

Access to Ultralarge-Pore Ordered Mesoporous Materials through Selection of Surfactant/Swelling-Agent Micellar Templates

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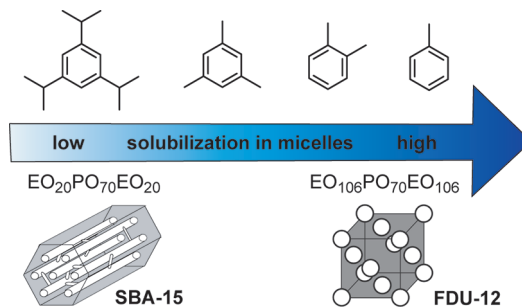
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CONSPECTUS

The surfactant-micelle-templating method has revolutionized the synthesis of high-surface-area materials with mesopores (diameter 2–50 nm) that have well-defined shapes and sizes. One of the major benefits of this method is the ability to tailor the pore size by manipulating the size of the templating micelles. The uniform pores typically form ordered arrays.

Although the choice of surfactant can tune the size of the micelles, it is more convenient to use a single surfactant and tailor the micelle size by adding a swelling agent. Unfortunately, the swelling agent tends to induce disorder or heterogeneity in the resulting structures, which can make this approach difficult to implement. We hypothesized that the swelling agents that are moderately solubilized within the micelles of a particular surfactant could generate well-defined micelle-templated structures with significantly enlarged pores.

Using this idea, we could judiciously select candidate swelling agents from families of compounds whose extent of solubilization in the surfactant micelles systematically changes with variations in the compound structure. Alkyl-substituted benzenes proved very useful as swelling agents, because their extent of solubilization in micelles of common Pluronic surfactants ($\text{EO}_m\text{PO}_n\text{EO}_m$; EO = ethylene oxide, PO = propylene oxide) significantly increases as the number or size of alkyl substituents decreases. On the basis of these principles, we identified 1,3,5-triisopropylbenzene and cyclohexane as swelling agents for the synthesis of ultralarge-pore SBA-15 silica (pore diameter up to 26 nm) and organosilicas with 2-D hexagonal structures of cylindrical mesopores. Moreover, we used xylene, ethylbenzene, and toluene as swelling agents for the synthesis of large-pore (pore diameter up to 37 nm) face-centered cubic silicas and organosilicas with spherical mesopores. During the early stages of the synthesis, the entrances to large cylindrical and spherical mesopores of these materials were much smaller than the inner pore diameter. Therefore we can often use calcination at sufficiently high temperatures (400–950 °C) to produce closed-pore silicas. Using hydrothermal treatments, we can obtain materials with large pore entrance sizes. In Pluronic-templated synthesis, we observed the propensity for formation of single-micelle-templated nanoparticles as the ratio of the framework precursor to surfactant decreased, and this process afforded organosilica nanotubes and uniform hollow spheres with inner diameters up to ~21 nm. Consequently, the adjustment of variables in the micelle-templated synthesis allows researchers to tailor the pore size and connectivity and to form either periodic pore arrays or individual nanoparticles.

