

Hexagonal to Mesocellular Foam Phase Transition in Polymer-Templated Mesoporous Silicas

John S. Lettow,[†] Yong Jin Han,[‡] Patrick Schmidt-Winkel,[‡] Peidong Yang,[‡]
Dongyuan Zhao,[‡] Galen D. Stucky,^{*,‡} and Jackie Y. Ying^{*,†}

Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, and Department of Chemistry, University of California,
Santa Barbara, California 93106

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We have investigated the phase transition between two distinct mesoporous silicas: SBA-15, comprising a hexagonally packed arrangement of cylindrical pores (6–12 nm in diameter), and mesocellular silica foams (MCF), consisting of spherical voids (22–42 nm in diameter) interconnected by “windows” of ~10 nm. Both SBA-15 and MCF are formed using an amphiphilic triblock copolymer (Pluronic P123) as a template. The synthesis conditions for the two materials are identical, except substantial trimethylbenzene is added to form MCF. We find that the phase transition occurs at an oil–polymer mass ratio of 0.2–0.3. Although the pore structures and pore sizes change dramatically, the mean surface curvature of the system remains essentially the same throughout the transition.

Introduction

The lack of stable materials with well-defined pores between the microporous (<20 Å) and macroporous (>500 Å) regimes was first addressed with the discovery of the M41S materials by Mobil researchers in 1992.¹ However, the pores of the surfactant-templated M41S silicates (20–40 Å) are at the lower end of the mesoporous regime.² The development of SBA-15 silicas^{3a} and mesostructured cellular foams (MCF)⁴ has extended the range of mesoporous materials well past 40 Å. SBA-15 and MCF materials are synthesized with polymer templates and are related by a phase transition from a hexagonally ordered cylindrical mesoporous structure to the mesocellular foam structure.⁴

In the synthesis of MCM-41-type materials, surfactant molecules with small, usually ionic hydrophilic headgroups and hydrophobic alkyl tails are used to template ordered arrays of pores in silica. Diblock and triblock copolymers, with much longer hydrophobic chain lengths than those of surfactants, have been used to template inorganic materials with pore diameters up to ~70 Å.³ In particular, polymer-templated syntheses utilizing a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer have been successfully developed to create a well-defined mesoporous silica material, termed SBA-15.^{3a,c} The use of poly-

(alkylene oxide) amphiphiles introduces a number of new effects that are important to the phase behavior of these micellar systems and the silica materials they template. First, the hydrophilic group is a long chain rather than a single polar group, so that hydration and entropy effects are very important in determining the shape of the hydrophilic block and the volume that it occupies. The specific nature of PEO and PPO interactions with water is also important. Both PEO and PPO are more soluble in water at low temperatures. PPO is relatively insoluble in water by 20 °C, whereas PEO solutions do not form a second phase until ~90 °C.⁵

The differences between ionic surfactant micelles and PEO–PPO–PEO micelles noted above profoundly affect their interactions with hydrophobic “swelling agents”. The swelling agents are introduced to supramolecular-templated systems in order to increase the pore size of the inorganic material by preferential solubilization of the additive in the micelle core. 1,3,5-Trimethylbenzene (TMB or mesitylene) has been used previously to swell the pores of surfactant-templated MCM-41 materials.¹ The swelling process maintains the hexagonally packed structure of the cylindrical pores in MCM-41 while increasing pore diameters from 40 to 100 Å. When TMB is added to a PEO–PPO–PEO templated system, the hexagonally packed pore structure is maintained only for very low concentrations of TMB. Upon increasing the oil–polymer ratio, a new mesocellular foam phase is obtained.⁴ The MCF phase possesses a system of interconnected pores with diameters of 220–420 Å. In this work, we describe the synthesis conditions of these materials and propose a mechanism for the phase transition of SBA-15 with *p6mm* symmetry and pore sizes of 40–120 Å to MCF with well-defined pores ranging from 220 to 420 Å in diameter.

