

Macroscopic Shear Alignment of Bulk Transparent Mesostructured Silica

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Transparent aligned composite or porous silica structures are desirable for use as membranes or as host materials for optical dyes, conducting polymers, and large molecules. However, few bulk aligned structures with orientational order have been produced.^{1–4} Moreover, those that have been produced are generally not transparent and thus are not useful for optical applications.

Creating orientational order within materials generally requires that they be processed in an externally applied field. For example, bulk aligned silica–surfactant mesophases have been prepared by using strong magnetic fields to orient low-molecular-weight liquid crystal precursors,^{2,5} though these materials are unfortunately not transparent. A number of transparent mesostructured silica thin films and fibers with macroscopic alignment have been synthesized by using interactions at air–(water, oil, or mica) interfaces,^{6–9} surface effects,^{10–12} or extensional flow.¹³ However, these techniques are not well suited to the formation of aligned bulk materials. Surface interactions, for example, generally do not extend far from the interface into the bulk, and practical considerations limit the use of extensional flow to alignment within thin fibers. Monolithic materials with large domain sizes have been reported, though the domains are not uniformly aligned with respect to one another and require lengthy annealing times.^{1,14} Shear alignment is not possible for these materials, because mesophase formation occurs after gelation of the silica. In this Communication, we describe a procedure for producing bulk mesoscopically ordered silica with high degrees of macroscopic alignment and transparency using capillary flow or parallel plate shearing.

Typically, silica/block-copolymer mesophase syntheses require evaporation of alcohol species produced by hydrolysis of inorganic alkoxide precursors before the structure-directing agents can self-assemble.^{10,11,15,16} As noted above, sample fluidity is lost, because self-assembly occurs after gelation, thus precluding effective shear alignment. Feng et al. recently demonstrated that by hydrolyzing the alkoxide precursors and removing the alcohols under vacuum prior to mixing with the structure-directing block-copolymer solution, a viscous but still fluid mesophase with hexagonal or lamellar order can be produced before gelation occurs.¹⁷

Mesoscopically ordered silica-block copolymer composites were formed under acidic solution conditions with amphiphilic poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) [EO₁₀₆PO₇₀EO₁₀₆] (Pluronic F127) triblock copolymer mixed with butanol and cyclohexane, which act as hydrophobic swelling agents. The concentrations of the swelling agents are important variables in establishing the final structure: 0.0, 0.16, and 0.20 g of swelling agent/g of F127 led to cubic, hexagonal, and lamellar mesophases accordingly. A typical hexagonal mesophase was prepared as follows: 2.0 mL of tetraethoxysilane (TEOS) was mixed with 2.0 mL of HCl (pH 1.4) and the mixture stirred until homogeneous. The sample was placed under vacuum until ~80% of the ethanol produced by the hydrolysis of the TEOS was removed. This solution was added directly to a mixture of 0.75 g of F127 polymer/0.15 mL of butanol/0.15 mL of cyclohexane and mixed manually for several minutes until the triblock copolymer had completely dissolved. While the resulting material was highly viscous, centrifugation for 10 min at 3000 rpm was sufficient to remove any bubbles, yielding a colorless transparent gel with strong birefringence (except for the cubic phase).

Highly aligned bulk hexagonal or lamellar mesophases were synthesized by using the silica/block copolymer mixture described above and a simple capillary shear-flow technique demonstrated by Davidson et al.¹⁸ The procedure involved using a vacuum to draw the viscous silica mixture 2–4 cm into a capillary tube, aligning the silica/block-copolymer mesophase by shearing. A variety of capillary tube diameters and geometries were evaluated, including 0.5, 0.7, and 1.0 mm cylindrical quartz X-ray diffraction (XRD) capillaries, as well as 0.3, 0.5, 0.75, and 1.0 mm rectangular optical glass capillaries (Vitrocom). In all cases, the transparent as-synthesized samples showed highly oriented birefringence along the capillary axes. When annealed for 3 days and calcined in air at 450 °C for 6 h, the samples prepared within the 0.5 mm cylindrical capillaries yielded large transparent pieces ~1–2 cm long. Large transparent, crack-free pieces were also obtained in better yield via calcination at 350 °C for 36 h with a 0.25 °C/min temperature ramp. Thinner samples were less prone to cracking, and cylindrical capillaries appeared to produce more robust materials than the flat optical capillaries.