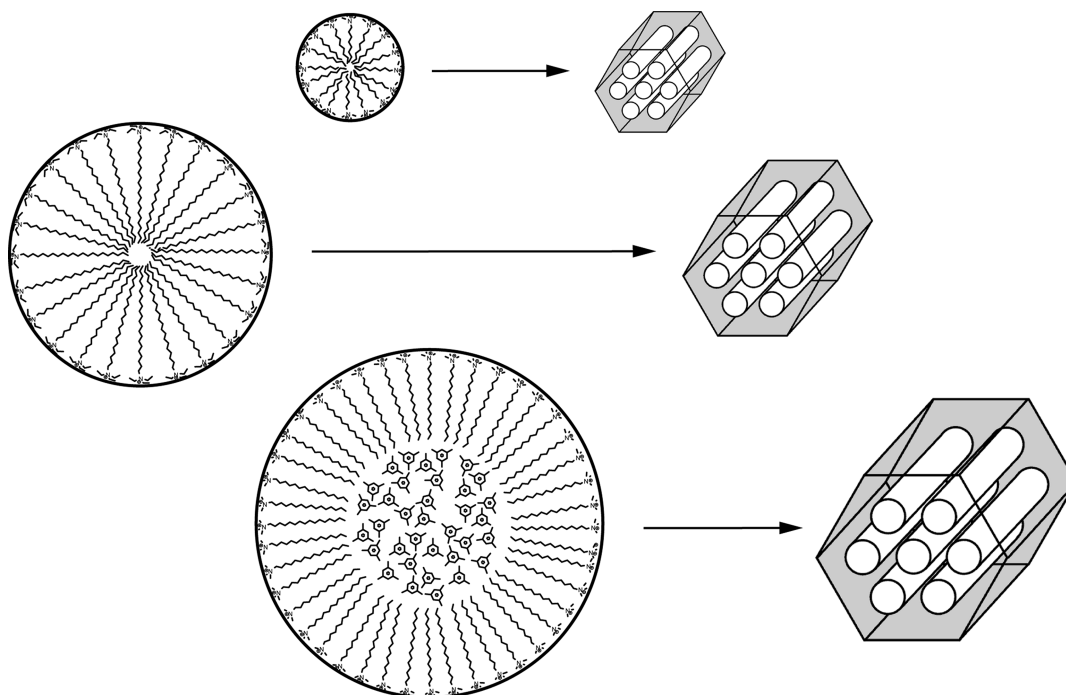


Introduction

In the early 1990s, a breakthrough in the synthesis of high-surface-area porous materials was made on the basis of the realization that pores in solid materials can be templated by surfactant micelles of uniform size and shape.^{1–3} In particular, Mobil scientists disclosed that alkylammonium

surfactants can assemble with silicate species into structures in which periodic arrays of surfactant micelles are occluded in three-dimensionally cross-linked silicate frameworks.¹ One of the resulting materials was MCM-41 silica with a two-dimensional (2-D) hexagonal structure of cylindrical mesopores (see Scheme 1) of diameter from 2 to 7 nm.^{1,4,5}

SCHEME 1. Adjustment of Pore Size in Micelle-Templated Synthesis of Porous Materials by Using Surfactants of Different Chain Lengths (Top and Middle) and by Adding Micelle Swelling Agents (Bottom)



It should be remarked that pores of width below 2 nm, between 2 and 50 nm, and above 50 nm are classified as micropores, mesopores, and macropores, respectively. The pore diameter of MCM-41 and other surfactant-templated materials can be tuned by adjusting the diameter of the templating micelles (see Scheme 1).^{1,2} It was initially postulated that preformed micellar arrays template the inorganic frameworks that form around them,¹ although subsequent studies showed that this mechanism of formation of ordered mesoporous materials (OMMs) is operational primarily in concentrated surfactant solutions⁶ that are rarely employed. A breakthrough in the understanding of the formation of OMMs came with the hypothesis of a cooperative assembly mechanism based on the charge density matching between the surfactant and the framework precursor with possible mediation by small ions.^{4,7} The identification of the above formation mechanism was a key to many further advances, including the synthesis of OMMs of a variety of framework compositions.^{8,9} The introduction of nonionic surfactants further extended the scope of surfactant-templated synthesis of OMMs.^{6,10} Surfactants with hydrophilic poly(ethylene oxide), PEO, block(s) and a hydrophobic part (typically an alkyl chain or a polymeric moiety, such as poly(propylene oxide), PPO) have attracted much attention.^{6,10–12} In particular, the use of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers,

commercially available as Pluronics, brought major advances in OMM synthesis.^{12,13} Pluronics are a vast family of surfactants available with different molecular weights and contents of hydrophobic domains, which form various assemblies in solutions, including spherical and cylindrical micelles, which may be arranged in periodic structures.¹⁴ Large contents of PEO facilitate the formation of high-curvature spherical micelles, whereas large contents of PPO promote lower-curvature assemblies, such as cylindrical micelles, although the structures are dependent on concentration and temperature.¹⁴ The best known OMM templated by Pluronics is SBA-15 silica with a 2-D hexagonal structure of cylindrical mesopores, which is typically synthesized using Pluronic P123 (EO₂₀PO₇₀EO₂₀) surfactant.¹² While SBA-15 exhibits a honeycomb structure similar to that of MCM-41,¹ a different nature of the surfactant “head-group”, which consists of PEO blocks, has profound structural implications. Namely, the framework of the templated material occludes the PEO chains of the surfactant,¹⁵ apparently forming around them,^{10,16} instead of interacting with the surfactant only at a sharply defined framework/surfactant interface, as is the case for alkylammonium surfactant templates.⁷ The presence of PEO chains in the silica wall of as-synthesized SBA-15 was the basis of the explanation of the presence of micropores in the walls and interconnections between the mesopores of SBA-15.^{16,17} The discovery

of SBA-15 was followed by the development of other block-copolymer-templated mesoporous silicas, including SBA-16 with spherical mesopores arranged in body-centered cubic structure ($Im3m$ symmetry)¹² and a cubic close-packed structure with $Fm3m$ symmetry (known primarily as FDU-12¹⁸ or KIT-5¹⁹). A number of periodic mesoporous organosilicas (PMOs) with various organic groups homogeneously distributed in the silica-analogous frameworks were also synthesized using block copolymer surfactants.²⁰ In addition, a large number of OMMs with nonsilica frameworks have been obtained.¹³ SBA-15 has attracted exceptionally high attention in the scientific community,²¹ which is related to the fact that its pore size (typically ~ 10 nm) is larger than that of MCM-41 and other alkylammonium-templated materials (typically 2–5 nm), which is desirable in many applications.^{21,22} Moreover, SBA-15 has a superior hydrothermal stability,¹² its surfactant template is cheap and readily available, its synthesis is well-reproducible, and the unique pore connectivity creates vast opportunities in the synthesis of inverse replicas, such as ordered arrays of nanowires of carbon and many other compositions,^{17,23} as well as nanotubes of carbon.²⁴ While the pore diameter of typical SBA-15 is sufficiently large for many applications, even larger pore sizes provide additional opportunities and benefits, for instance in catalysis^{22,25} and immobilization of biomolecules.²⁶