Experimental Procedure

The synthesis of both SBA-15 and mesocellular foam materials has been reported elsewhere.^{3a,4} For this study, all samples were prepared by first dissolving PEO–PPO–PEO triblock copolymer (EO₂₀PO₇₀EO₂₀, BASF Pluronic P123, MW = 5800, 2.0 g, 0.4

[†] Massachusetts Institute of Technology.

[‡] University of California, Santa Barbara.

* To whom correspondence should be addressed (G.D.S., fax: 805-893-4120; e-mail: stucky@chem.ucsb.edu; J.Y.Y., fax: 617-258-5766; e-mail: jyying@mit.edu).

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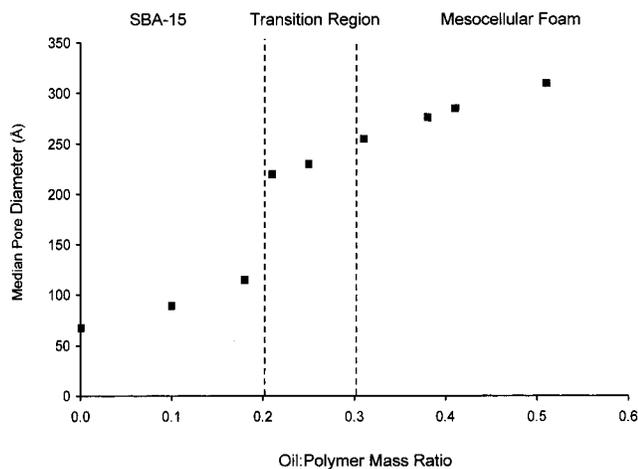


Figure 1. Variation in the median pore diameter of mesoporous silicas synthesized at different oil–polymer ratios. Pore sizes were determined from N_2 adsorption data using the BdB–FHH method.⁷

mmol) in 75 mL of 1.6 M HCl at 35–40 °C. Amounts of TMB (Aldrich) ranging from 0 to 1 g were then added to the polymer solution, and the mixture was stirred for at least 1 h. Tetraethyl orthosilicate (TEOS, Aldrich, 4.25 g, 21 mmol) was added as the silica source. After the mixture was stirred for 24 h at 35–40 °C and aged for 24 h at 100–120 °C, the solids were collected by filtration and dried in air. The resulting powder was calcined at 500 °C for 6 h to produce the mesoporous silica material.

The calcined mesoporous silica materials were characterized by nitrogen adsorption analysis, small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), and transmission electron microscopy (TEM). Nitrogen adsorption experiments were performed on a Micromeritics ASAP 2010 instrument, while a Siemens SAXS instrument (sample-to-detector distance 60 cm, nonmonochromated Cu source operating at 40 kV and 30 mA) was used for structural analysis. DLS studies were performed with an argon-ion laser and the results were analyzed with a BI-9000AT correlator software package from Brookhaven National Laboratory. For TEM studies, a JEOL JEM-200CX microscope (W filament, 200 kV) was employed.

Results and Discussion

Previous experiments determined the polymer, TEOS, and acid concentration ranges over which hexagonally ordered SBA-15 material will form.^{3a} In this study, we fixed the polymer, acid, and TEOS concentrations and added varying amounts of TMB or “oil”, with the oil–polymer mass ratio ranging from 0 to 0.5 in order to investigate the SBA-15 to mesocellular foam phase transition.

A significant increase in the pore size of the mesoporous material is observed at an oil–polymer ratio of ~ 0.2 (see Figure 1). The pore diameters reported in Figure 1 were determined by nitrogen adsorption and were verified with TEM. To determine the pore size of the silica materials from the nitrogen adsorption data, we used two different models. In the low oil concentration regime, the pores were modeled as long straight cylinders (see Figure 2a).^{6,7} For oil-to-polymer ratios above 0.2, the hysteresis in the nitrogen adsorption and desorption isotherms is significantly larger, as shown in Figure 2b and c. In the higher oil concentration regime, we used a modification of the Broekhoff–de Boer (BdB) model that treats the pores as

