthesis. Since these macroscale syntheses of mesoporous silica use low molecular weight surfactants as the structure-directing agents, the resulting materials normally have small mesopore sizes (~2 nm), which impose limitations on many of their potential applications.

Herein we report a simple procedure to synthesize mesoporous silica fibers with large pores using amphiphilic block copolymers of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)^{20,21} as the structure-directing agents. The fibers have three-dimensional (3D) hexagonal cage and simple two-dimensional (2D) hexagonal channel structures depending on the choice of the copolymer surfactants. These fibers have a uniform mesoporous structure and the pore channels are uniaxially aligned. The pore sizes are as large as 63 Å and the diameter of these fibers can be varied from submicron to several hundred microns.

Mesoporous silica fibers were prepared by drawing a gel strand from a highly viscous amphiphilic polymer/silicate solution. Tetraethoxysilane (TEOS, Aldrich) was used as the silica source. Poly(alkylene oxide) block copolymers HO(CH₂CH₂O)₁₀₆(CH₂CH(CH₃)O)₇₀(CH₂-CH₂O)₁₀₆H (designated EO₁₀₆PO₇₀EO₁₀₆, BASF, Pluronic F-127) and HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂-CH₂O)₂₀H (designated EO₂₀PO₇₀EO₂₀, BASF, Pluronic P-123) were used as structure-directing agents. The gel solution was prepared using the compositions (in moles): 1 Si(OEt)₄, 3–4 EtOH, 1–2 H₂O, 0.005–0.015 HCl, 0.006–0.011 polymer. A typical preparation was as follows: 2 g of polymer was dissolved in 4.69 g of ethanol (EtOH), then 0.94 g H₂O and 0.15 g HCl (2M) were added with stirring, resulting in a clear solution. To this solution was added 6.25 g of TEOS slowly with stirring. The mixture was aged without stirring for 4 h at 80 °C in a 50 mL beaker. Longer aging times are necessary at lower temperatures. The viscosity of the solution increases during aging, because of partial hydrolysis and condensation of the silica and solvent evaporation. A glass rod or pipet tip was then dipped into the highly viscous gel solution and withdrawn to form the silica/copolymer fibers. The fibers were air-dried for 1 week. The polymer structure-directing agents were removed by calcination at 450 °C for 4 h in air.

Figure 1 shows several images of the as-synthesized and calcined silica fibers. The fibers can be either free-

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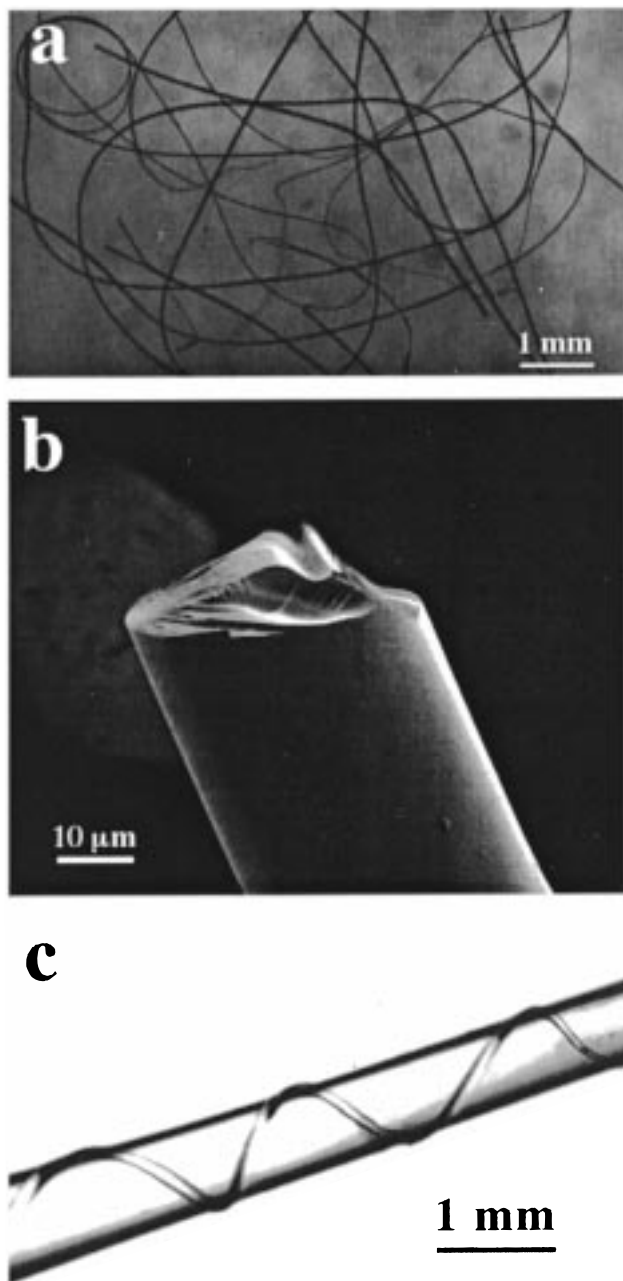