While the micelle-templated synthesis of OMMs had become a new paradigm in the synthesis of well-defined porous materials already in 1990s, it is surprising that the application of surfactant micelles to template individual hollow nanoparticles (nanospheres or nanotubes) has been explored mostly during the last 5 years. First examples of the single-micelle templating of nanoparticles typically involved silicas and custom-made surfactant templates.^{27–30} However, it was recently realized that one can also use Pluronic surfactants to synthesize silica-cross-linked micelles³¹ and that the resulting materials not only are stable in solution³¹ but can survive surfactant removal and thus be converted to mesoporous materials.^{32–36} Most of the work in this regard involved silicas or organosilicas (although, for instance, hollow titania nanospheres have been developed³⁷) and spherical micelles, but more recently, examples of silica and organosilica nanotubes templated by cylindrical micelles of Pluronic^{34–36} have been reported. The single-micelle-templated nanoparticles (whether as-synthesized or surfactant-free) are highly suitable as delivery vehicles for therapeutic substances, supports in heterogeneous catalysis, and anode materials for Li-ion batteries.^{31,34,38} In some cases,

agents that suppress cross-linking between the nanoparticles were used to avoid aggregation,³¹ suggesting that consolidated materials form from single-micelle-templated nanoparticles.

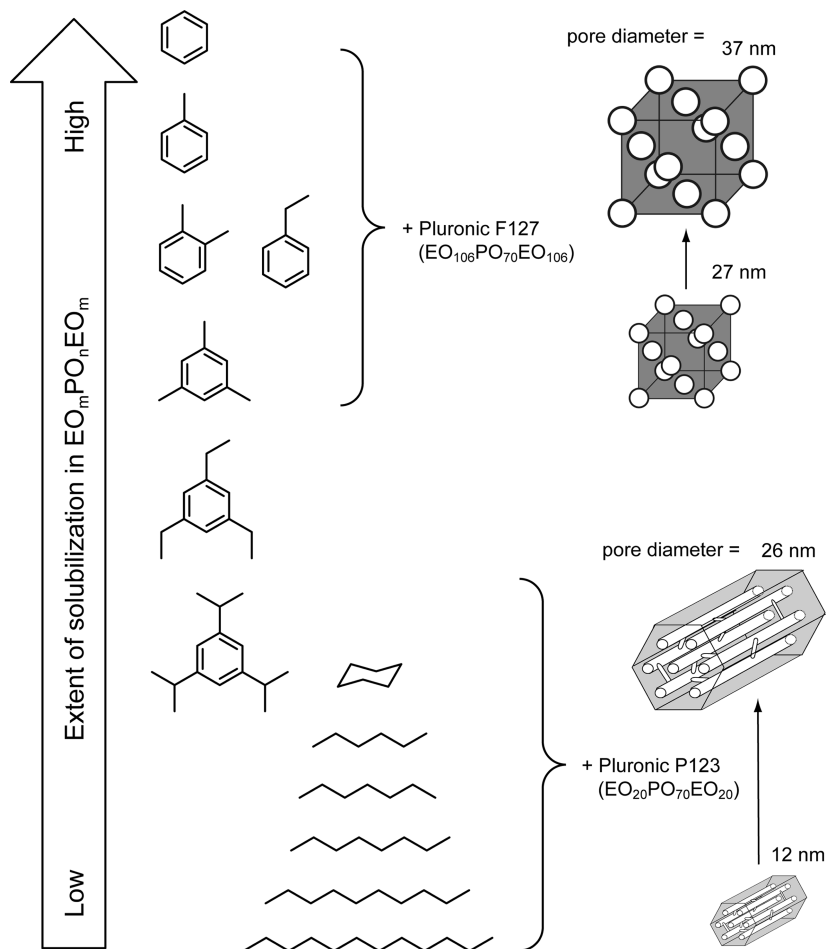
Swelling Agents in Micelle-Templated Synthesis

One of the most spectacular signatures of the micelle-templated synthesis of OMMs is the ability to tailor the pore size through the use of micelle swelling agents (micelle expanders), which increase the size of the micelles (Scheme 1). A variety of compounds were shown to act as micelle expanders, including benzene and its alkyl-substituted derivatives^{1,12,39–42} (most notably, 1,3,5-trimethylbenzene, TMB), linear hydrocarbons,^{43–45} cyclic hydrocarbons,^{41,46} and long-chain amines.⁴⁷ While micelle expanders readily increase the mesopore size and volume of micelle-templated materials,^{12,47} their action typically results in the lowering of the degree of structural ordering (often dramatically)⁴⁷ or in the change of the structure type (e.g., from SBA-15 to a mesocellular foam).⁴⁸