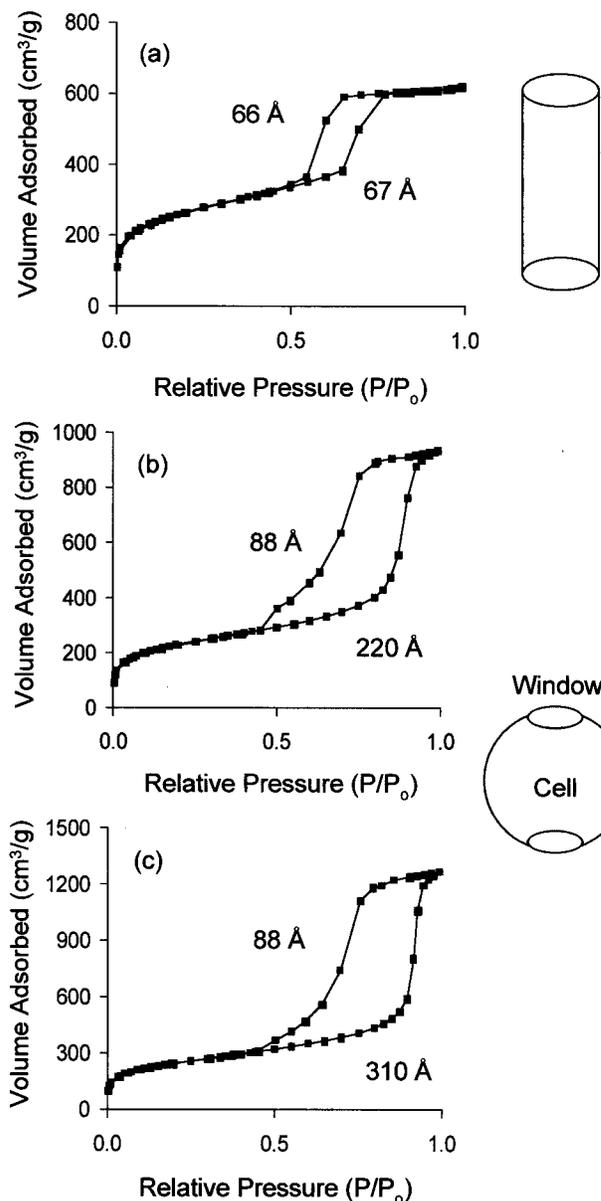


Figure 2. N_2 adsorption–desorption isotherms of mesoporous silicas synthesized at oil–polymer mass ratios of (a) 0.00, (b) 0.21, and (c) 0.50.

spherical cells with smaller openings or windows.^{7,8} In the modified model of the N_2 sorption data, termed BdB–FHH analysis,⁷ we derive cell sizes from the adsorption branches of the isotherms, while the desorption branches give the window sizes. In addition, the TEM images (Figures 3a–c) show a change in pore morphology in the oil–polymer range of 0.2–0.3. The walls of the cylindrical pores begin to buckle with approximately the same periodicity as the pore diameter, forming spherical nodes down the length of the pores as illustrated in Figure 3b.

SAXS data indicate a large shift in the d spacing of the primary scattering peak in the transition region of oil–polymer = 0.2–0.3, supporting the TEM and nitrogen adsorption data that also show distinct changes in pore size. However, the SAXS pattern of a sample synthesized with an oil–polymer ratio of 0.21 can still be indexed to the $p6mm$ space group characteristic of the SBA-15 material (Figure 4b). At an oil–polymer ratio of 0.5, the SAXS pattern (Figure 4c) does not match the $p6mm$ space