Figure 1. (a) Optical image of calcined mesoporous silica fibers synthesized using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ triblock copolymers as the structure-directing agents. (b) Scanning electron microscope image of the circular cross section of a calcined mesoporous silica fiber. (c) Optical image of an as-synthesized helical mesoporous silica fiber synthesized using $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ as the structure-directing agent. The fiber was wound around a glass rod.

standing or wound into different morphologies, such as the helical forms as shown in Figure 1c. They normally have circular cross sections with smooth outer surfaces (Figure 1b). The fiber diameter has excellent uniformity along the longitudinal axis, which can be varied from submicron to several hundred microns by modifying the solution composition and drawing speed.

Powder X-ray diffraction (XRD) patterns of the as-synthesized and calcined fibers prepared using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ block copolymers are shown in Figure 2. The diffraction pattern for the as-made fibers shows two low angle peaks at $d = 138$ and 124 Å. After calcination, six peaks can be resolved with d spacings of 115,

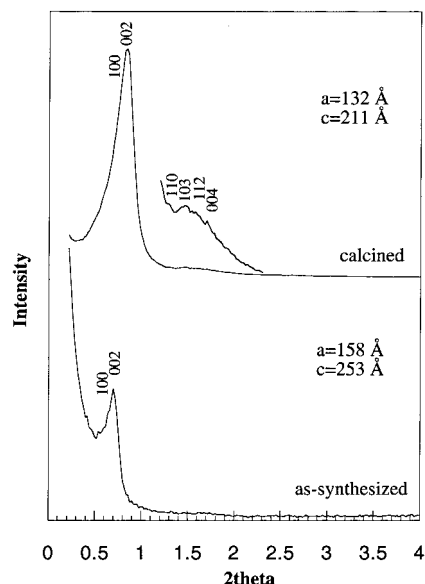


Figure 2. Powder X-ray diffraction patterns for as-made and calcined mesoscopically ordered silica fibers synthesized using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ as the structure-directing agent.

67.2, 59.9, 56.1, and 51.9 Å. These peaks cannot be indexed into the reflections of either a 2D hexagonal or a cubic structure.^{13,21} Instead, they can be indexed as the (100), (002), (110), (103), (112), and (004) reflection of a 3D hexagonal cage structure. This 3D hexagonal structure has a unit cell of $a = 132$ Å and $c = 211$ Å, with $c/a = 1.60$. Accordingly, the two peaks for the as-synthesized fibers can be indexed as the (100) and (002) reflections of a 3D hexagonal structure with unit cell of $a = 158$ Å and $c = 253$ Å. The 3D hexagonal structure and the lattice parameters were further confirmed by transmission electron microscope (TEM) imaging on thin-sliced sections of the fibers. Lattice images recorded along three different zone axes are shown in Figure 3 with their corresponding electron diffraction patterns. These electron diffraction and X-ray diffraction patterns can be indexed in the space group $P6_3/mmc$. The pore system reflects the symmetry of the silica framework structure. Along the [0001] zone axis, 6-fold symmetry can be clearly seen. Along the $[1\bar{2}1\bar{3}]$ and $[01\bar{1}1]$ zone axes, slightly distorted hexagonal and rhombohedral arrays of pores are observed. This structure shows a close similarity to the common hexagonal close-packed structure.

Polarized optical microscopy was used to study the pore orientation within the fibers. It was found that maximum light transmission occurred with the fiber oriented 45° to the polarizers (Figure 4), and complete extinction occurs when the fiber is oriented either parallel or perpendicular to the analyzer (image not shown). This indicates that the pores are uniaxially aligned along the hexagonal optical axis, i.e., 6-fold symmetry axis.

Previous cubic (V_1), isotropic, and 2D hexagonal structures have been observed in the Pluronic $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ /water/solvent system^{22,23} and only a cubic mesostructure ($Im\bar{3}m$) was observed during our previous