Low-Temperature Synthesis of Ordered Mesoporous Materials

In 2005, it was reported that Pluronic block copolymers combined with appropriate swelling agents afford ordered mesoporous silicas with unusually large pore sizes when the initial step of the synthesis (in which the material forms) takes place at ~ 15 °C.^{40,45} In particular, it was shown that the lowering of the initial temperature from 25–40 °C to 14–15 °C in the synthesis of FDU-12 silica with face-centered cubic structure of spherical pores templated by Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) in the presence of TMB (see Scheme 2) allows one to increase the unit-cell parameter from ~ 30 to 44 nm and to double the pore diameter, reaching 27 nm.⁴⁰ At that time, this was the largest pore size achieved for highly ordered mesoporous silica. The resulting materials were dubbed large-pore FDU-12 (LP-FDU-12). The pore size was adjustable by selecting initial synthesis temperature and further tuned using hydrothermal treatments.^{40,49} Another important finding was the formation of highly ordered large-pore SBA-15 (LP-SBA-15) with (100) interplanar spacing, d_{100} , of ~ 14 nm (d_{100} multiplied by 1.155 gives the unit-cell parameter, which is the distance between the pore centers) and pore diameter ~ 15 nm (much higher than ~ 10 nm for typical SBA-15) using Pluronic P123 and hexane at 15 °C (see Scheme 2).⁴⁵ While even larger pore diameter had been achieved for

SCHEME 2. Experimental or Extrapolated Extent of Solubilization of Aliphatic and Aromatic Hydrocarbons (Swelling Agent Candidates) in $\text{EO}_m\text{PO}_n\text{EO}_m$ Block Copolymers, And the Corresponding Ordered Mesoporous Structures with Tunable Pore Sizes Templated by Pluronic P123 and F127 Surfactants



SBA-15 using PEO–poly(methyl acrylate) surfactants,⁵⁰ the synthesis with hexane proved to be well-reproducible and convenient.^{22,51} More importantly, different linear hydrocarbons were found suitable as swelling agents and the pore size increased as the alkyl chain length decreased (Scheme 2),^{45,52} which was noted⁴⁵ to be consistent with the order of the extent of solubilization of alkanes in Pluronic micelles.^{53,54} The correlation between the extent of solubilization of compounds and their swelling action in OMM synthesis was a very important insight, because previous studies tacitly assumed that one can control the extent of swelling, and thus the pore diameter, through the adjustment of the amount of the swelling agent added.

Selection of Swelling Agents in Low-Temperature Synthesis

We further explored the low-temperature syntheses of large-pore SBA-15 and FDU-12. One of the conclusions

was that even though the swelling agent (hexane) was used in large excess in the synthesis of LP-SBA-15, the actual uptake of hexane by Pluronic P123 micelles was small.⁵¹ Moreover, no appreciable increase in the uptake of the swelling agent (TMB) was apparent as the temperature was lowered in the LP-FDU-12 synthesis, while the pore size increased substantially.⁴⁹ It was concluded that a limited extent of solubilization of the swelling agents in the micelles contributed to the retention of highly ordered mesoporous structures despite significant pore size increases.⁵¹ It was hypothesized⁴¹ that an excessive and thus poorly controlled uptake of the swelling agent by the micelles was a problem that was encountered in many attempts to significantly increase the pore size of OMMs and resulted in loss of structural uniformity or in pore structure change.^{39,47,48} Since the initially reported low-temperature syntheses appeared to involve no major swelling agent uptake, there emerged an opportunity to further enhance the swelling

agent uptake to achieve even larger pore sizes while retaining well-defined periodic structures.⁴¹ The concept was implemented through considerations of the extent of solubilization of different compounds in Pluronic micelles, which allowed for the identification of a new series of swelling agents belonging to alkyl-substituted benzenes and an “extension” of the linear hydrocarbon series (see Scheme 2).⁴¹ In particular, the extent of solubilization of alkyl-substituted benzenes was reported to decrease as the number or size of alkyl substituents increased (for benzene, toluene, ethylbenzene, and xylene).⁵⁴ It was hypothesized that the same trend is valid for compounds with a larger number or size of alkyl substituents, including TMB, 1,3,5-triethylbenzene (TEB), and 1,3,5-trisopropylbenzene (TIPB), which are expected to be a continuation of the series with decreasing extent of solubilization (Scheme 2).⁴¹ In addition, the solution data⁵⁴ indicated that a cyclic aliphatic compound (cyclohexane) exhibits an extent of solubilization in Pluronics appreciably higher than its linear counterpart (hexane). Thus, it was proposed⁴¹ to employ cyclohexane as an “extension” of the linear hydrocarbon series of swelling agents.