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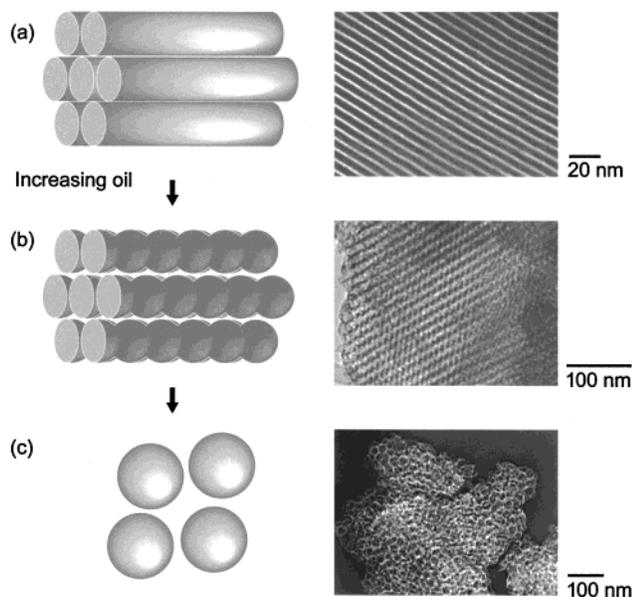


Figure 3. Progression of the morphological transition in P123-templated materials swollen by TMB. The proposed schemes of formation and TEM micrographs of the mesoporous silicas synthesized at oil–polymer mass ratios of (a) 0.00, (b) 0.21, and (c) 0.50 are illustrated.

group, and can instead be simulated by scattering due to monodisperse spheres characteristic of the mesocellular foam material.⁴

The sudden increase in pore size with no mesophase change in SAXS pattern found in the transition region between SBA-15 and MCF is caused by the nodding of the cylindrical pore walls. Light scattering and small-angle neutron scattering (SANS)⁹ results indicate that the micelles formed by the polymer/HCl/TMB/water mixture are spheres up to an oil–polymer ratio of 0.5. Hydrodynamic micelle diameters, determined by light scattering, increase from 17 to 25 nm when the oil–polymer ratio is increased from 0 to 0.5. Because the micelles that eventually form the cylindrical templates for SBA-15 begin as spheres, there must be a morphological change upon the addition of TEOS. Similar sphere-to-rod transitions after the addition of TEOS have been seen in surfactant-templated systems,¹⁰ and this transition has been explained by ionic interactions between the surfactant headgroups and charged silica precursors. The interactions screen the charge from neighboring headgroups, thereby reducing the repulsion between headgroups and the effective area that they occupy. This effect decreases the curvature of the micellar surface, allowing the silica precursor/surfactant pairs to form cylindrical rods rather than spheres. For nonionic PEO–PPO–PEO triblock copolymers, the effective areas occupied by the amphiphile head and tail groups also determine the micelle shape, but the dominant forces are local solvation effects.

We can use the geometric explanation of amphiphile packing at interfaces developed by Israelachvili¹¹ and

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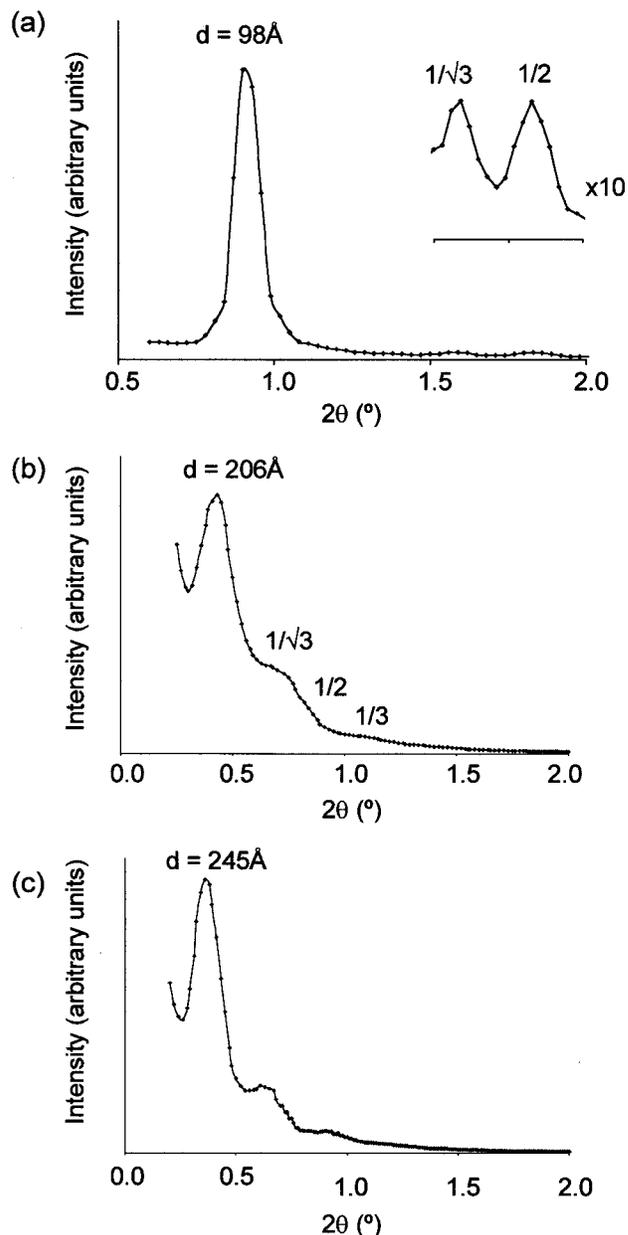