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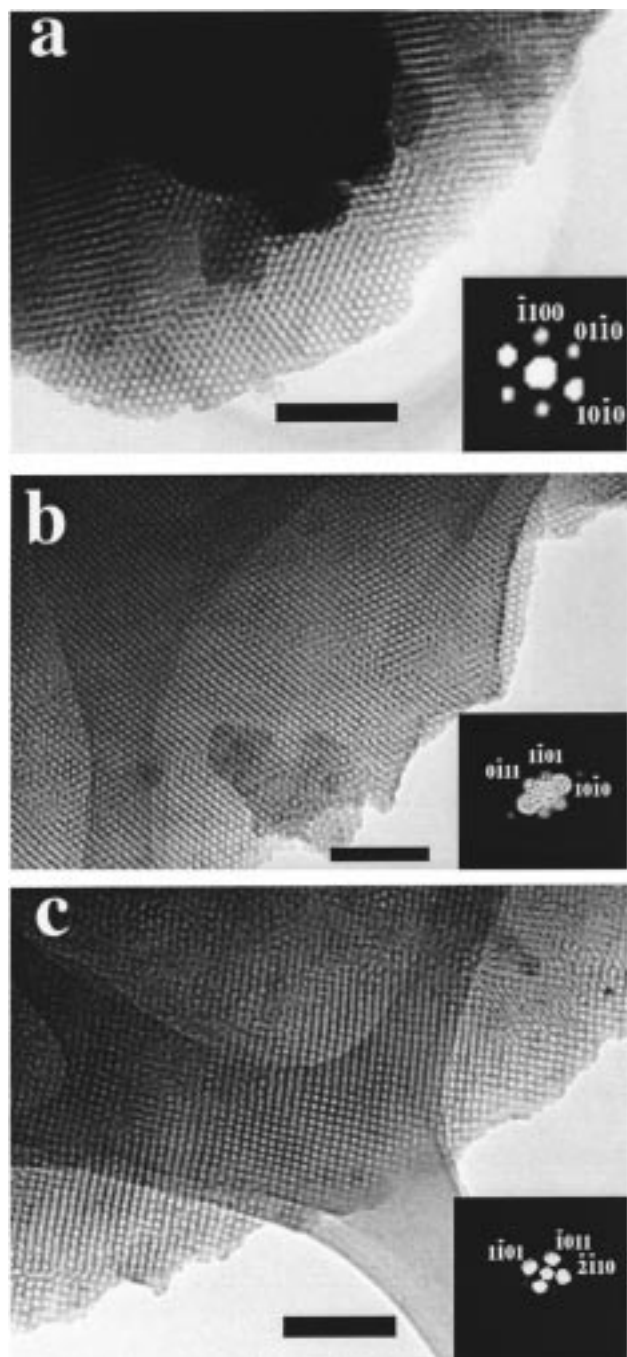


Figure 3. TEM micrographs recorded along three different zone axes (a) [0001], (b) [1213] and (c) [0111] of calcined mesoporous silica fibers with a 3D hexagonal cage mesostructure prepared using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$. The corresponding electron diffraction patterns are shown in the insets. The scale bars correspond to 100 nm.

powder and film syntheses of mesoporous silica that were prepared using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ as the structure-directing species.^{13,24} It has been established by comparing a large number of surfactants that when the local effective surfactant packing parameter $g = V/a_0l$ (V is the total molecular volume of the hydrophobic surfactant chains plus any cosolvent species present, a_0 is the effective surfactant headgroup area at the hydrophilic-



Figure 4. Polarization image of calcined 3D hexagonal mesoporous silica fibers prepared using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$. The fiber axis is oriented 45° with respect to the upper and lower polarizers.

hydrophobic micelle aggregate interface, and l is the kinetic surfactant tail length) is less than $1/3$, globular aggregates are preferred. This is consistent with the formation of cubic or 3D hexagonal phases^{25,26} in concentrated lyotropic systems.²⁷ When compared to other poly(alkylene oxide) surfactants, $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ has a much larger effective hydrophilic EO headgroup. This is expected to yield a small effective g value that will favor the formation of cubic or 3D hexagonal arrays of globular aggregates, as opposed to a hexagonal rod mesostructure. However, under the clearly nonequilibrium conditions used to prepare the fibers here, numerous concurrent kinetic processes occur to complicate meso- and macroscale material organization. Nevertheless, appreciable control can be excised over mesostructural ordering and macroscopic morphology by optimizing different synthesis and processing conditions, including pH, solution composition, temperature, and fiber drawing rate. In this way, mesophase self-assembly, silica polymerization, solvent evaporation, and fiber drawing may be balanced to achieve the meso- and macroscopic structural features desired.