We proposed the following approaches to implement the above considerations in OMM synthesis.^{41,42} If there is a known synthesis involving a swelling agent, which leads to well-defined OMM product, one can substitute the proven swelling agent with the one that would solubilize to a somewhat greater extent in the surfactant used. This approach led to the identification of xylene, ethylbenzene, and toluene as superior swelling agents in the Pluronic F127 templated synthesis of LP-FDU-12 silica with face-centered cubic structure, allowing us^{42,55} to reach the unit-cell parameter of 56 nm vs 44–51 nm reported by others with previously used TMB,^{25,40} and pore diameter of 37 nm. The aforementioned unit-cell parameters were close to those achieved using a custom-made surfactant,⁵⁶ whereas the pore diameters were even higher than in the latter case. In addition, the application of xylene and toluene in the synthesis of large-pore periodic mesoporous organosilicas (PMOs) with face-centered cubic structures resulted in major increases of their unit-cell parameter and pore size⁵⁷ in comparison to the TMB-based synthesis.^{57,58}

A similar reasoning played a role in the identification of TIPB as a superior swelling agent to substitute hexane in LP-SBA-15 synthesis,⁴¹ although in that case, there were no literature data found to establish whether TIPB or hexane is solubilized in Pluronics to a greater extent, and additional considerations also played a role. Namely, another consideration was to identify OMM syntheses in which an

excessive uptake of the swelling agent was observed (for instance, the synthesis of SBA-15 with TMB that results in a limited pore size increase with retention of 2-D hexagonal structure, followed by a transition to mesocellular foams⁴⁸) and to implement a swelling agent that exhibits a lower extent of solubilization. This reasoning pointed to TIPB as a promising swelling agent candidate for the synthesis of LP-SBA-15 (see Scheme 2). The use of TIPB resulted in ultralarge-pore SBA-15 (ULP-SBA-15) with (100) interplanar spacing up to 26 nm,⁴¹ which by far exceeds d_{100} for LP-SBA-15 discussed above.^{45,50,52} Shown in Figure 1a are small-angle X-ray scattering (SAXS) patterns for a series of SBA-15 silicas with d_{100} from 14 to 26 nm synthesized by decreasing an initial synthesis temperature from 17 to 12.25 °C (Figure 1d). At temperatures of 14 °C or lower, it was found beneficial to increase the relative quantity of TIPB in the synthesis mixture; otherwise the mesopore size increase was accompanied by the development of an increasing fraction of mesopores of smaller size at the expense of the volume of the uniform mesopores and their ordering. The SAXS patterns became less resolved as the unit-cell size increased, but even silica with d_{100} of 26 nm exhibited three peaks or shoulders, whose relative positions pointed to 2-D hexagonal ordering, as confirmed by transmission electron microscopy (TEM).⁴¹ Shown in Figure 1b are nitrogen adsorption isotherms of the considered series of SBA-15 samples.⁴¹ As the unit-cell size increased, the position of the capillary condensation steps on the isotherms shifted to higher relative pressures (from $p/p_0 = 0.86$ to 0.94), indicating the pore diameter increase, which was reflected on pore size distributions (PSDs) calculated from the isotherms (see Figure 1c). These PSDs were calculated using a method that overestimates the size of cylindrical mesopores in the considered pore size range, and more reliable estimates of the pore diameters were from 14 to 26 nm for the discussed SBA-15 silicas,⁴¹ being close to d_{100} values that are shown in Figure 1d.

One can predict the suitability of a swelling agent for a particular surfactant by considering the structure of the surfactant and the order of the extent of solubilization for a family of swelling agent candidates in the pertinent type of surfactants.^{41,42} In particular, Pluronic P123 (EO₂₀PO₇₀EO₂₀) surfactant used in the synthesis of SBA-15 and other materials with cylindrical mesopores has ~70 wt % of hydrophobic PPO domains that accommodate the hydrophobic swelling agent. Consequently, Pluronic P123 exhibits a much higher extent of solubilization of hydrocarbons in comparison to Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆), which has only ~30 wt %