Figure 4. SAXS patterns of mesoporous silicas synthesized with oil–polymer mass ratios of (a) 0.00, (b) 0.21, and (c) 0.50.

Mitchel and Ninham¹² to describe the changes in micelle shape with the additions of acid, ethanol, and TMB. The geometric model is based on the idea of a surfactant packing factor that determines the curvature of the micelle surface and therefore the micelle shape. The packing factor (P) is defined by the ratio of the effective cross-sectional area of the tail (hydrophobic) group, a_T , to that of the head (hydrophilic) group, a_H .

$$P = \frac{a_T}{a_H} \quad (1)$$

For $P < 1/3$, micelles with highly curved surfaces, i.e., spheres, are formed. When $1/3 < P < 1/2$, micellar structures with less surface curvature would assemble, usually as cylinders.

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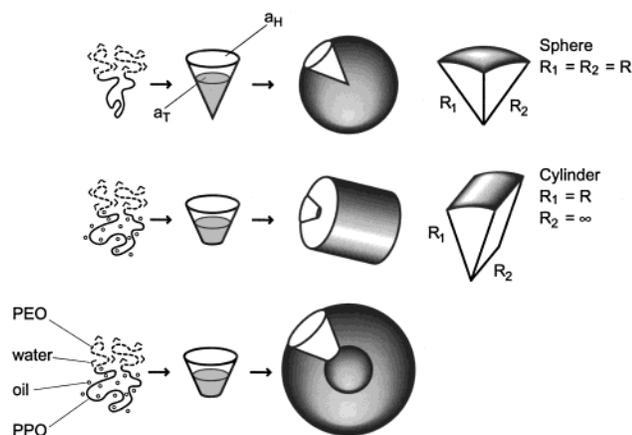


Figure 5. Schematic diagrams showing the effects of local solvation environments on the packing factor of the amphiphilic triblock copolymer, P123. (a) The PEO segments of the polymer are fully hydrated, leading to the formation of spherical micelles. (b) HCl present in the reaction mixture dehydrates the PEO segments, and ethanol and oil solvate the PPO segments, thus increasing the packing factor and leading to cylindrical micelles. (c) Increasing the oil content leads to formation of microemulsion droplets with oil cores. Because of the large radius of the microemulsion droplets, their mean surface curvature is similar to that of the cylindrical micelles formed in (b). The radii of curvature for a sphere and a cylinder are defined to the right of the schemes.

The cross-sectional areas of the head and tail groups are affected by their local environments and, therefore, the packing factor and micelle shape are changed by the addition of selective swelling agents. When the Pluronic P123 polymer is mixed with water at or above room temperature, it forms micelles with PPO cores and hydrated PEO coronas. The PPO core contains only a small amount of water, according to the neutron scattering results of Goldmints et al.¹³ and Liu et al.,¹⁴ whereas the PEO corona is hydrated by approximately three water molecules hydrogen-bonded to each ethylene oxide (EO) unit,¹⁵ and a total hydration of approximately 19–25 water molecules per EO unit due to mechanical entrapment.¹⁶ The high hydration number of the PEO chains leads to a large effective hydrophilic volume and thus a decreased value of the packing factor relative to that of the dry polymer. Therefore, P123 forms spherical micelles in aqueous solutions, as is shown schematically in Figure 5a.