Synthesis routes based on aging/gelation of silica oligomers within a lyotropic liquid-crystalline phase have proven to be useful for the fabrication of monolithic mesoporous silica with different macroscopic shapes.¹⁴⁻¹⁶ In this liquid crystalline templating process, a preexisting surfactant liquid crystal phase is required for the formation of the mesophase silica. In our process, the

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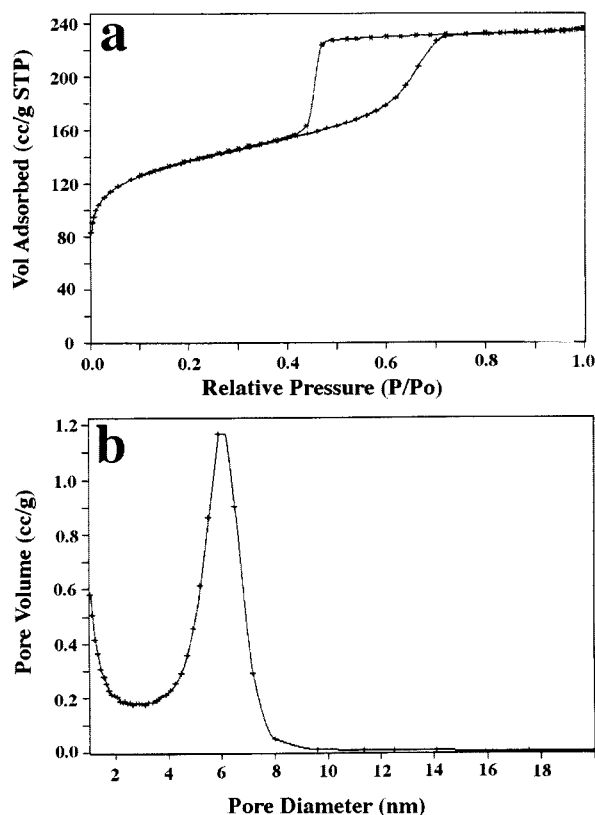


Figure 5. (a) Nitrogen adsorption and desorption isotherms for 3D hexagonal mesoporous silica fibers synthesized using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$. (b) The pore size distribution of the mesoporous silica fibers calculated using the Barrett–Joyner–Halenda (BJH) model from the adsorption branch of the isotherm.

formation mechanism of the fibers involves cooperative self-assembly of the amphiphilic block copolymer and the silicate polyions. This process is believed to occur first at the air–fiber interface, followed by progressive conversion of the entire fiber to a mesophase structure with the evaporation of the solvent. During and after the rapid solvent evaporation, the mesophase is maintained by diffusion barriers and further silica framework gelation.¹⁸ An attractive aspect of the current process is the utilization of the viscoelastic rheological properties of the self-assembled silica–block copolymer mesophases, which allows the fiber spinning without the addition of other gel-forming agents.

N_2 adsorption/desorption isotherms obtained on the 3D hexagonal silica fiber powders show typical type IV curves with a large H_2 hysteresis (Figure 5). This type of isotherm is characteristic of an open interpenetrating pore system with cage structures.^{24,25} These calcined fibers have a N_2 Brunauer–Emmett–Teller (BET) surface area of $580 \text{ m}^2/\text{g}$, a mean pore size of 6.3 nm , and a single point ($p/p_0 = 0.983$) pore volume of $0.56 \text{ cm}^3/\text{g}$. These fibers, to our knowledge, have the largest

known pore sizes for silica mesophase fibers. In addition, this is also the first example of mesoporous fibers with a supercage structure. An important feature of the cage arrangements is their connectivities, which permits molecules to diffuse freely either parallel or normal to the fiber axis. This makes these fibers potentially useful in applications such as remote chemical/biological sensors or fibrous catalyst supports.

We have also used other poly(alkylene oxide) block copolymers as structure-directing agents for processing mesoscopically ordered silica fibers. Powder XRD and TEM results (not shown here) indicate that fibers with a 2D hexagonal ($p6mm$) structure can be formed when $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ species are used as the structure-directing agents. For such fibers, d_{100} XRD spacings of 98 and 78 \AA are observed before and after calcination, respectively. Furthermore, N_2 adsorption/desorption isotherms obtained on the fiber powders show typical type-IV curves with H_1 hysteresis. BJH analyses show that these calcined fibers exhibit a mean pore size of 43 \AA , a pore volume of $0.62 \text{ cm}^3/\text{g}$, and a BET surface area of $720 \text{ m}^2/\text{g}$. The mean pore size of these fibers is substantially larger than fibers synthesized using CTAC as the surfactant.¹⁸ TEM experiments indicate that the pore channels are aligned preferentially along the fiber axis.

In summary, a simple process has been employed as a generalized approach for making fibers with large and accessible pores using amphiphilic block copolymers as the structure-directing agents. These uniaxially aligned fibers have either 3D hexagonal cage or 2D hexagonal channel structures and have pore sizes ranging from 40 to 63 \AA . The structures of the amphiphilic block copolymers (e.g., the relative hydrophilicity of the blocks, molecular weight, etc.) can be modified using well-established techniques of polymer chemistry to tune the pore sizes and mesostructural ordering of the resultant mesoporous silica fibers. The combination of surfactant self-assembly chemistry and polymer processing^{1,13} provides simple and versatile synthetic approaches for creating nanostructured hybrid inorganic/organic materials.

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