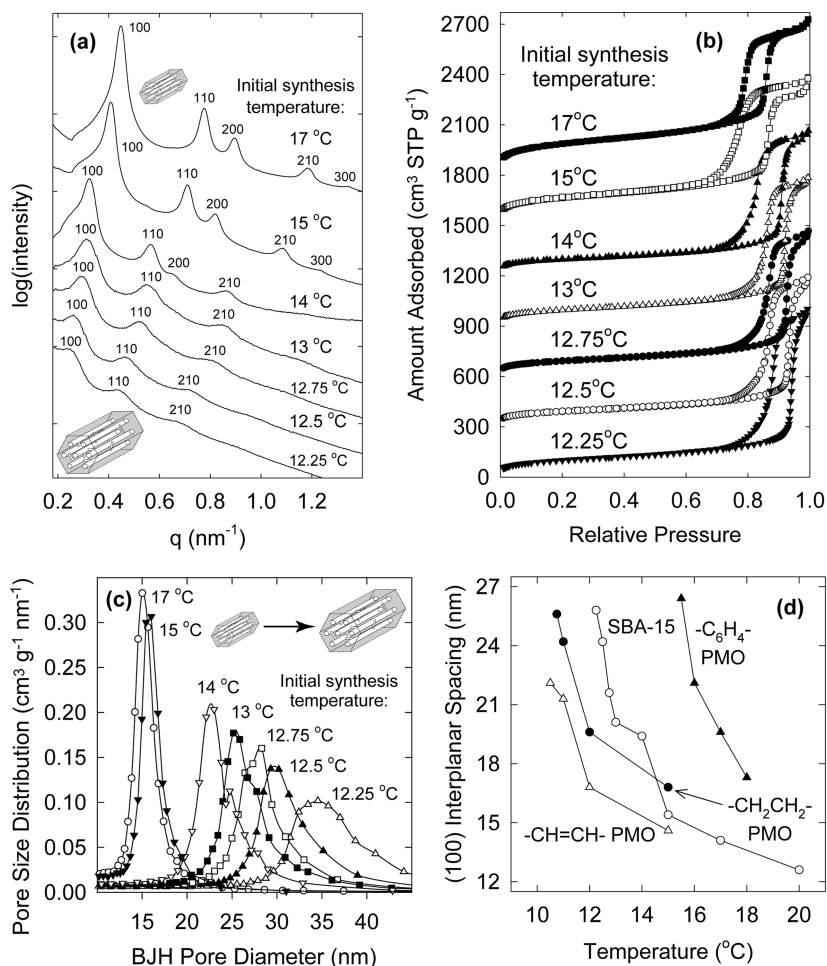


FIGURE 1. (a) Small-angle X-ray scattering patterns, (b) nitrogen adsorption isotherms (shifted vertically for clarity), and (c) pore size distributions for SBA-15 silicas synthesized with triisopropylbenzene as a swelling agent at different initial temperatures (figures adapted from ref 41); (d) (100) interplanar spacing vs initial synthesis temperature for SBA-15 and for ethenylene-, ethylene-, and phenylene-bridged periodic mesoporous organosilicas (data taken from refs 41 and 46).

PPO,⁵⁴ and is suitable for the synthesis of FDU-12 and other materials with spherical mesopores.⁴² Therefore, Pluronic P123 should be combined with a swelling agent that solubilizes to a lower extent in Pluronics (e.g., TIPB or cyclohexane),^{41,46} and Pluronic F127 should be combined with a swelling agent having a significant tendency to solubilize in Pluronics (e.g., xylene, ethylbenzene, or toluene) (see Scheme 2).^{42,55} Otherwise, the swelling action may be too strong (for Pluronic P123 and other surfactants with high PPO content), resulting in poorly defined very large pore products, or too weak (for Pluronic F127 and other surfactants with low PPO content), resulting in no appreciable pore size enlargement⁵⁷ or lack of tendency to induce the formation of OMM. It should be noted that the order of the extent of solubilization of aromatic and aliphatic hydrocarbons in surfactants that was discussed above is expected to be a general feature of block copolymer surfactant solutions and

is not restricted to Pluronics.^{53,54} The synthesis strategy for ultralarge-pore OMMs outlined above was very successful at subambient temperatures (10–20 °C),^{41,42,46,55,57} but its applicability at room temperature or above remains to be fully evaluated, although there is some evidence for it from PMO synthesis.⁵⁹

Synthesis of Large-Pore Periodic Mesoporous Organosilicas

As discussed above, our study identified TIPB and cyclohexane as swelling agents used in conjunction with EO₂₀-PO₇₀-EO₂₀ surfactant.⁴¹ This identification allowed us to develop a family of PMOs with 2-D hexagonal structures of unprecedented unit-cell size (d_{100} from 15–18 to 22–26 nm, see Figure 1d) and methylene, ethylene, ethenylene, and phenylene bridging groups.⁴⁶ Notably, cyclohexane was found much more suitable for PMOs with aliphatic