Without the addition of oil, P123 templates cylindrical cavities in silica networks. It is well established that the presence of certain ions (such as Cl^-) in the aqueous solution decreases the solubility of the PEO block.¹⁷ The reduction in PEO block solubility decreases a_H and leads to a micelle with less surface curvature. In addition to salt effects, the presence of ethanol released by the hydrolysis of TEOS will also influence the micelle shape. At relevant temperatures, PPO is soluble in ethanol but not in water, therefore, there will be some ethanol present at the hydrophilic/hydrophobic interface and in the core of the micelle. We propose that the dehydrating effects of HCl addition and the swelling effects of ethanol on the PPO core lead to an increase in the packing factor of the

P123 amphiphiles and a reduction in micelle curvature, allowing cylindrical micelles to form. When small amounts of oil are added to the synthesis mixture, the oil will further swell the hydrophobic PPO blocks, resulting in the formation of larger cylindrical micelles. This theory is supported by prior work in which the addition of small amounts of oil or other swelling agents has been shown, both experimentally and theoretically, to induce the sphere-to-rod transition in micelle structure.^{18,19} Figure 5b provides a schematic diagram of the swelling of the PPO blocks to form cylindrical micelles.

The transition from cylindrical micelles back to spherical micelles that yields mesocellular silica foams is driven by the requirement to cover an increasing volume of oil with a fixed amount of polymer. The oil swells out the PPO chains until saturation, and then pure oil cores are formed at the center of the micelles. To cover the oil droplets with the minimum amount of polymer, the micelles become more spherical, yielding the noded structure shown in Figure 3b that reduces the overall surface-to-volume ratio. Figure 1 shows that the diameter of the spherical nodes that form at an oil–polymer ratio of 0.21 is ~ 220 Å, and that the diameter of the cylinders that form at an oil–polymer ratio of 0.19 is ~ 110 Å. By the transition from cylinders of 110 Å diameter to spheres of 220 Å diameter, the overall surface-to-volume ratio of the system decreases by $\sim 30\%$. In addition, the mean curvature of the system (H_c , defined in eq 2 and Figure 5) remains almost unchanged by the transition.

$$H_c = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

The mean curvatures of the system at oil–polymer ratios of 0.19 and 0.21 are 0.0045 and 0.0046 \AA^{-1} , respectively. The maintenance of the mean curvature indicates that the packing factor does not change significantly during the transition. The progression of mesoporous structures obtained by increasing oil concentration is shown in the schemes of Figure 3a–c.

Mesoporous materials templated by PEO–PPO–PEO triblock copolymers form a novel mesocellular foam phase when substantial TMB is added. The transition between the hexagonally structured SBA-15 silica and the mesocellular foam occurs at a TMB–polymer mass ratio of 0.2–0.3. The gradual transition to the MCF phase is characterized by a sharp increase in the pore size, whereas a hexagonal structure ($p6mm$) is still observed in the SAXS pattern. Transmission electron micrographs reveal buckling in the walls of the cylindrical pores for oil–polymer ratio of ~ 0.2 . The increased hysteresis in the N_2 adsorption/desorption isotherms also indicates a change in pore morphology. We propose that the change in pore morphology, without an accompanying mesophase change in SAXS pattern, is due to the formation of a noded structure in the cylindrical pores while they maintain their hexagonal packing (see scheme in Figure 3b). As the TMB concentration increases, the nodes separate into spherical micelles and aggregate to form the mesocellular foam material. The mesophase change is thought to be driven by the need to decrease micelle surface-to-volume ratio as more oil is added to a solution with a fixed amount of polymer, but the transition results in a negligible change in the mean curvature of the polymer-stabilized oil–water interface.

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