Structure identification and quantitative analyses of the orientational ordering of the silica-EO₁₀₆PO₇₀EO₁₀₆ mesophases with respect to the shear direction were provided by transmission X-ray diffraction patterns recorded on two-dimensional image plates.¹⁴ The degree of mesophase alignment was determined from the full-width-at-half-maximum (fwhm) line width of each two-spot pattern, measured around the azimuthal angle and deconvolved for 5° finite-beam-size effects. For hexagonal phases, the fwhm refers to the distribution of lengthwise orientations of the cylindrical aggregates, and for lamellar phases, the distribution of layer alignments.

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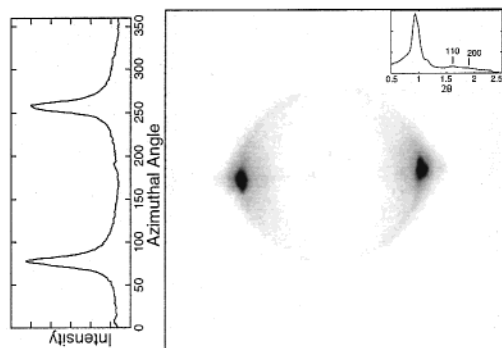


Figure 1. Transmission XRD pattern of a calcined transparent mesoporous silica rod (0.5 mm diameter) prepared by capillary flow. On the left is the scattering intensity distribution plotted as a function of azimuthal angle, which shows that the mesopores are oriented longitudinally along the rod axis with a distribution of 9° fwhm. The distinct reflections and higher order peaks (see inset) establish that the sample has a uniform hexagonal mesostructure. The reflection at 1.16° arises from a hexagonal region at the surface that radially rings the rod periphery and which has contracted more than the bulk region in the center of the sample.

Transmission XRD studies of the aligned samples demonstrate the effectiveness of capillary shear flow for orienting silica-block copolymer mesophases. For the hexagonal phase, the XRD patterns (not shown here) of transparent as-synthesized silica/ $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ samples displayed two well-defined spots indicating orientational ordering along the shear direction, with a typical distribution of 12° fwhm and $d_{100} = 123 \text{ \AA}$. Upon calcination, the samples formed in the 0.5 mm capillary tubes remained transparent and also yielded two distinct spots, as shown in Figure 1, with a fwhm of 9° and $d_{100} = 81 \text{ \AA}$. The degrees of alignment in these samples, 12° as-synthesized and 9° calcined, are higher than those produced with cone-and-plate shearing of neat EO-PO-EO block copolymers ($\sim 20\text{--}30^\circ$ fwhm).¹⁹ The XRD patterns of the silica samples remained identical when the X-ray beam was translated over their entire 0.5 to 2.0 cm lengths, indicating that the ordering is maintained throughout the materials. The d_{110} and d_{200} peaks (Figure 1, inset) confirm that the hexagonal phase was preserved following calcination.

Interestingly, the XRD pattern in Figure 1 also contains a weak 6-fold reflection pattern at a slightly smaller d spacing than the intense two-spot feature, indicating that there are hexagonally packed tubes oriented radially around the sample cylinder as well. By translating the X-ray beam to the extreme edge of the cylindrical sample, the weak six-spot pattern was enhanced, while the intense two-spot pattern was diminished. This suggests that at the surface of the sample, the C_6 axis of the hexagonal phase wraps around the macroscopic sample cylinder, rather than aligning with the shear direction. Such radial orientational order at a curved air-silica interface has been observed previously for low-molecular-weight surfactant/silica mesophases.^{8,20} From the relative intensities of the different spot patterns, it is estimated that less than a few percent of the sample is oriented in this circular configuration. A core-shell model of the mesophase tube alignment in the bulk cylinders agrees with polarizing optical microscopy measurements, which show uniform birefringence at the sample edges, with highly oriented birefringent inner cores.