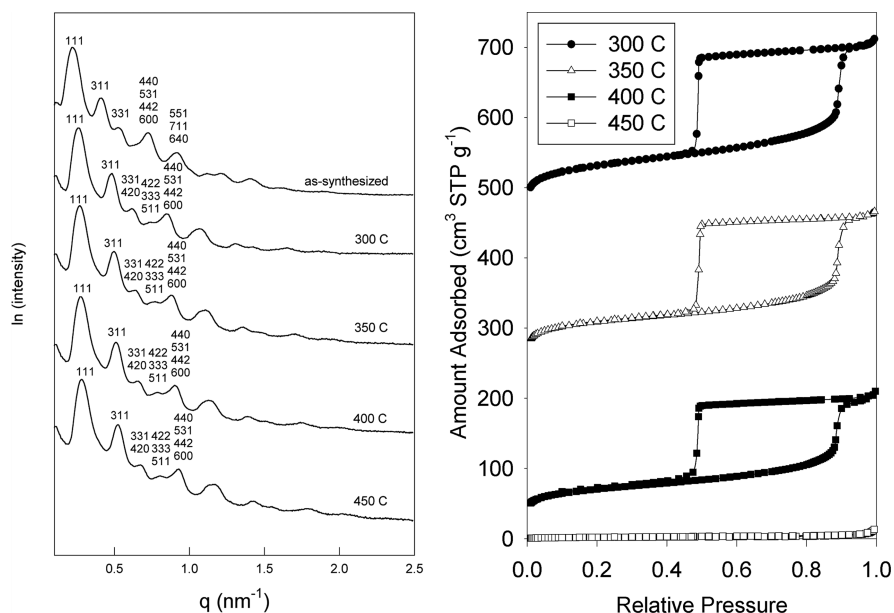


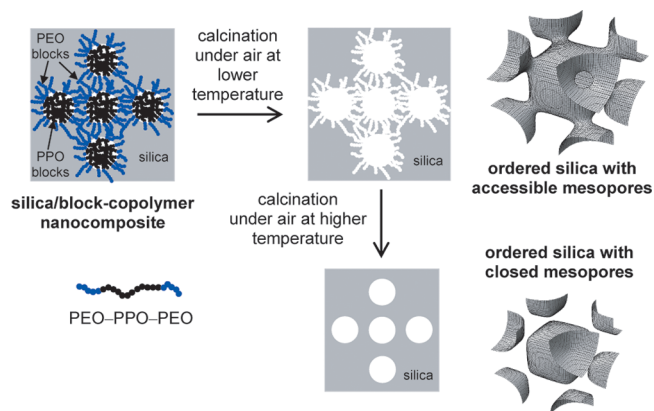
FIGURE 2. Small-angle X-ray scattering (left) and nitrogen adsorption isotherms (shifted vertically for clarity) (right) of FDU-12 silica of face-centered cubic structure, which was as-synthesized or calcined at different temperatures (300–450 °C). Reprinted with permission from ref 42. Copyright 2010 American Chemical Society.

bridging groups than it was for pure silicas. While cyclohexane did not afford large-pore PMOs with aromatic bridging groups, TIPB was found highly suitable for this purpose. In most cases, the unit-cell size of PMOs increased as the initial synthesis temperature decreased (see (100) interplanar spacings in Figure 1 d), allowing us to generate families of PMOs with a wide range of unprecedented unit-cell sizes and pore diameters (up to ~ 20 nm). In addition, highly ordered ethylene-bridged organosilicas with $Fm3m$ structure and unit-cell parameters of up to 43 nm, as well as moderately or weakly ordered PMOs with unit-cell parameters up to ~ 50 nm, were successfully obtained using $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ and xylene or toluene as swelling agents.⁵⁷ Such large-unit-cell PMOs have not been reported before. For these cubic PMOs, the pore diameter was controllable through the adjustment of the inorganic salt concentration in the synthesis mixture.

Ordered Mesoporous Silicas with Closed Mesopores

One of remarkable features of block-copolymer-templated ordered mesoporous silicas is the adjustability of their pore entrance sizes.^{18,40,42,49,55,60,61} While the large pore entrance size is advantageous in many applications,^{18,25} the ability to decrease the pore entrance size or possibly close it to obtain a closed-pore material is also important, for instance, in the development of low-dielectric-constant materials.^{61–63} We have developed a thermally induced

SCHEME 3. Mechanism of Thermally-Induced Pore Closing in Ordered Mesoporous Silicas Templated by PEO–PPO–PEO Block Copolymers



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pore closing method^{42,55,61,63,64} in which a mesoporous silica with spherical pores accessible through narrow entrances is selected and as its calcination temperature increases, the material shrinks without the loss of structural ordering (see SAXS patterns in Figure 2), and its mesopores become inaccessible above a certain temperature, as seen from gas adsorption (see Figure 2). It was proposed that the shrinkage decreases the dimensions or perhaps completely sinters the connections between the mesopores, which originate from spaces where PEO blocks of the surfactant template resided in the as-prepared material (see Scheme 3), making the mesopores inaccessible to gas molecules from

the surrounding. The thermally induced pore closing can be achieved not only for spherical mesopores, but for cylindrical mesopores with plugs inside them or with caps at the pore ends.⁶⁴ Such structural features appear to be present in some SBA-15 silicas prepared without a hydrothermal treatment, and thus a closed pore SBA-15 silica was obtained after calcination at ~ 950 °C.⁶⁴

Synthesis of Single-Micelle-Templated Hollow Nanoparticles

As an extension of the work on consolidated (and typically ordered) mesoporous silicas and organosilicas that were discussed above, a family of hollow organosilica nanoparticles and nanotubes was prepared at sufficiently low organosilica-precursor/block-copolymer–surfactant ratios.³⁵ In particular, it was demonstrated³⁵ that in the Pluronic-F127-templated synthesis of ethylene-bridged organosilicas (with Si–CH₂–CH₂–Si moieties) in the presence of TMB, the lowering of the ratio of the organosilica precursor to the surfactant led to a transition from a well-ordered face-centered cubic structure with spherical mesopores to individual or somewhat aggregated hollow spherical nanoparticles with mesopores of similar diameter. It should be noted that in two studies of silicas, a possibility of a transition from individual particles to consolidated structures through the adjustment of the ratio of the framework precursor to the surfactant was indicated on the basis of TEM.^{30,65} It was hypothesized³⁵ that at low organosilica-precursor/PEO–PPO–PEO–surfactant ratios, the precursor is solubilized in the surfactant micelles and its concentration on their surfaces is not high enough to lead to any significant cross-linking between the resulting nanoparticles, which hinders the consolidation into larger particles. The inner diameter of the nanospheres was adjusted by varying the micelle swelling agent (TMB, xylenes, toluene, and benzene), allowing us to obtain pore diameters up to ~ 21 nm, which are unprecedented for single-micelle-templated organosilica spheres synthesized using Pluronics, and approached only by those for nanospheres synthesized by custom-made surfactants.³⁸ By using low framework-precursor/surfactant ratios, hollow spherical nanoparticles were obtained also for methylene-, ethylene-, and phenylene-bridged organosilicas (with Si–CH₂–Si, Si–CH=CH–Si, and Si–C₆H₄–Si bridging moieties) (see TEM in Figure 3). The approach involving the adjustment of the framework-precursor/surfactant ratio was extended on ethylene-bridged organosilica nanotubes templated by Pluronic P123 surfactant in the presence of cyclohexane as a swelling agent (see TEM in Figure 3).³⁵

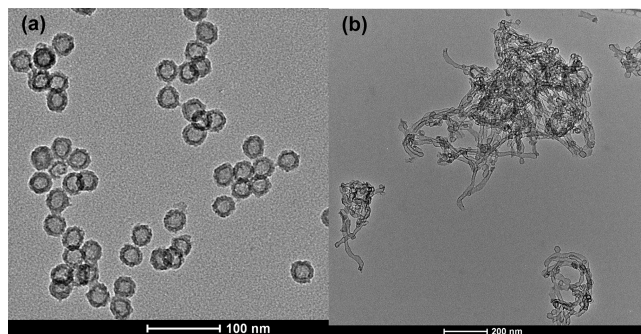


FIGURE 3. (a) Methylene-bridged organosilica hollow nanospheres and (b) ethylene-bridged organosilica nanotubes synthesized using PEO–PPO–PEO surfactants and micelle swelling agents. Reprinted with permission from ref 35. Copyright 2012 American Chemical Society.

It was attempted to directly synthesize hollow pure silica spheres using the above strategy, but the use of Pluronic F127 in combination with xylenes did not immediately render the desired material. However, when a block copolymer with a higher fraction of the hydrophilic domain (Pluronic F108, EO₁₃₂PO₅₀EO₁₃₂) was used in combination with xylenes as a swelling agent, hollow silica spheres (inner diameter ~ 23 nm) were obtained.³⁵

Conclusions

The application of swelling agents in the micelle-templated synthesis of well-defined mesoporous materials offers a remarkable opportunity for tailoring the pore diameter in a wide range without the need to use different surfactants. The swelling agents can be selected from families of compounds exhibiting systematic trends in the extent of solubilization in surfactants of a particular composition, so that the surfactant micelles are expanded in a controlled manner without inducing size or shape heterogeneity. EO_mPO_nEO_m triblock copolymers (such as Pluronics) are compatible with aliphatic and aromatic swelling agents. For Pluronics with high fractions of the hydrophobic block (for instance, P123, EO₂₀PO₇₀EO₂₀), it is advantageous to use swelling agents that solubilize in them to low or moderate extent in order to avoid excessive swelling. This identification opened the avenue to SBA-15 silica and periodic mesoporous organosilicas with very large cylindrical mesopores. On the other hand, Pluronics with low fractions of the hydrophobic block (for instance, F127, EO₁₀₆PO₇₀EO₁₀₆) work well with more potent swelling agents, allowing one to synthesize silicas and organosilicas with unusually large spherical mesopores. The synthesis of these large-pore materials was primarily explored under subambient temperature, adjustment of which often allowed for the pore size tailoring in a

wide range. The resulting large-pore silicas and organosilicas with spherical and cylindrical mesopores have thick walls, and their thermal treatment may lead to the formation of closed-pore silicas with retention of the original pore shape and symmetry. The use of judiciously selected surfactant/swelling-agent pairs combined with the adjustment of framework-precursor/surfactant ratio allows one to obtain large-pore hollow spherical and tubular nanoparticles of organosilica and silica templated by single micelles.

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BIOGRAPHICAL INFORMATION

Michał Kruk was born on March 20, 1970, in Lublin, Poland. He received his M.S. in chemistry from Maria Curie-Skłodowska University in Lublin, Poland, in 1994 and his Ph.D. in chemistry from Kent State University (KSU), Kent, Ohio, in 1998. He worked as a postdoctoral fellow at KSU in 1998–2003 and as a visiting assistant professor at Carnegie Mellon University, Pittsburgh, Pennsylvania, in 2003–2005. From 2005, he has worked at the College of Staten Island of the City University of New York, Staten Island, New York, where he is now an associate professor. He has published 110 papers in scientific journals and 31 articles in books. His research interests are in the synthesis and characterization of well-defined porous materials.

FOOTNOTES

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The authors declare no competing financial interest.

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