Macroscopic alignment of bulk silica-block copolymer mesophases was also achieved by parallel-plate shearing. For this procedure, the viscous centrifuged gel was placed into a Teflon parallel-plate shear device and oscillated at 1 Hz with a 3 cm stroke length for 30 min. Afterwards, the transparent gel was allowed to dry open to the atmosphere. After 3 days, a $2.5 \times 7.5 \times 0.1 \text{ cm}^3$ slab was created with uniform birefringence

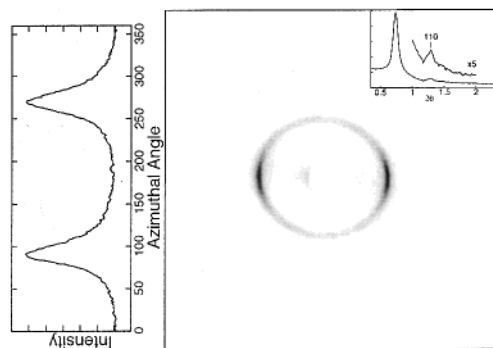


Figure 2. XRD pattern of a calcined mesoporous silica slab ($2.5 \times 7.5 \times 0.1 \text{ cm}^3$) prepared by parallel-plate shearing. The intense (saturated) arcs and inset indicate that the material has an aligned hexagonal mesostructure, while the diffuse ring reflects a small contribution from randomly oriented components. The azimuthal scattering intensity on the left shows that the mesopores are aligned along the shear direction and in the plane of the sample with a 26° fwhm distribution.

along the shear direction. The XRD patterns acquired for silica/ $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ mesophases processed under parallel-plate shearing show that these samples were also macroscopically aligned, though to a lesser extent than the materials prepared with the capillary shearing method. In addition, the parallel-plate-sheared samples are comprised of a mixture of hexagonal and lamellar mesophases. The hexagonal phases had d_{100} spacings of $\sim 120 \text{ \AA}$ with higher order d_{110} and d_{200} peaks and were aligned along the shear direction with a distribution of 46° fwhm. The lamellar phase was oriented with its sheets parallel to the surface of the sample and had a substantially larger d spacing, $d_{100} = 206 \text{ \AA}$, consistent with higher local concentrations of the hydrophobic swelling agents, likely due to incomplete mixing. After calcination, the bulk slab became opaque, but retained its shape. X-ray analysis (Figure 2) showed that only the hexagonal phase remained, retaining alignment along the shear direction, with a fwhm of 26° and $d_{100} = 118 \text{ \AA}$. These results are consistent with the collapse of the lamellar regions upon removal of the block copolymer. The degree of alignment of the hexagonal phase after removal of the block copolymer is comparable to that of other shear-alignment studies of neat polyglycol block copolymers.^{19,21} The bulk orientationally ordered silica/ $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ composites and calcined mesoporous silicas prepared by capillary flow or oscillatory-parallel plate shearing yield alignment distributions ($\sim 9^\circ$ and 26° , respectively) that are significantly better than previously demonstrated for mesostructured silica/surfactant systems ($\sim 50^\circ$).^{2,5}

These highly aligned transparent composites or porous mesostructured silicas produced by capillary flow or parallel-plate shearing show promise as host matrices for a variety of electrically or optically active chemical guest species. Beneficial properties of such bulk silica materials include uniform $50\text{--}200 \text{ \AA}$ mesostructural organization, anisotropic orientational ordering over macroscopic length scales ($>$ millimeter), thermal stability, optical transparency, processability, and for porous materials, high internal surface areas. Efforts are underway to incorporate active species into such bulk composites and porous solids to examine the anisotropic properties of these host-guest systems.

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